Plasmonic hot electrons generated by a dimer of silver nanoparticles:

increased energy and orientational selectivity

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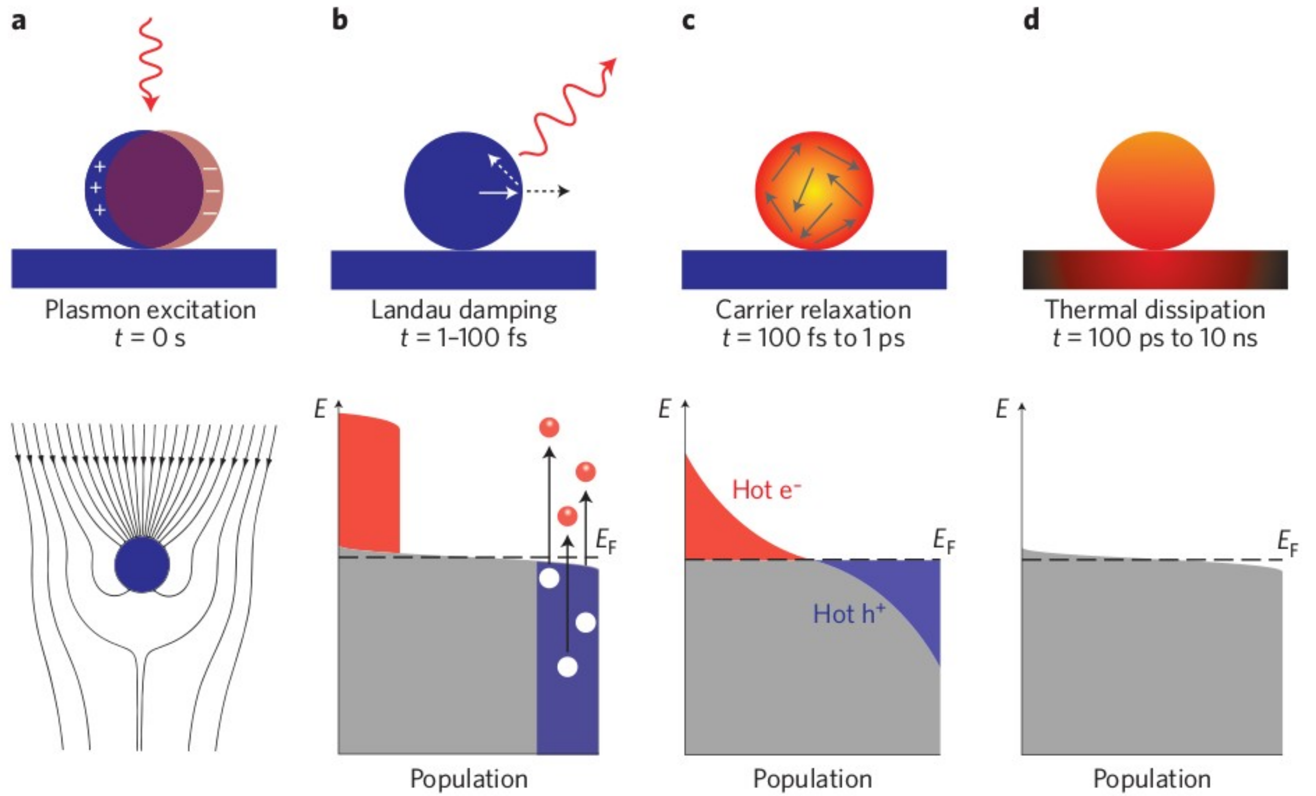
J. Phys. Chem. C. **2125** (43), 23991–24000 (2021)

Or-nano conference, Strasbourg, 26/10/23

Context and objectives

What are plasmonic hot electrons ?

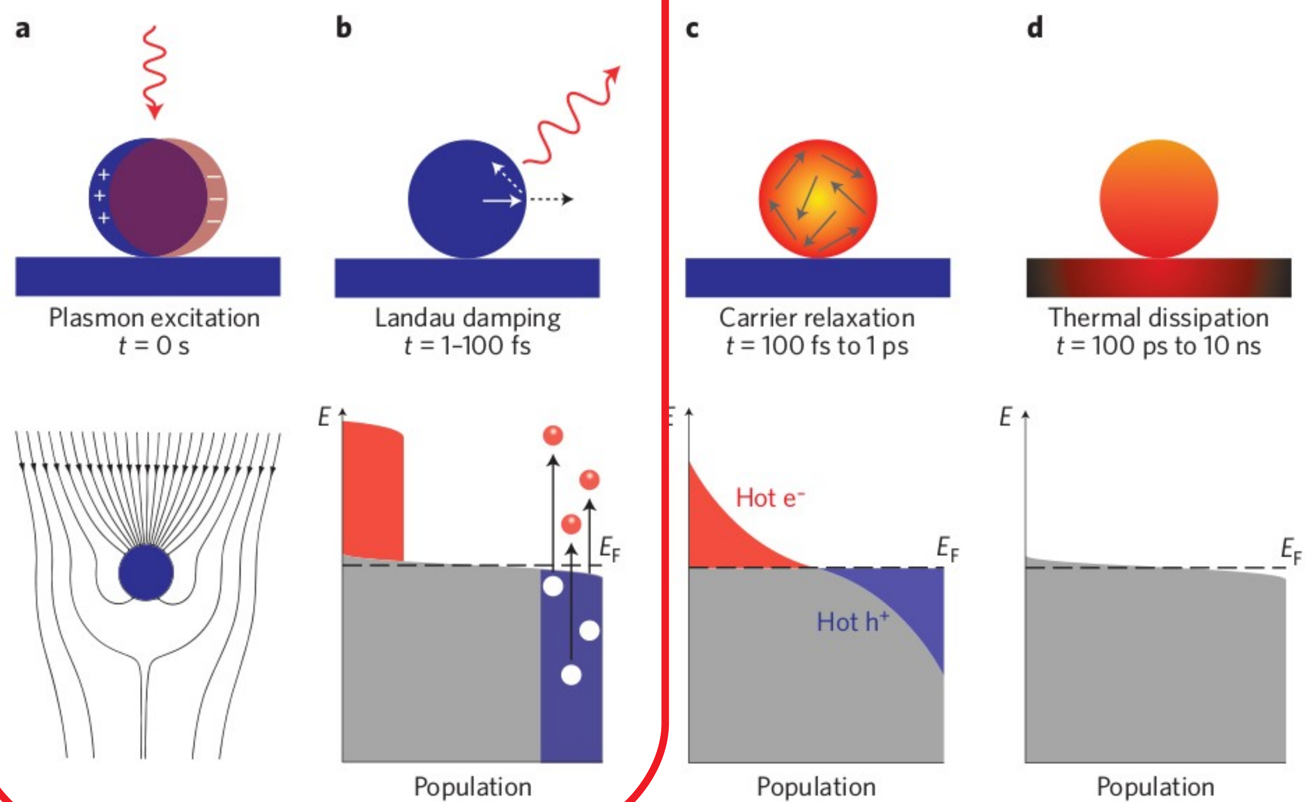


from *Nature Nanotechnology* **10**, 25–34 (2015)

Context and objectives

What are plasmonic hot electrons ?

Collective excitation (LSPR) ⇒ Individual excitations



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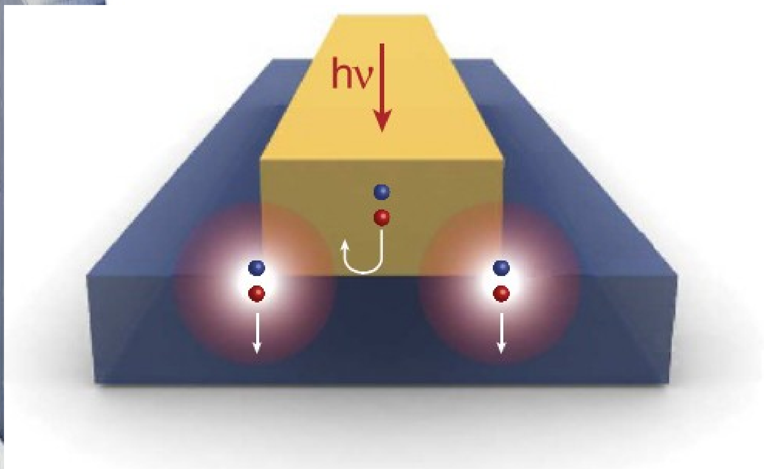
Context and objectives

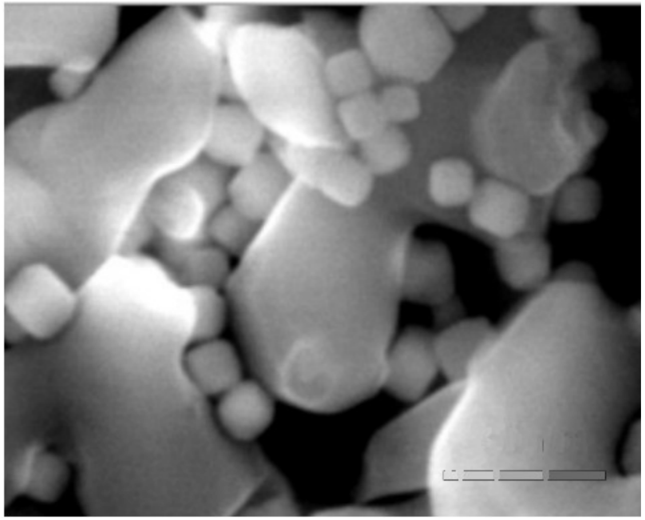
Application of plasmonic hot electrons

Optimization of photoelectric yields



Generation of plasmonic hot carriers
Au nanostructure on TiO_2 substrate
Zheng et col. – Nat. Com. ***6****, 7797 (2015)*

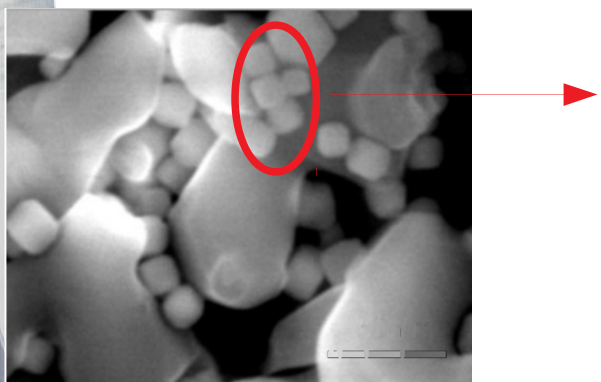
Plasmonic photocatalysis



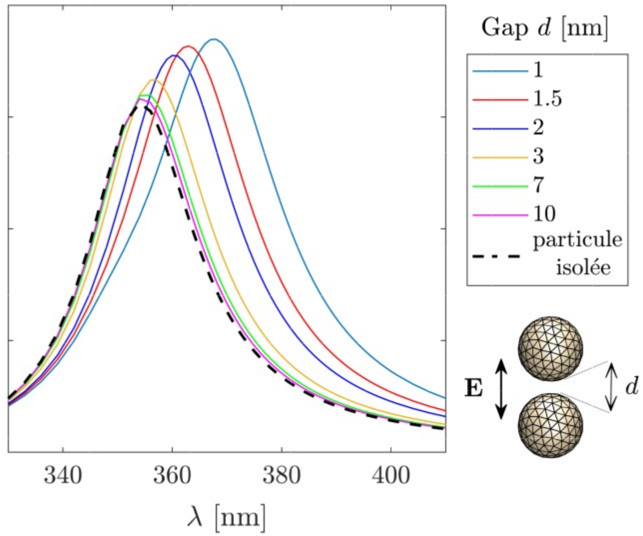
Ethylene epoxidation catalyzed by
silver nanocubes under visible light
Christopher et coll. - Nat. Mater. ***11****, 12 (2012)*

Context and objectives

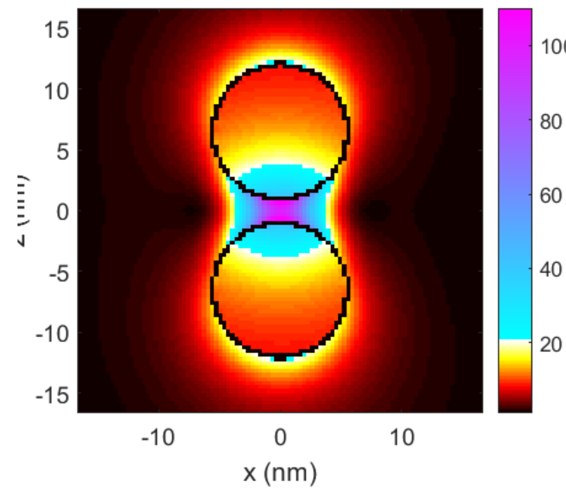
Interacting nanoparticles



Realistic photocatalyst



Redshift and increase of the absorption peak



« Hot spot » : strong exaltation of the electric field between the nanoparticles

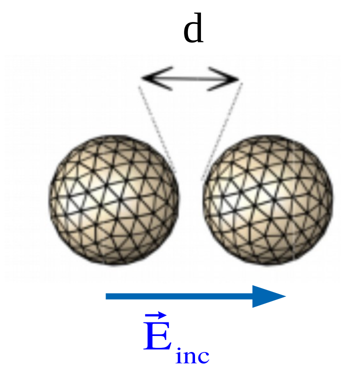
What are the effect of the inter-particle interactions on the hot carrier generation ?

MNPBEM toolbox: U. Hohenester and A. Trügler, *Comp. Phys. Commun.* **183**, 370 (2012).
Simulation parameters : silver NPs in air, D = 5 nm, gap = 1 nm.

Our theoretical model

Investigated system

- Dimer of spherical silver NPs in air, D = 5 nm, gap d
- Longitudinal incident field
  - I = 1 mW/µm²
  - λ ~ 350-400 nm (E < W_0 => no photoemission)



Method

- ~ 7500 atoms => too big for TD-DFT
- Semi-classical method adapted from literature

Electronic properties
from quantum mechanics
(Schrödinger equation)

Optical properties
from classical physics
(Maxwell's equations)

M. S. Maurice *et al.*, J. Phys. Chem. C. 2125 (43), 23991–24000 (2021)
A. Manjavacas *et al., ACS Nano* **8**(8), 7630–7638, 2014
L. V. Besteiro *et al., J. Phys. Chem. C* 120, 19329–19339, 2016

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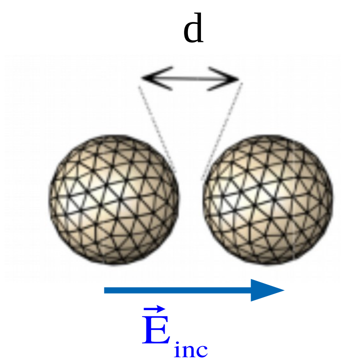

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Electronic properties from quantum mechanics (Schrödinger equation) ← **Perturbation theory** → **Optical properties** from classical physics (Maxwell's equations)

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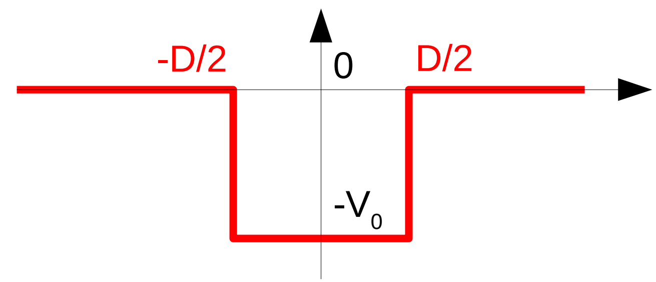
Our theoretical model

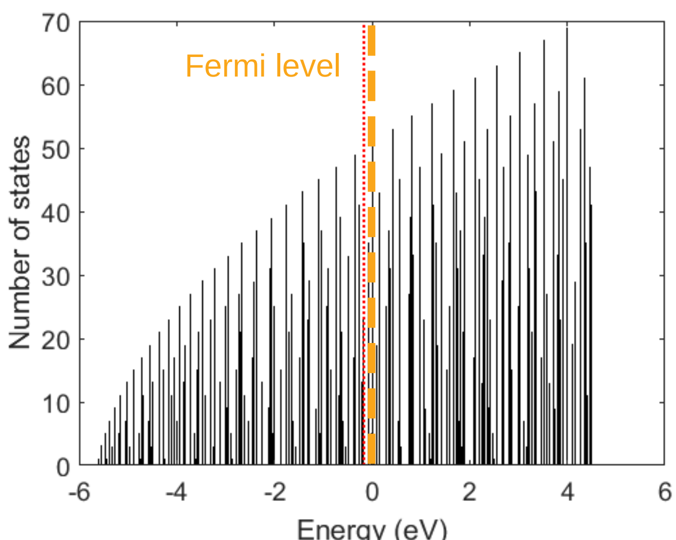
1. Electronic states of the nanoparticle

- Hypotheses
  - Only conduction electrons (5s)
  - Independent electrons
  - Jellium model (spherical finite potential)
  - No perturbation by the second NP

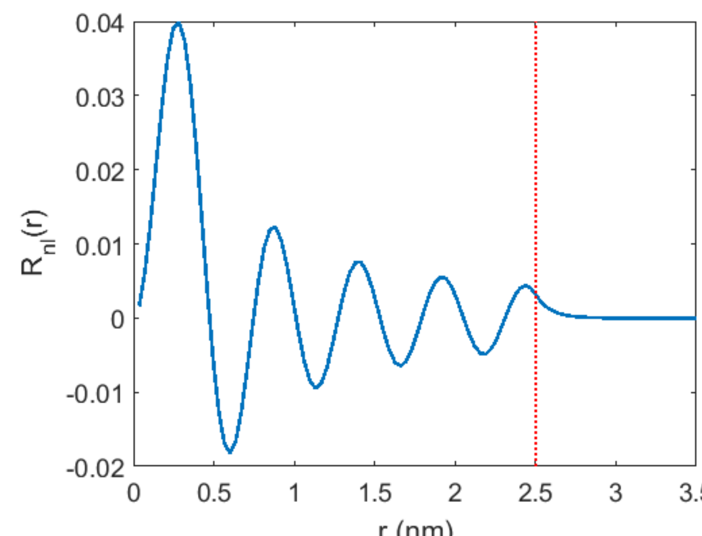


- Semi-analytical resolution of the Schrödinger equation

=> energies ε_i ,wave functions $\varphi_i(\mathbf{r})$ and occupancies at fundamental state



Density of states for a 5-nm Ag particle

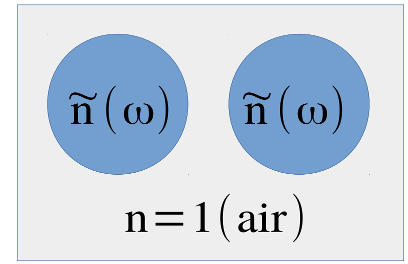


Radial part for the last occupied state

Our theoretical model

2. Optical properties

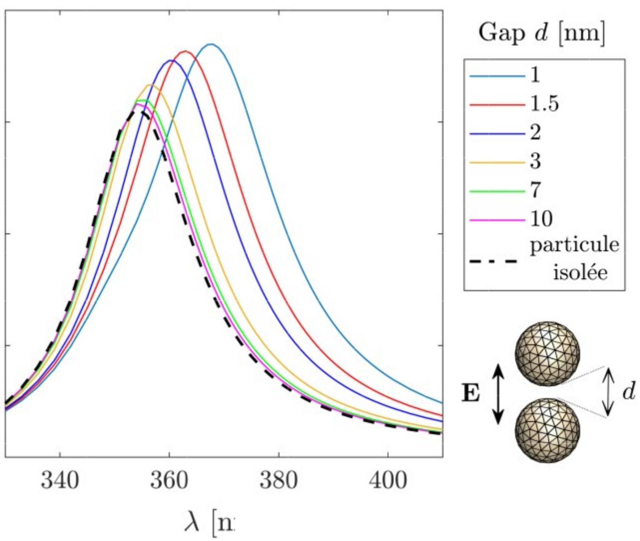
- Hypotheses
  - Homogeneous refractive index $\tilde{n}(\omega)$ for the metal
  - Abrupt interfaces
  - No tunneling between NPs



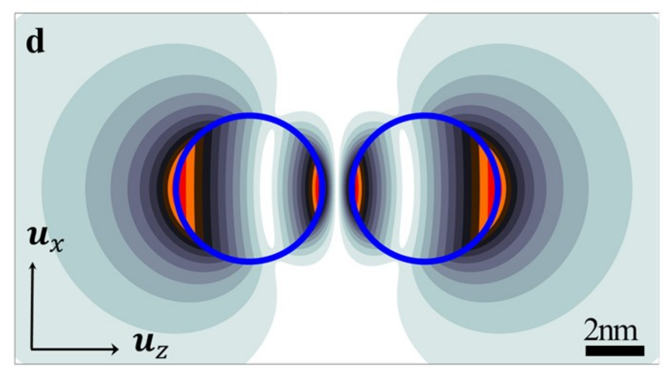
- Numerical resolution of the Maxwell equations

  => optical cross-section

  => optical potential inside and outside the NPs $V_{tot}(\mathbf{r},\omega)$



Absorption cross-section for increasing gaps



Optical potential at LSPR for dimer (d = 1 nm)

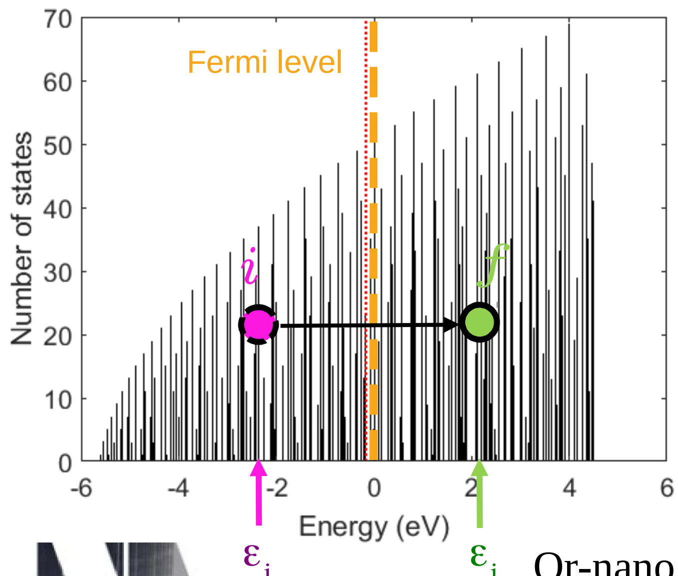
Our theoretical model

3. Time-dependent perturbation theory

- Optical potential => perturbation of the electronic states
  => electron transfer from occupied to empty states

- Hypotheses :
  - optical potential $V_{tot}(\mathbf{r},\omega) \ll$ jellium potential V_0
  - linear response (single-photon absorption)

- Numerical computation of the **transition rates between states** $\Gamma_{\varphi_i \to \varphi_f}(\omega)$



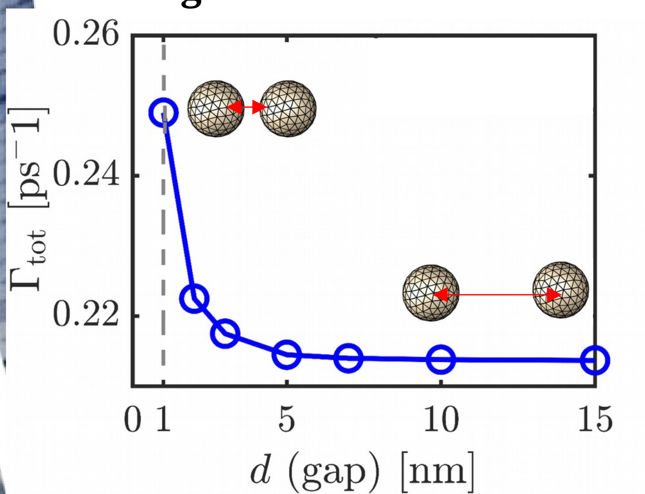
$$\Gamma_{\varphi_i \to \varphi_f}(\omega) = \frac{4}{\tau_p} F(\varepsilon_i)(1 - F(\varepsilon_f)) \frac{|\langle \varphi_i(\mathbf{r})| e V_{tot}(\mathbf{r},\omega) | \varphi_f(\mathbf{r}) \rangle|^2}{(\hbar\omega - \varepsilon_f + \varepsilon_i)^2 + \hbar^2 \tau_p^{-2}}$$

Results

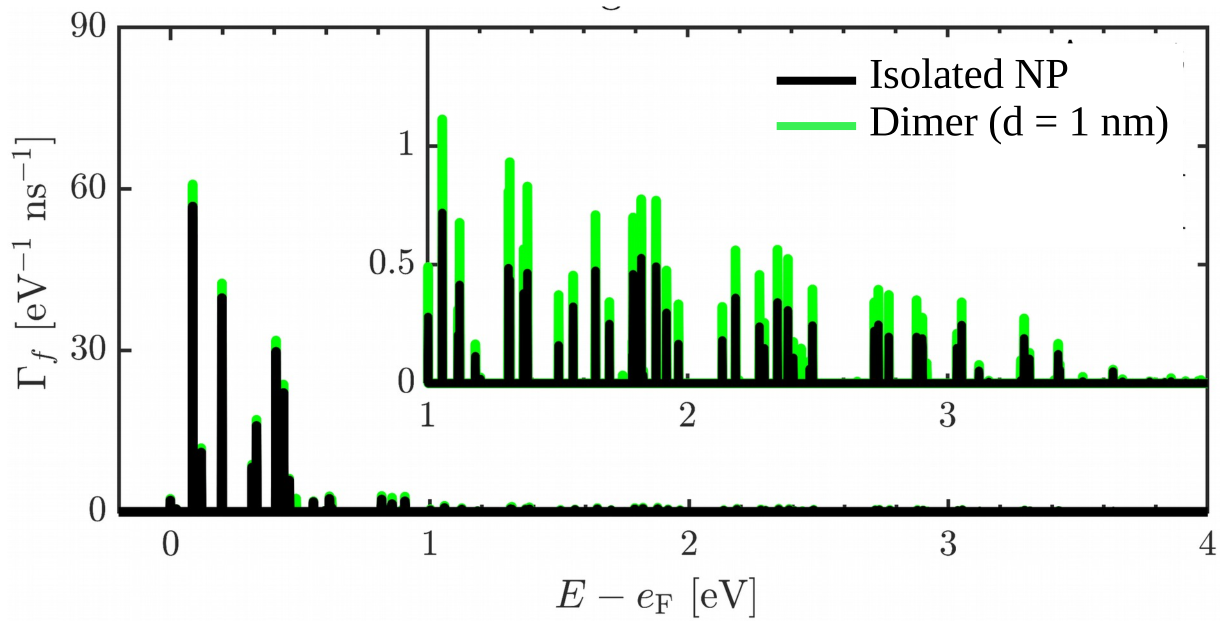
Generation rates

- Total generation rate : + 15%
- Increase at all energies
- Higher increase at high energies

Total generation rate of hot e-



Energy distribution of the generated hot e-

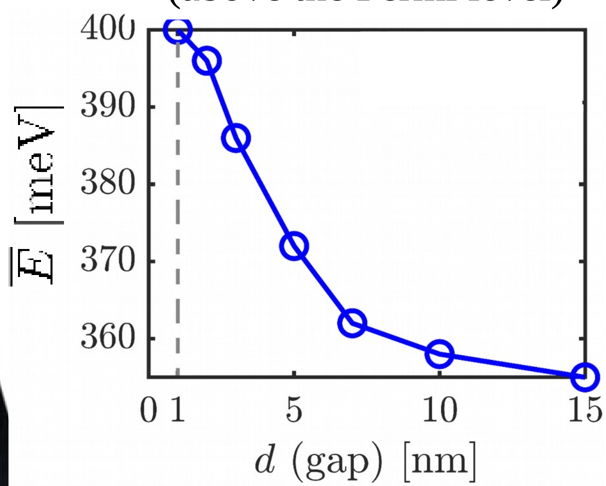


Results

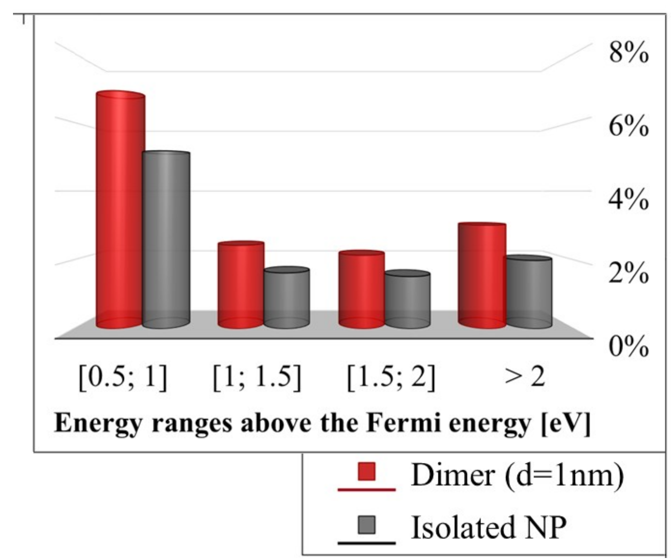
Energies

- Average energy of the hot electrons : 355 meV (single NP) => 400 meV (dimer)
- « Very hot electrons » with energies > 0,5 eV above the Fermi level :
  10 % (single NP) => 15 % (dimer)

Average energy of hot e-
(above the Fermi level)

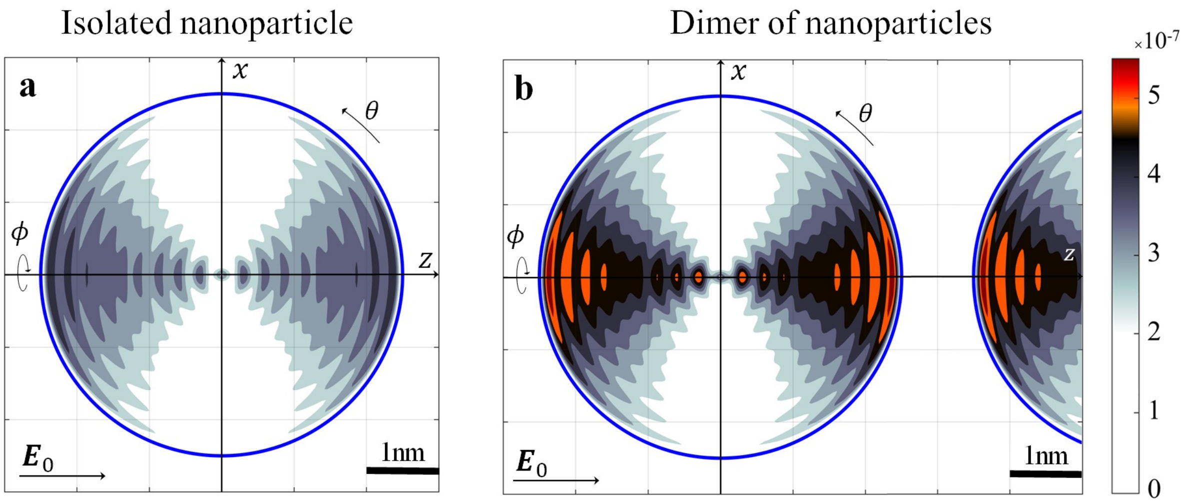


Proportion of « very hot electrons »



Results

Spatial distribution



- Slight increase in the hot electron spill-out : 1 % => 2 %
- Directionality
  - hot electrons preferentially generated in the direction of the incident field
  - effect enhanced in the dimer (+ 16%)
  - increase both in the gap and at the opposite side

Conclusions and perspectives

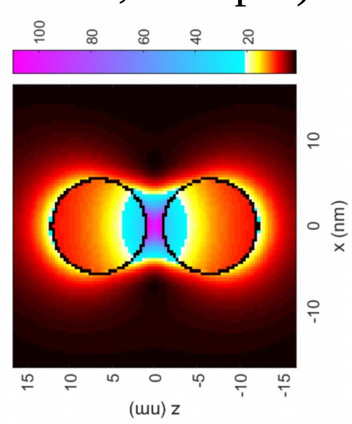
Semi-classical model for the generation of hot electrons

Electronic properties from quantum mechanics ← **Perturbation theory** → **Optical properties** from classical physics

=> Physical quantities: generation rates, energies, spatial distribution

Effect of inter-particle interactions

Modified optical properties
(redshift, hot spot)

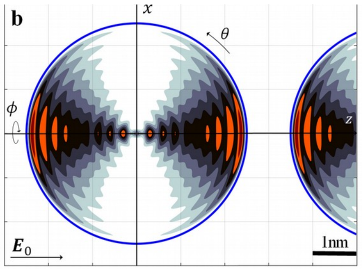


→

Improved hot e- generation

- ↗ Total generation rate
- ↗ Proportion of « very hot electrons »
- ↗ Directionality along the incident field direction

« Accessible » hot e- at the opposite side of the gap

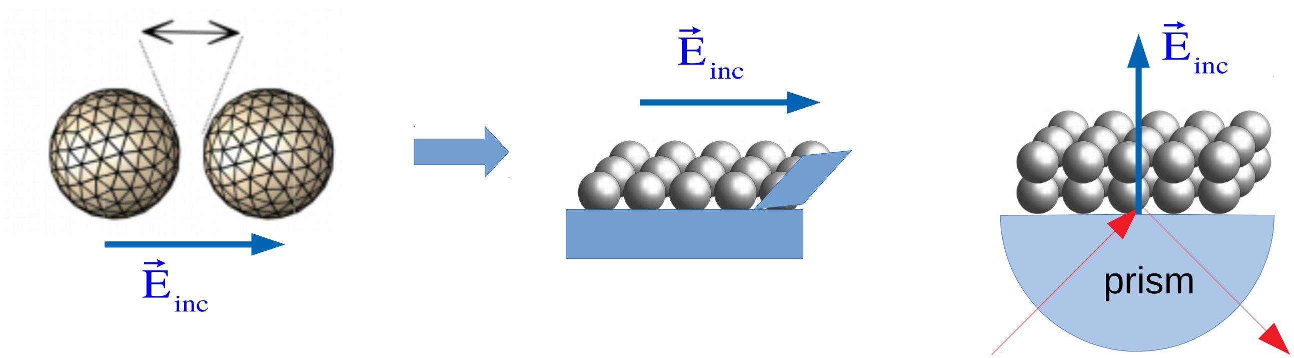


Conclusions and perspectives

Perspectives

– Compare with TD-DFT calculations (very small NPs)

– Explore relations between optical properties and hot electron generations
  => conception of new systems to improve hot electron generation



– Simulate electron transfer to adsorbed molecules (effective hamiltonian)

– **Experiments ?**

More details?

Orientational Selectivity of Hot Electrons Generated by a Dimer of Plasmonic Nanoparticles

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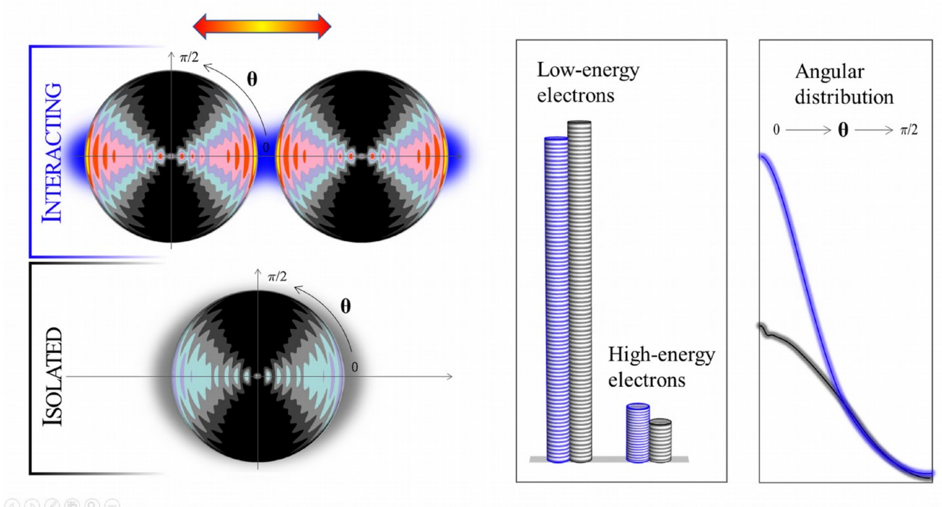

Thank you for attention !