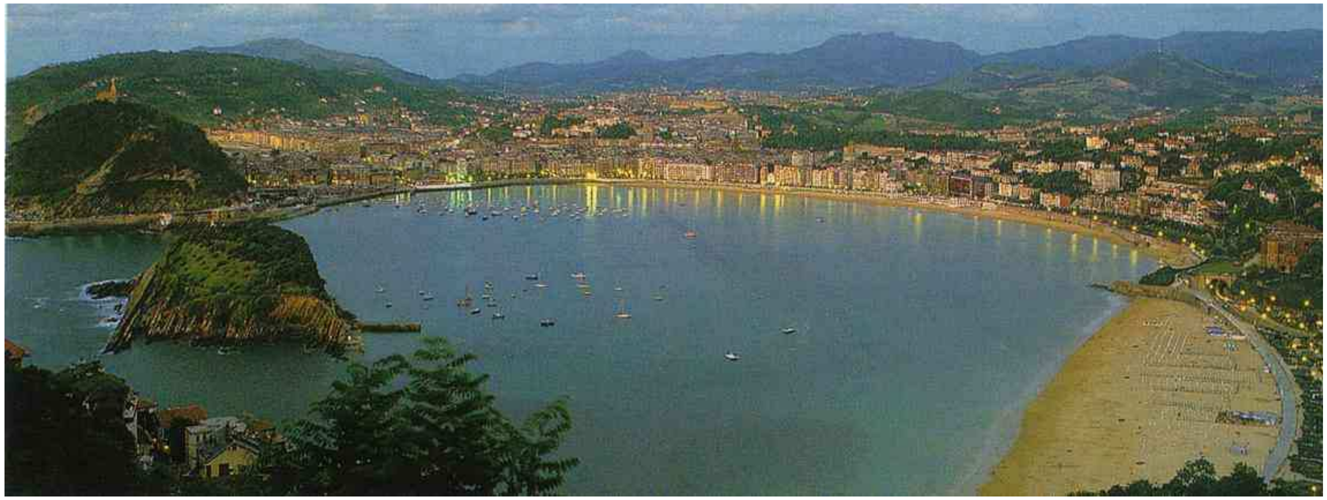

Size-dependent effects in the electron dynamics of metal clusters

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San Sebastián

ASEVA workshops 2006
WS-19: Physical and Chemical properties of Nanoclusters
Avila (Spain), September 25-27 2006

physics in San Sebastián

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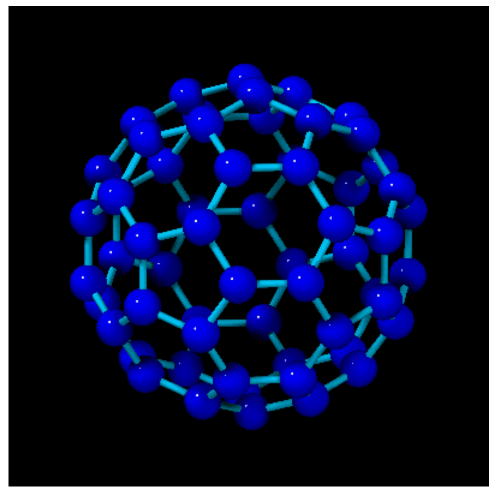
clusters as crossroads

physics

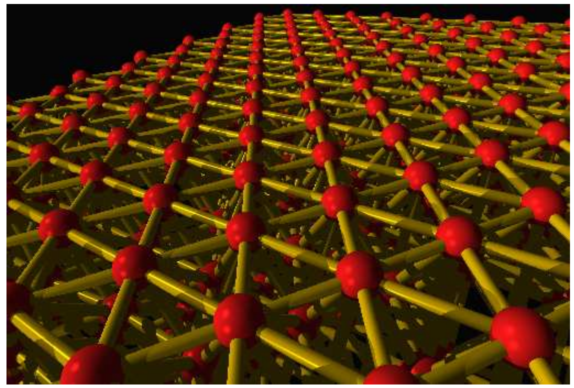
atoms and molecules

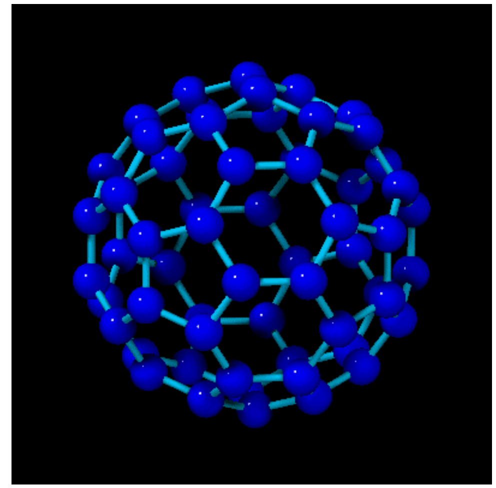


solid state

chemistry

clusters vs. bulk



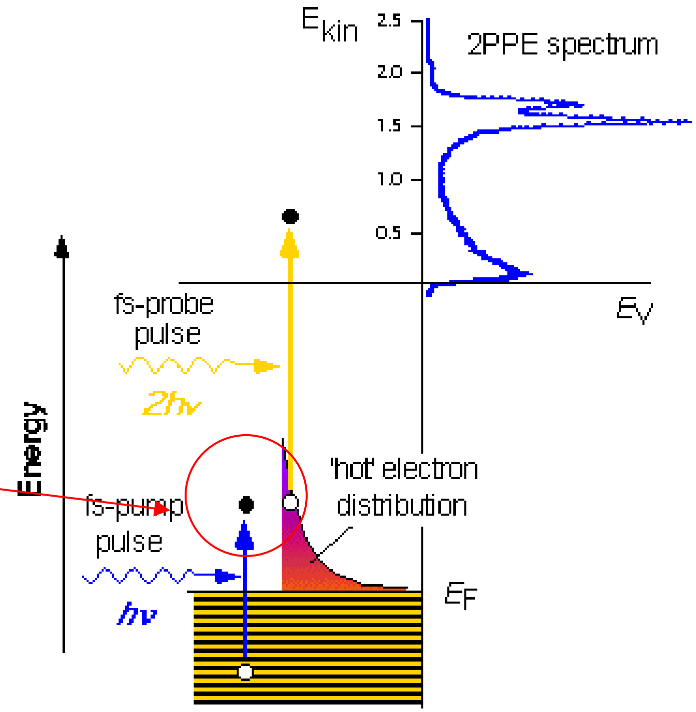


	metal single crystals	metal clusters
geometric structure	simple	complex
electronic structure	electron bands	discrete spectrum
chemical properties	fixed	**tunable**
optical properties	continous behavior	Mie: resonance behavior

lifetime of electronic excitations: 2PPE pump-probe experiments

a first (pump) laser pulse populates an unoccupied state and a second (probe) laser pulse photoemits the electron.

lifetime of the excitation



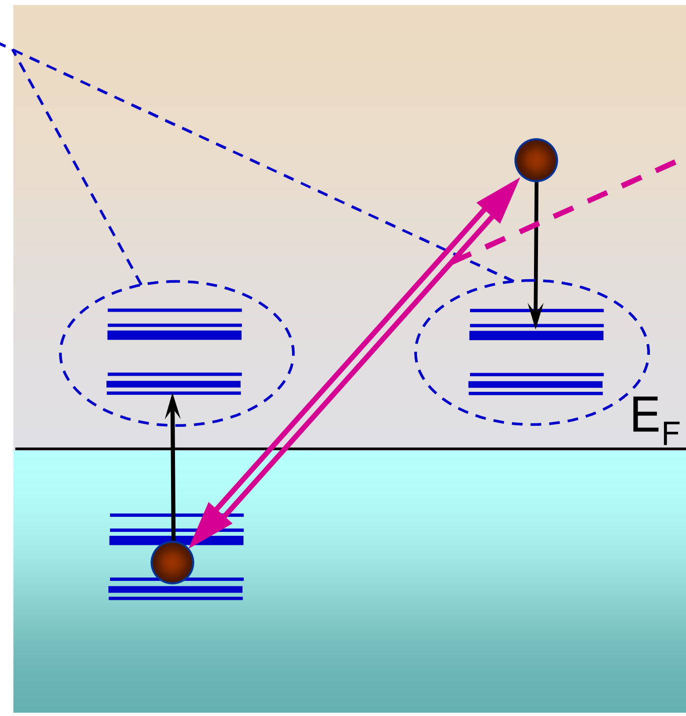
two main channels compete in electron relaxation:

electron-electron scattering
electron-phonon interaction

competition between them determines photochemical activity, for instance ... but also energy transfer, electron transfer across interfaces, etc.

decay of excitations in a FEG: density of states vs. screening

density of states
↓
more DOS
↓
more phase space available
↓
more probability for the process
↓
shorter lifetimes



screening
↓
more DOS
↓
more screening
↓
weaker interaction
↓
longer lifetimes

Free electrons
Quinn (1962)

$$\tau \approx \frac{263\, r_s^{-5/2}}{(E-E_F)^2} \propto \frac{n^{5/6}}{(E-E_F)^2}$$

questions to solve:

how does the lifetime of electronic excitations change when moving from infinite to finite nano-sized systems?

which is the dependence with size of the electronic excitation lifetimes?

lifetimes in clusters vs. lifetimes in solids: DOS effects

discretization of levels

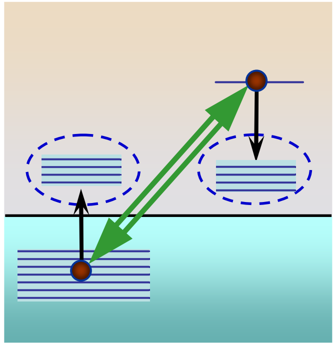
↓

less phase space available

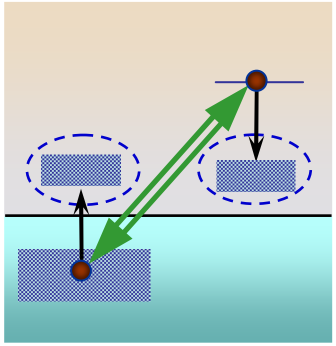
↓

longer lifetimes

clusters



FEG



$\tau_{cluster} > \tau_{FEG}$?

continuum spectrum

↓

more phase space available

↓

shorter lifetimes

lifetimes in clusters vs. lifetimes in solids: screening effects

surface effects and less electron mobility

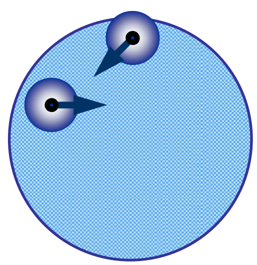
↓

less screening

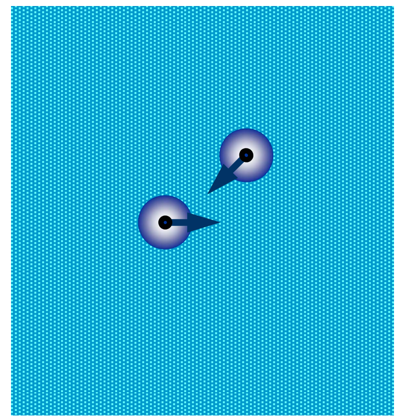
↓

shorter lifetimes

clusters



FEG



no surface, free electrons

↓

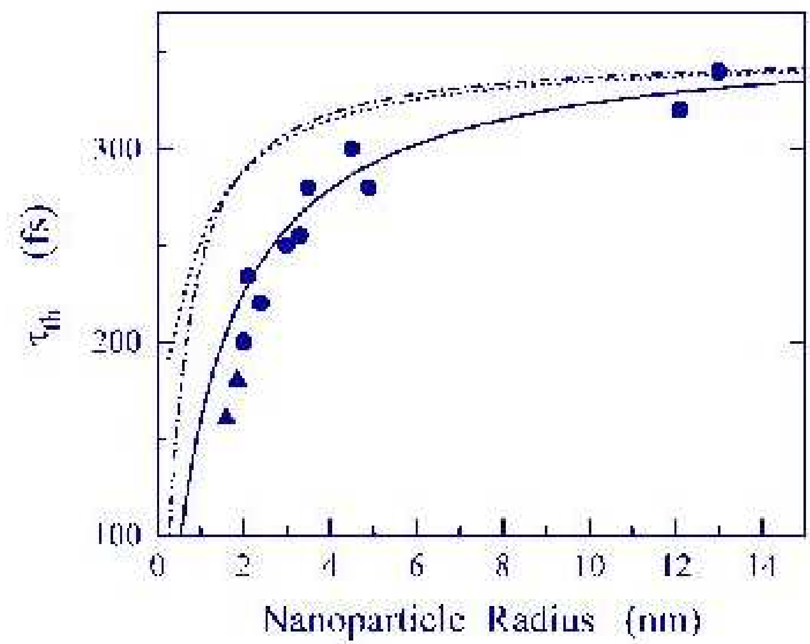
more screening

↓

longer lifetimes

$$\tau_{cluster} < \tau_{FEG} \, ?$$

experimental measurements of size-dependent electron dynamics



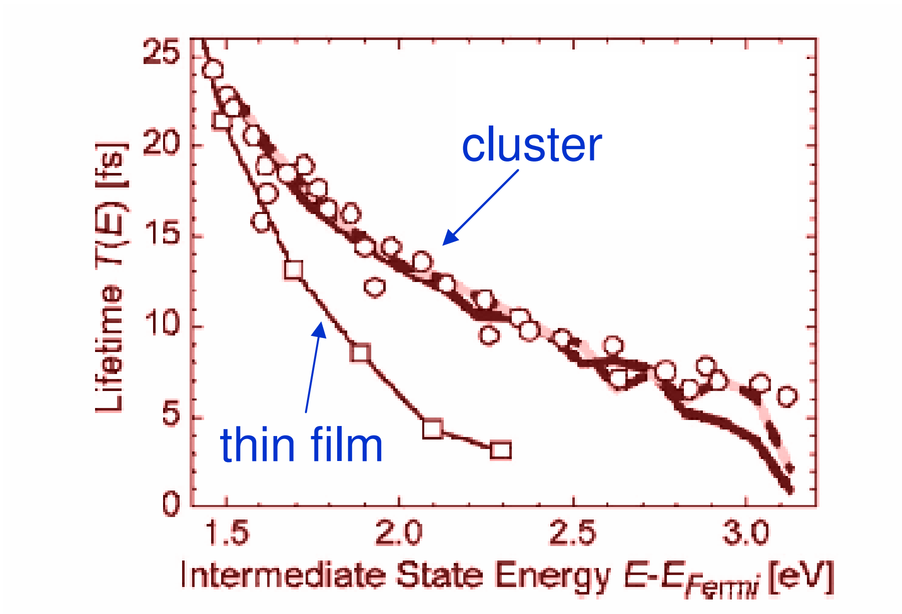
Ag nanoparticles

Voisin *et al.*,
Size-dependent electron-electron interactions in metal nanoparticles
*PRL **85**, 2200 (2000)*

*A sharp increase of the electron energy exchange rate is demonstrated for nanoparticles smaller than 5 nm.
... due to surface induced reduction of the Coulomb interaction screening.*

$$\tau_{cl} < \tau_{bulk}$$

experimental measurements of size-dependent electron dynamics



Ag 2nm nanoparticles

Merschdorf *et al.*,
Collective and single-particle dynamics
in time-resolved two-photon photoemission
PRB ***70****, 193401 (2004)*

*Experiments performed with TR 2PPES
on bulk Ag yield
significantly lower lifetimes
('as compared to clusters').*

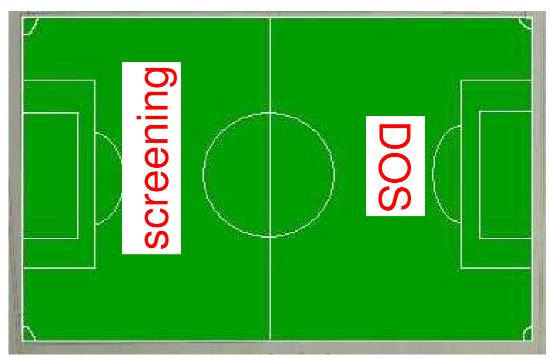
$$\tau_{cl} > \tau_{bulk}$$

lifetimes in clusters vs. lifetimes in solids

screening arguments: $\tau_{cluster} < \tau_{FEG}$?

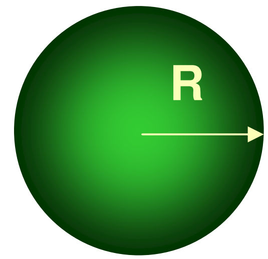
DOS arguments: $\tau_{cluster} > \tau_{FEG}$?

$$\tau_{cluster} \lessgtr \tau_{FEG} \, ?$$



1^{st} step: DFT calculation of a jellium cluster

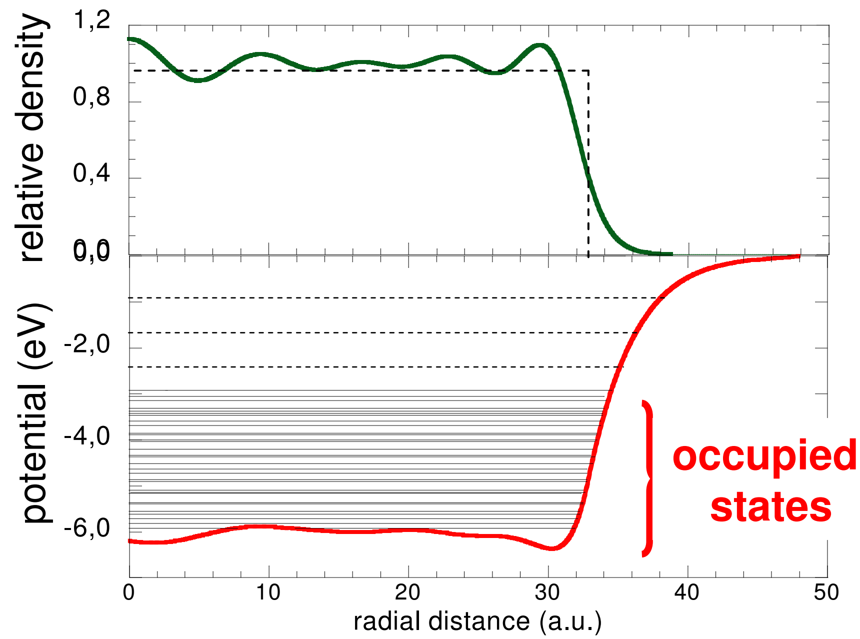
cluster is described in the jellium model (a background of constant positive charge)



Kohn-Sham equations solved self-consistently

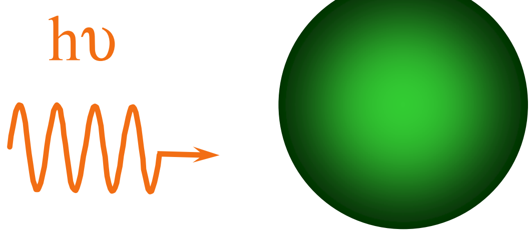
$$\left\{-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right\}\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{jellium}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

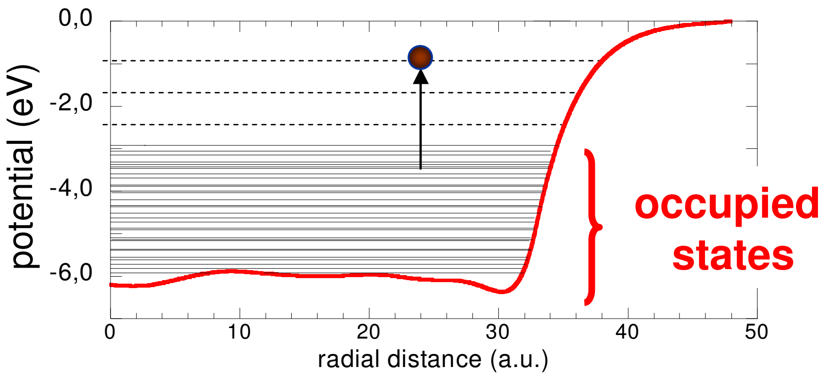


lifetimes of electronic excitations in metal clusters

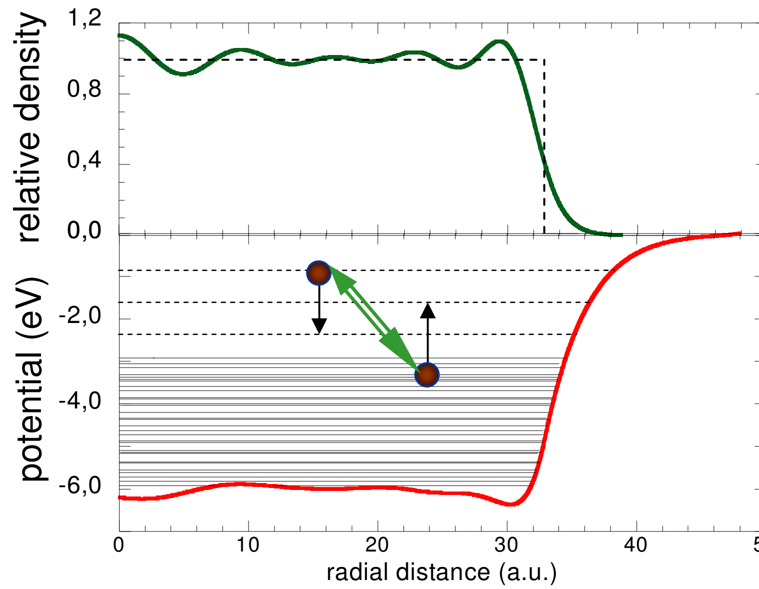
metallic clusters in excited electronic states



(excited by incident laser light, for instance)



decay of excitation through electron-electron interaction



2nd step: calculation of the linear response function χ(r,r',ω) and of the screened interaction W(r,r',w)

2a.- independent-particle response function $\chi_0(\mathbf{r},\mathbf{r}',\omega)$

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\varphi_2 \in occ.} \sum_{\varphi_3 \notin occ.} \left[\frac{\varphi_2^*(\mathbf{r})\varphi_2(\mathbf{r}')\varphi_3^*(\mathbf{r}')\varphi_3(\mathbf{r})}{\omega + \varepsilon_2 - \varepsilon_3 + i\delta} - \frac{\varphi_2(\mathbf{r})\varphi_2^*(\mathbf{r}')\varphi_3(\mathbf{r}')\varphi_3^*(\mathbf{r})}{\omega - \varepsilon_2 + \varepsilon_3 + i\delta} \right]$$

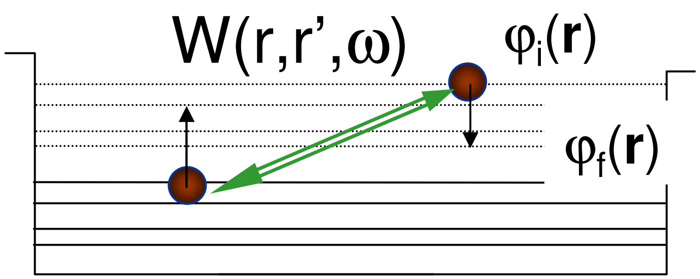
2b.- self-consistent calculation of $\chi(\mathbf{r},\mathbf{r}',\omega)$ in real space (RPA)

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi_0(\mathbf{r},\mathbf{r}',\omega) + \int d\mathbf{r}_1 d\mathbf{r}_2\, \chi_0(\mathbf{r},\mathbf{r}_1,\omega) \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \chi(\mathbf{r}_2,\mathbf{r}',\omega)$$

2c.- calculation of the screened Coulomb interaction $W(\mathbf{r},\mathbf{r}',\omega)$

$$W(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r}_1 d\mathbf{r}_2 \left[\frac{1}{|\mathbf{r} - \mathbf{r}_1|} \right] \chi(\mathbf{r}_1,\mathbf{r}_2,\omega) \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}'|} \right]$$

3rd step: calculation of the imaginary part of the self-energy GW approximation

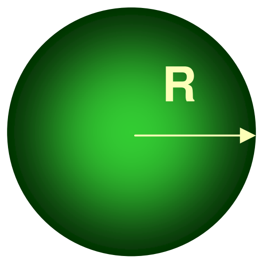


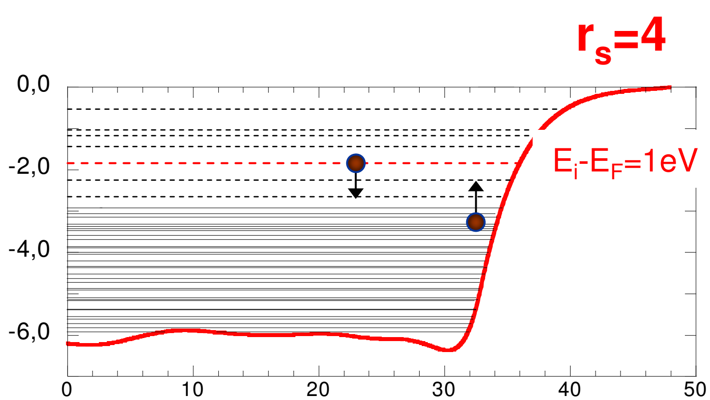
$\varphi_i(\mathbf{r})$ is a KS unoccupied wavefunction that represents the initial state in the decay
$\varphi_f(\mathbf{r})$ is a KS unoccupied wavefunction that represents the final state in the decay

calculation of the decay rate $\Gamma=\tau^{-1}$

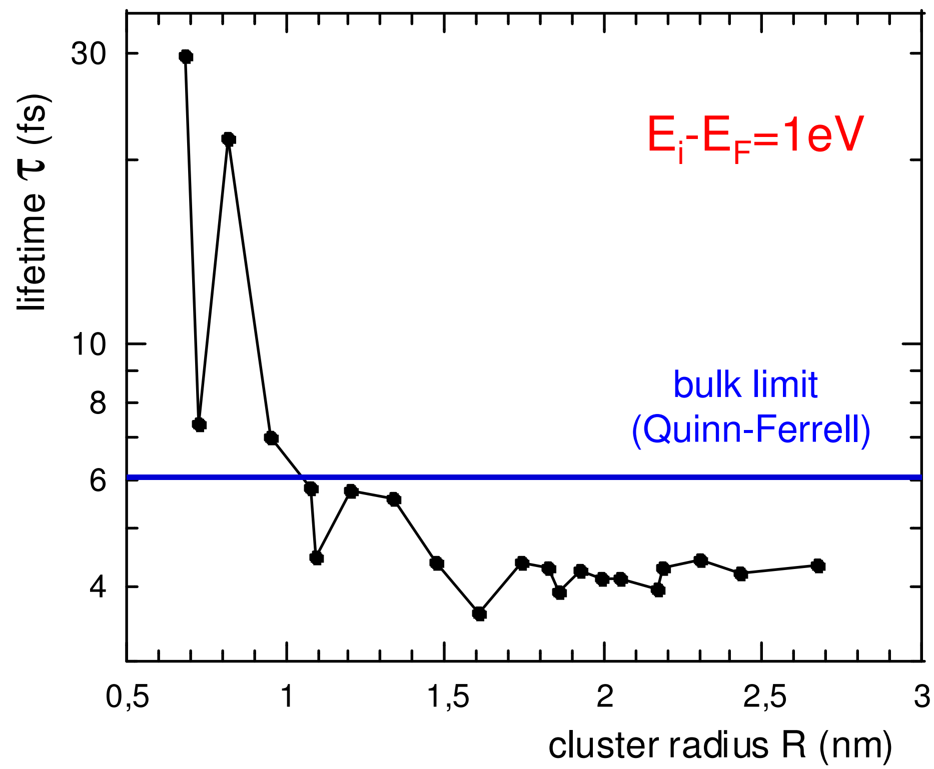
$$\Gamma_i = -2 \sum_{f \notin occ.} \int d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \varphi_f^*(\mathbf{r}') \mathrm{Im} W(\mathbf{r},\mathbf{r}',\omega) \varphi_i(\mathbf{r}') \varphi_f(\mathbf{r})$$

size-dependence of the decay rate for electrons excited ~1 eV above the Fermi level



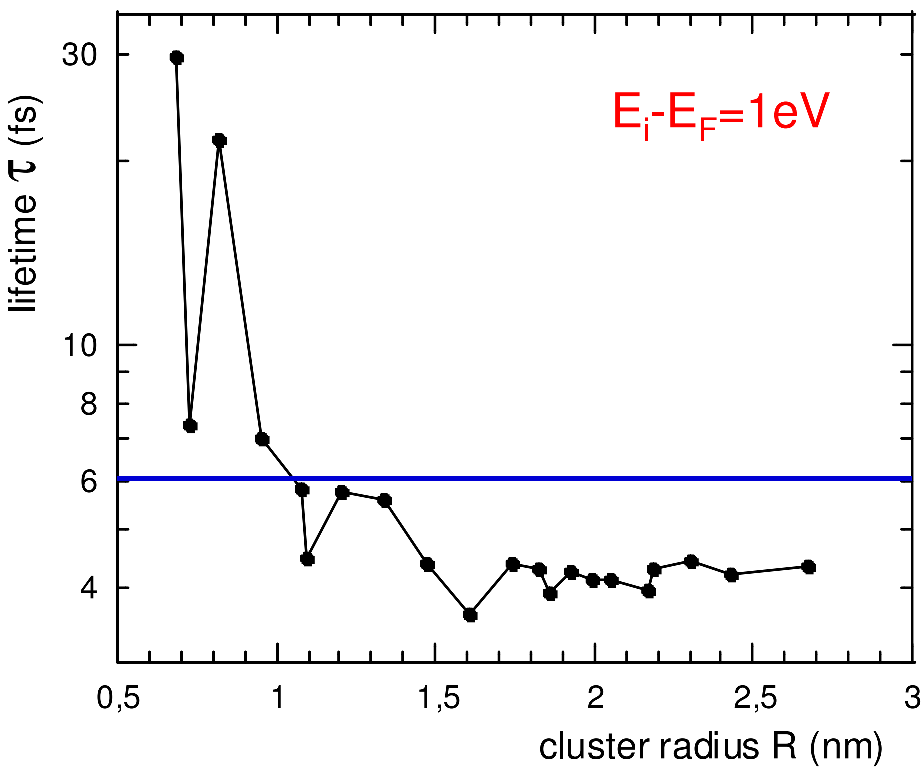


we sum over all possible final states



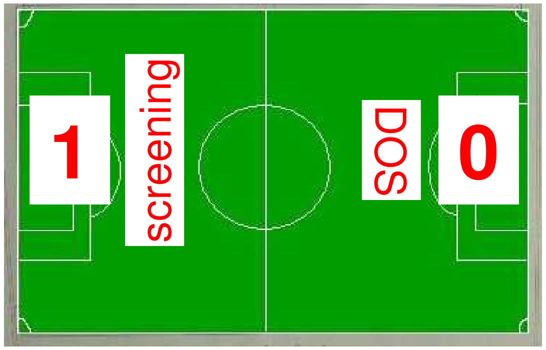
*Quijada et al., Nanotechnology **16**, 176 (2005)*

size-dependence of the decay rate for electrons excited ~1 eV above the Fermi level

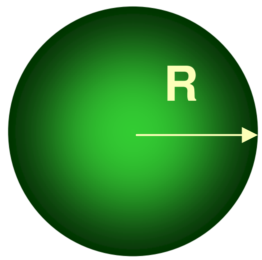


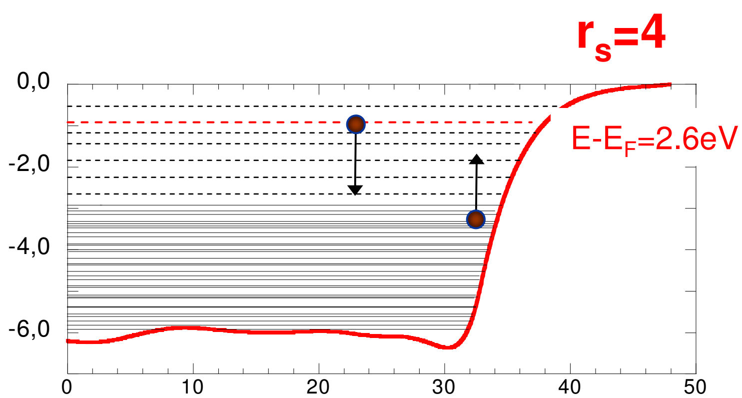
- electron lifetimes in clusters range between 3 and 30 fs for E~1 eV
- order of magnitude is similar in a FEG
- oscillations due to the discretization of levels

$$\tau_{cluster} < \tau_{FEG}!$$

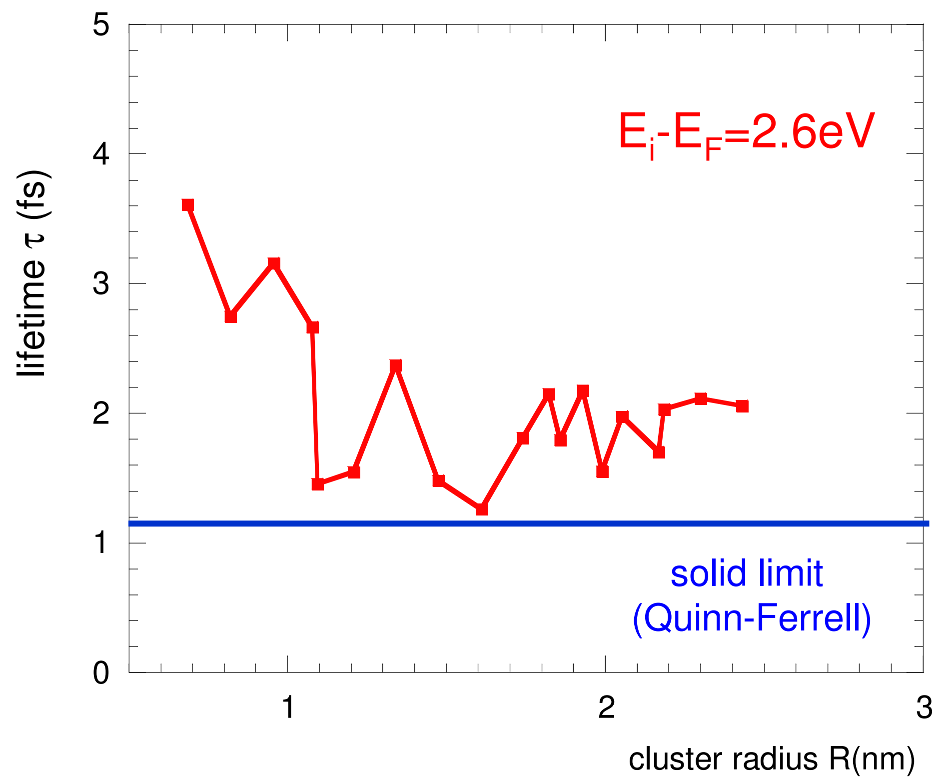


size-dependence of the decay rate for electrons excited ~2.6 eV above the Fermi level

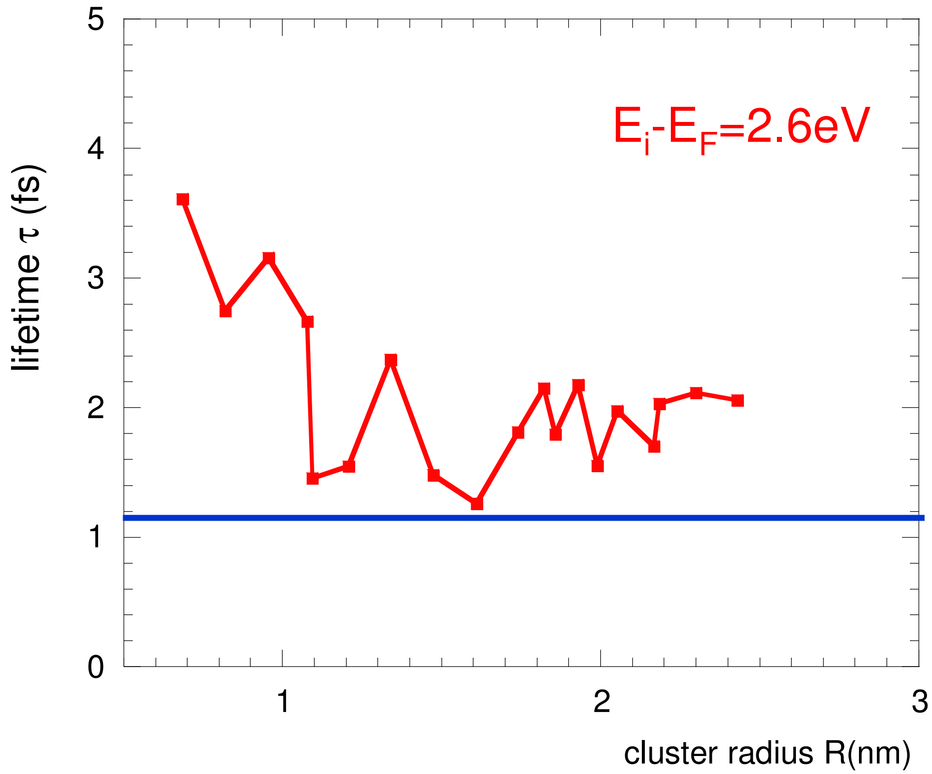




we sum over all possible final states

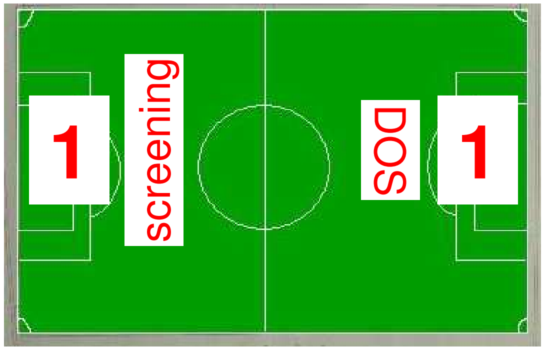


size-dependence of the decay rate for electrons excited ~2.6 eV above the Fermi level



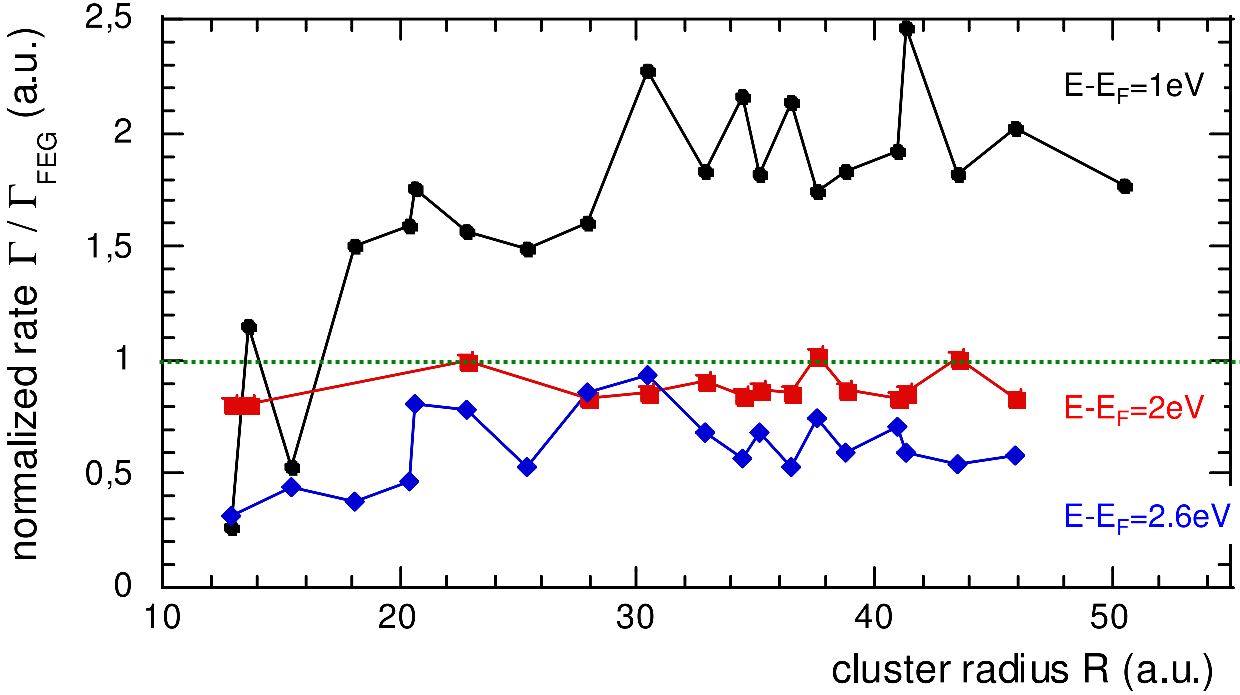
Electron lifetimes in clusters range are ~2fs for E~2.6eV (slightly longer than solids)

$$\tau_{cluster} > \tau_{FEG}!$$



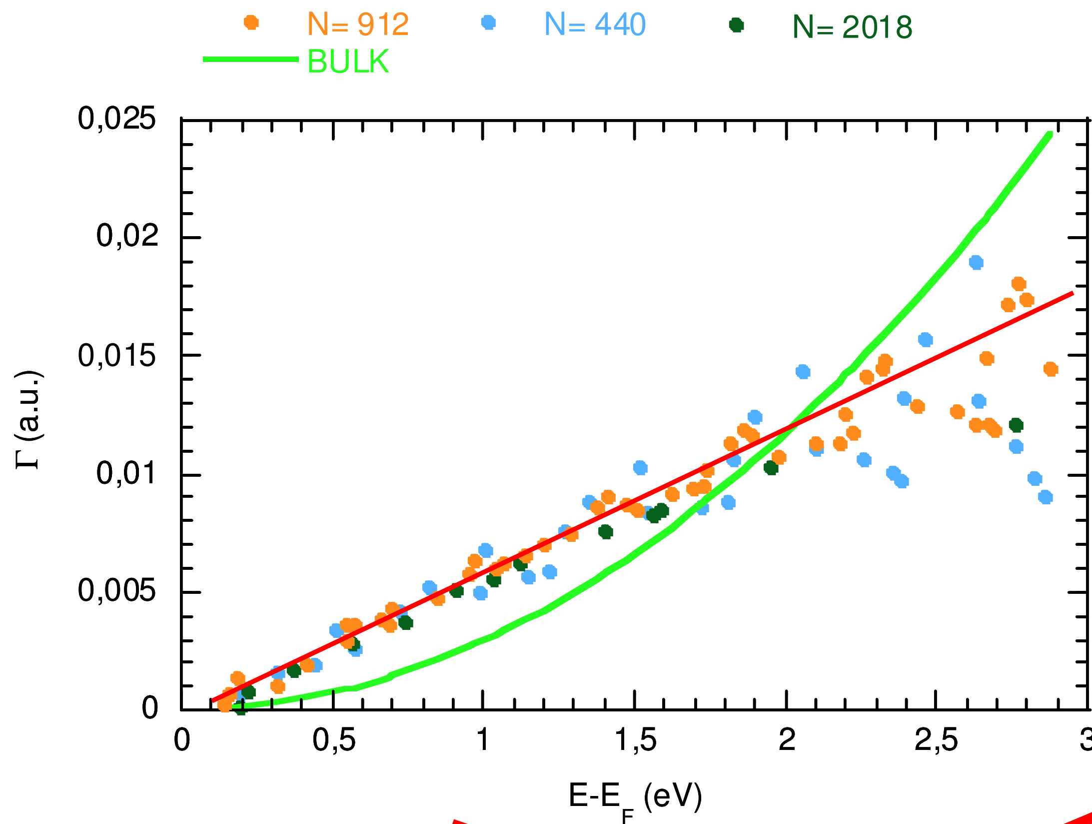
size-dependence of the decay rate for electrons

decay rate Γ normalized to the solid (FEG) value



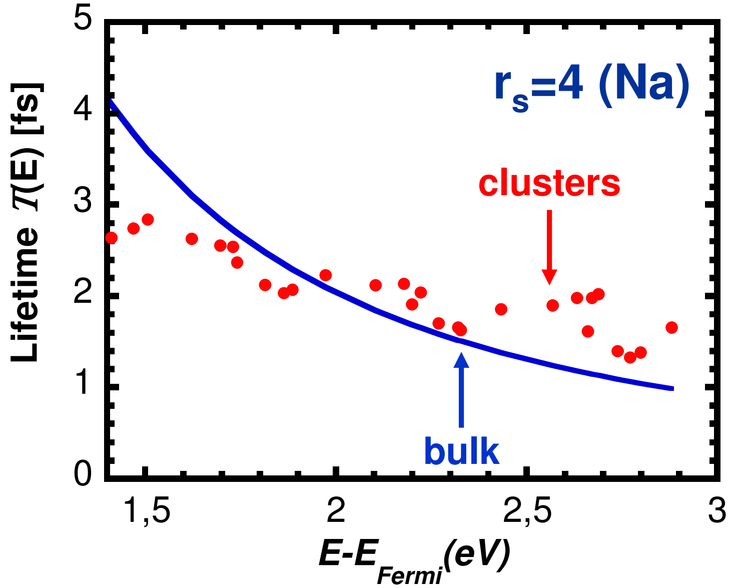
$$\tau_{cluster} \lessgtr \tau_{FEG} \,?$$

initial energy dependence of the decay rate

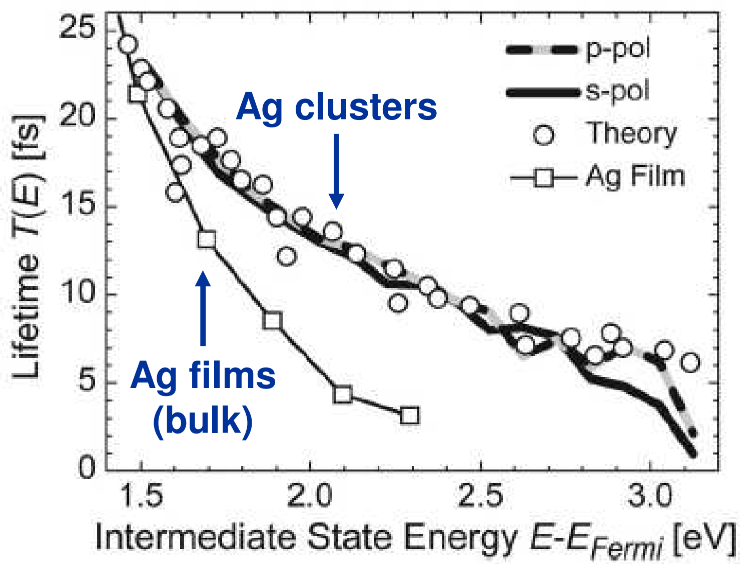


free electrons: $\tau \approx \frac{263\, r_s^{-5/2}}{(E-E_F)^2} \propto \frac{n^{5/6}}{(E-E_F)^2}$

comparison of lifetimes in solids and nanosized clusters



Theoretical calculation
for (gas-phase) Na clusters
of ~ 4nm diameter



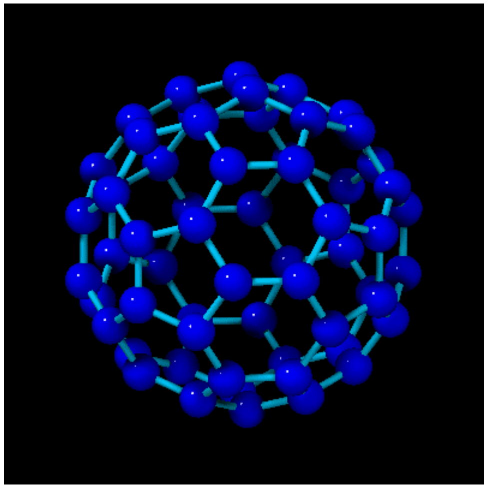
Experimental measurements
for (supported) Ag clusters
of ~ 2.2nm diameter
Merschdorf *et al.*,
PRB **70**, 193401 (2004)

electron lifetimes in metal nanoparticles: conclusions

- Electron lifetimes in metal clusters are of the order of few femtoseconds (not far from those in solids), for sufficiently large (nm) clusters

- Nevertheless, in this size range, there are apparent differences with respect to the free-electron gas: lifetimes can be either larger or shorter depending on the excitation energy

- There is not a clear winner in the screening versus DOS competition: the free-electron gas dependence $\tau \sim 1/(E-E_F)^2$ is broken!



thank you for your attention

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