Real-time TDDFT simulations within SIESTA

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Main objective

Apply "real-time" simulations within time-dependent density functional theory (TDDFT) to study electron and coupled electron-ion dynamics for solids and clusters

Keywords:

TDDFT to follow the electron dynamics:

- **Standard approach for electronic response of solids**
- **Similar results to RPA with less sophisticated (normal) XC kernels**

"Real-time" simulations (as opposite to frequency domain):

- **Arbitrary perturbations, i.e., non-linear regime available**
- **Need for very stable algorithms for time evolution**

"Ehrenfest dynamics" for the coupled electron-ion dynamics

DFT– (Kohn – Sham)

Independent particles in an effective potential

$$-\frac{1}{2}\nabla^2\,\psi_n(\vec{r})+V_{eff}(\vec{r})\,\psi_n(\vec{r})=\varepsilon_n\,\psi_n(\vec{r})$$

$$V_{eff}(\vec{r})=V_{ext}(\vec{r})+\Phi(\vec{r})+V_{xc}[\rho] \quad \textit{with} \quad \rho(\vec{r})=\sum_n^{N_e}|\psi_n(\vec{r})|^2$$

Hatree potential

$$\Phi(\vec{r})=\int d\vec{r}'^3\,\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

Exchange-correlation potential

$$V_{xc}(\vec{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

Extension to time dependent situations: Time dependent density functional theory

Time dependent quantum evolution can be obtained from a stationary point of the action $A(t_0,t_1)$

$$A = \int_{t_0}^{t_1} dt \left\langle \Psi(t) \middle| \frac{\partial}{\partial t} - \hat{H}(t) \middle| \Psi(t) \right\rangle$$

TDDFT

$$A = A[\rho(r,t), \Psi(r,t_0)]$$

E. Runge and E. K.U. Gross, PRL (84)

In practice, TDKS equations

$$-\frac{1}{2}\nabla^2 \psi_n(\vec{r},t) + V_{eff}(\vec{r},t)\,\psi_n(\vec{r},t) = i\frac{\partial}{\partial t}\psi_n(\vec{r},t)$$

$$V_{eff}(\vec{r},t) = V_{ext}(\vec{r},t) + \Phi(\vec{r},t) + V_{xc}[\rho(t), \vec{j}(t)]$$

Standard approximation (also in SIESTA)

So-called "adiabatic" ("static") approximation for the exchange-correlation potential

$$V_{\mathrm{xc}}[\rho](\mathbf{r},t) \cong \frac{\delta E_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_t]}{\delta \rho_t(\mathbf{r})} = V_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_t](\mathbf{r}).$$

Depends on instantaneous density

Electron dynamics in SIESTA I

TD-KS equations:

$$i\frac{\partial \Psi}{\partial t} = H\Psi$$

SIESTA (LCAO):

$$\Psi_i(r,t) = \sum c_i^{\mu}(t)\phi_{\mu}(r)$$

$$\rho(r,t) = \sum_{\mu,\nu} \rho_{\mu\nu}(t)\phi_{\mu}(r)\phi_{\nu}(r)$$

$$iS_{\mu\nu}\frac{\partial c^{\nu}}{\partial t} = H_{\mu\nu}c^{\nu} \quad \Rightarrow \quad i\frac{\partial c}{\partial t} = S^{-1}Hc$$

Electron dynamics in SIESTA II

Discretization of TD-KS equations:

$$i\frac{\partial c}{\partial t} = S^{-1}Hc$$

Forward propagation for dt/2

$$c(t_{n+1/2}) = c(t_n) - i\frac{\Delta t}{2}S^{-1}H(t_n)c(t_n)$$

Backwards propagation for dt/2

$$c(t_{n+1/2}) = c(t_{n+1}) + i\frac{\Delta t}{2}S^{-1}H(t_{n+1})c(t_{n+1})$$

$$H(t_{n+1}) = H(t_n) + O(\Delta t)$$

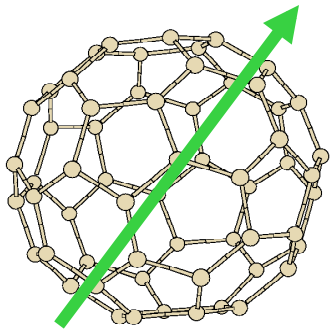
Crank-Nicholson

- **Unitary by construction**
- **Good energy conservation**
- **Time reversal symmetry**

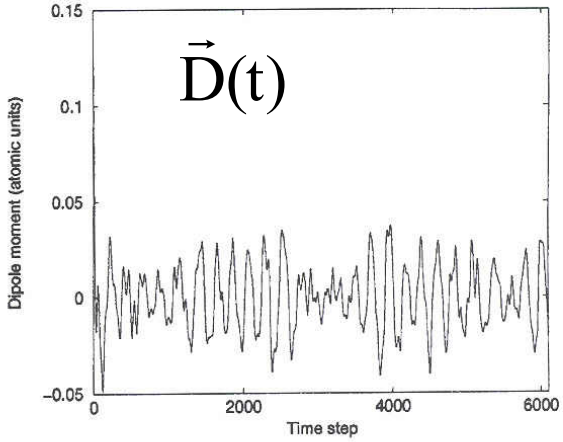
$$c(t_{n+1}) = \frac{1 - iS^{-1}H(t_n)\frac{\Delta t}{2}}{1 + iS^{-1}H(t_n)\frac{\Delta t}{2}}c(t_n)$$

Applications to calculate optical adsorption

A. Tsolakidis, D. Sánchez-Portal, R. M. Martin, PRB(2002), adapting a recipe by Yabana and Bertsch, PRB (1996)

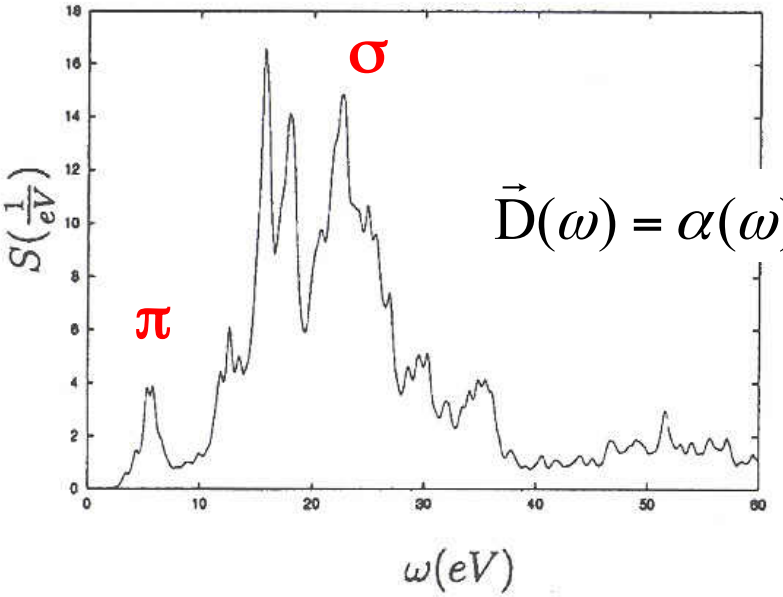


$\vec{E}$



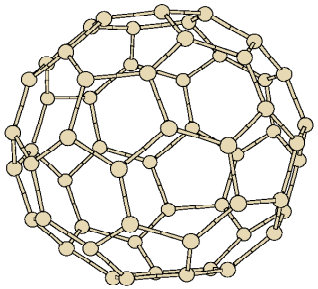
Low energy peaks with TDLDA

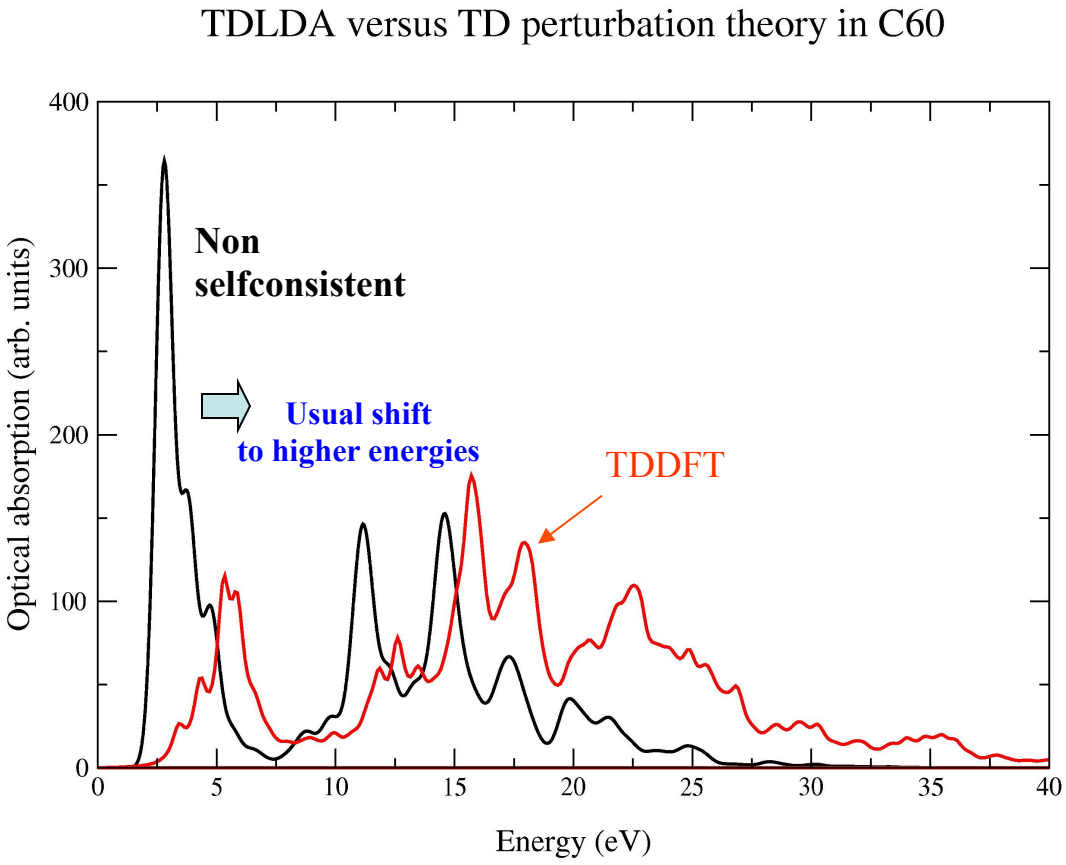
SIESTA	Yabana	Exp.
3.5	3.4	3.8
4.4	4.3	
5.4	5.3	4.8
5.8	6.0	5.8



$$\vec{D}(\omega) = \alpha(\omega)\,\vec{E}(\omega)$$

TDDDFT versus Kohn-Sham result

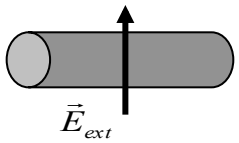




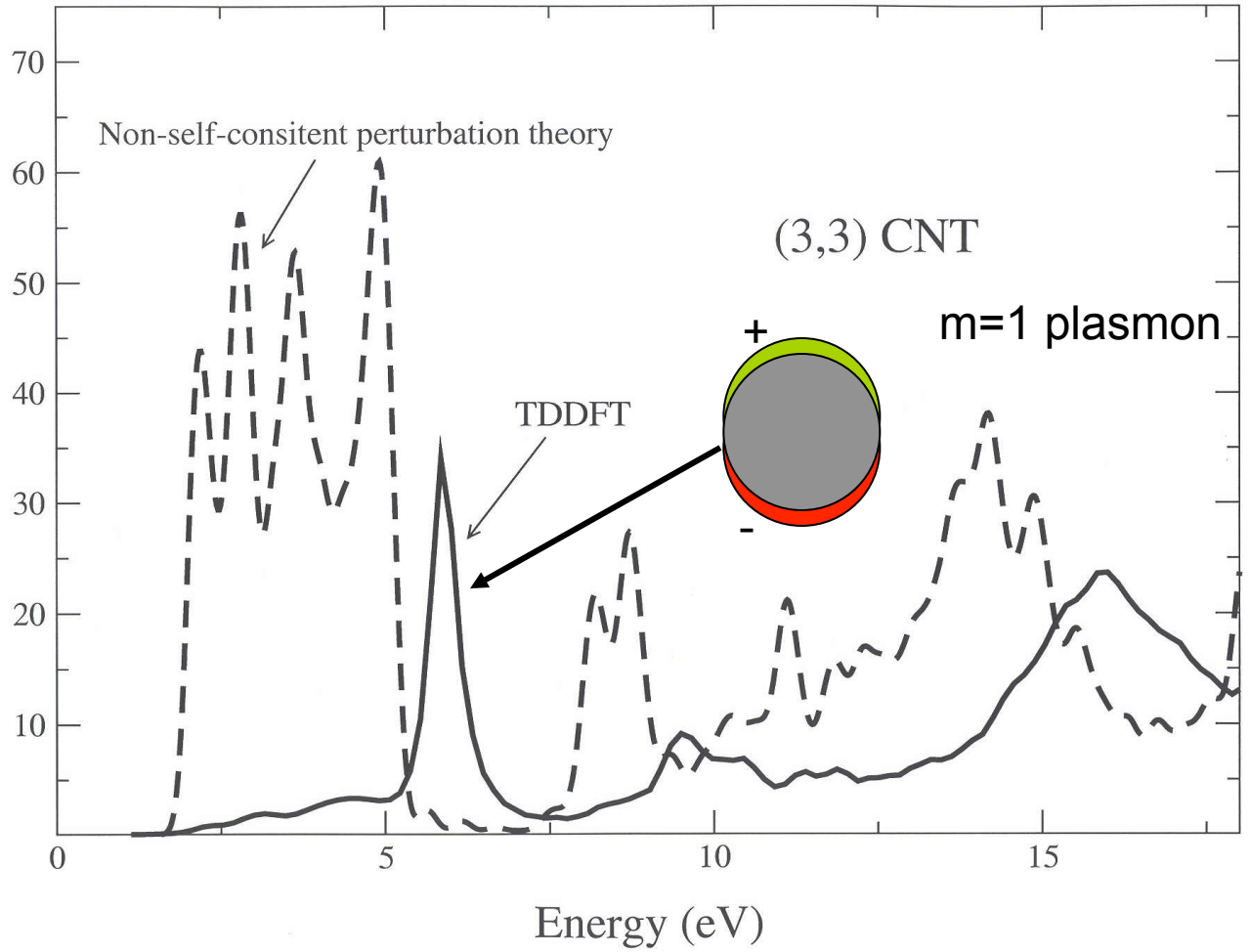
A. Tsolakidis, D. Sánchez-Portal, R. M. Martin,
Phys. Rev. B **66**, 235416 (2002)

Response of carbon nanotubes to a external field perpendicular to the axis

Strong depolarization effect

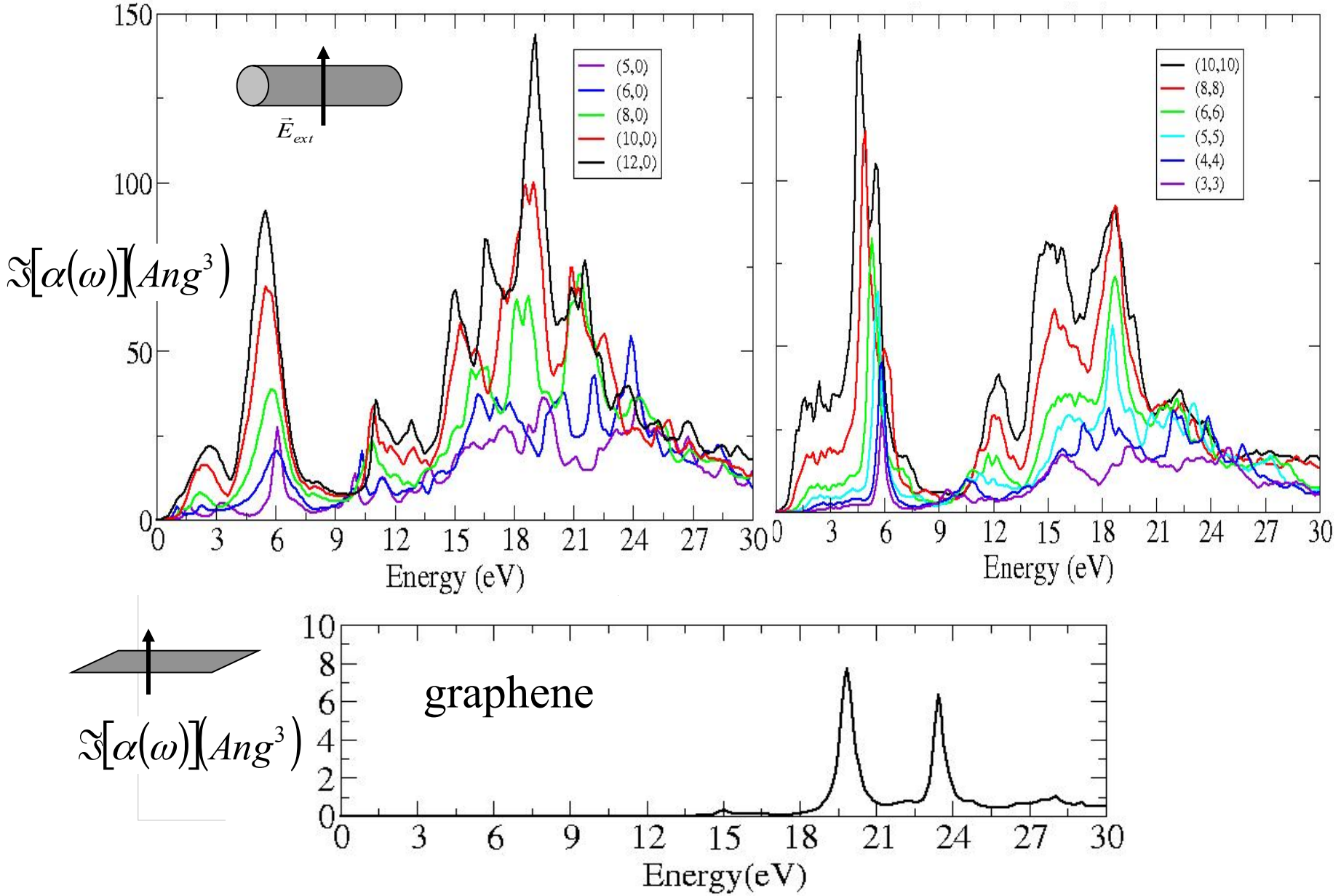


$$\Im[\alpha(\omega)](Ang^3)$$

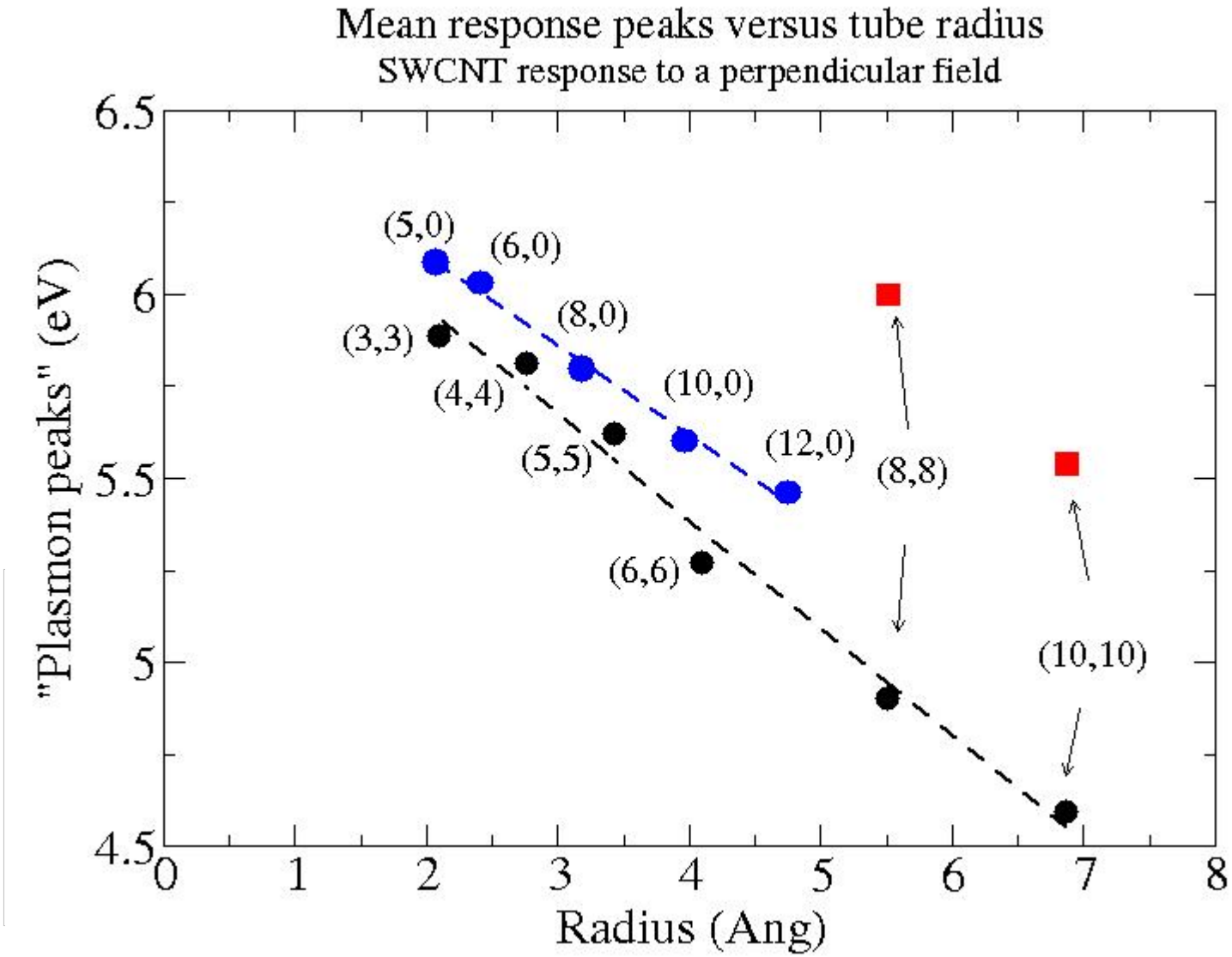


Our calculation for the (3,3) tube in very good agreement with the results L. Wirtz, *et al. (Electronic Properties of Novel Materials: XVIIth International Winterschool*, 2003) and Marinopoulus, Reining, Rubio,Vast, (PRL, 2003)

Results for SWCNT of larger diameters



m=1 π plasmon as a function of the tube radius



Key approximations for coupled electron dynamics

$$\psi(t) = \sum_{\mu} c^{\mu}(t)\,\phi_{\mu}(\vec{r} - \vec{R}_{\mu}(t))$$

$$\frac{\partial \psi}{\partial t} = \sum_{\mu} \frac{\partial c^{\mu}}{\partial t}\,\phi_{\mu} - c^{\mu}\,\vec{v}_{\mu}.\vec{\nabla}\phi_{\mu}$$

Basis set movement gives rise to additional terms, dependent on velocities, that are ignored in our case. Instead we perform the electron dynamics for static ions and project the wavefunctions from one set of atomic positions to the following (trick by Sankey and Tomfohr).

- Instead we use an approximate unitary projector operator [proposed by Tomfohr and Sankey, PSSb (2001)] to find the new coefficients of the wavefunctions in the translated basis set
- This works well when ion velocities are not "*very*" large
- Time step used for ion dynamics is sufficiently small

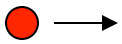
Application to study electronic stopping power in solids

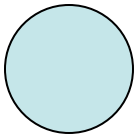
Computing the energy loss

TDDFT calculation of the energy loss as a function of the speed of the projectile
Very simple for a localized target:

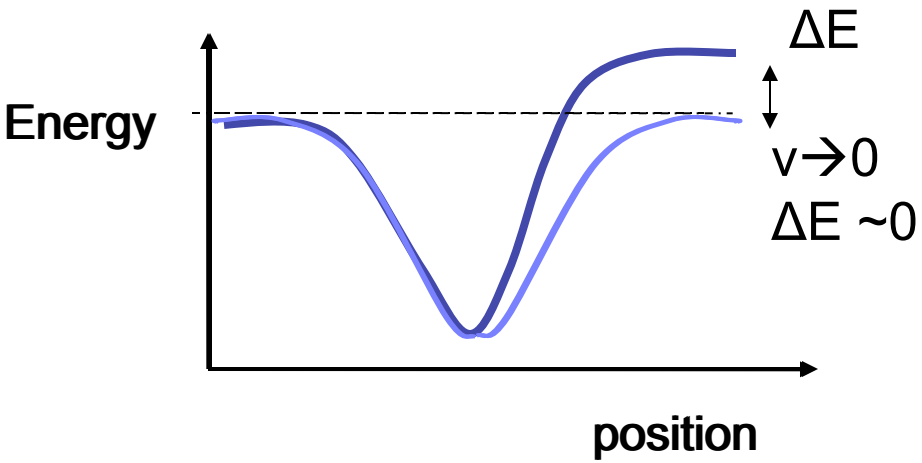
Add a perturbation and …..

1) Displace the perturbation with constant velocity and record the total energy
2) Compute the force on projectile and integrate



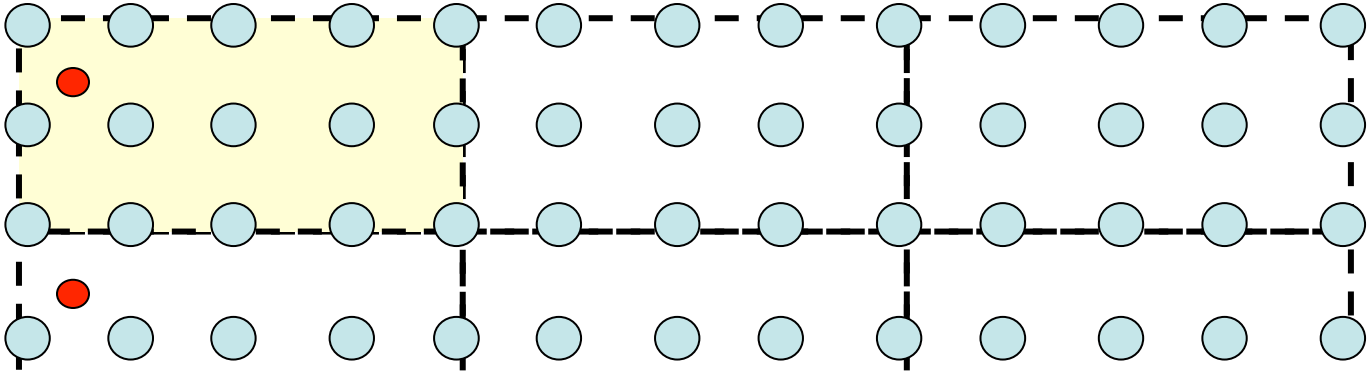


Localized scatterer



Will something similar work for a solid?

Solids ?



- **Periodic boundary conditions: finite size effects**
- **Initially static perturbation: transient effects** **?**

Achieving a stationary regime is necessary for a meaningful definition of the stopping power in solids:

$$\frac{dE}{dx} = \frac{1}{\mathrm{v}} \frac{dE}{dt}$$

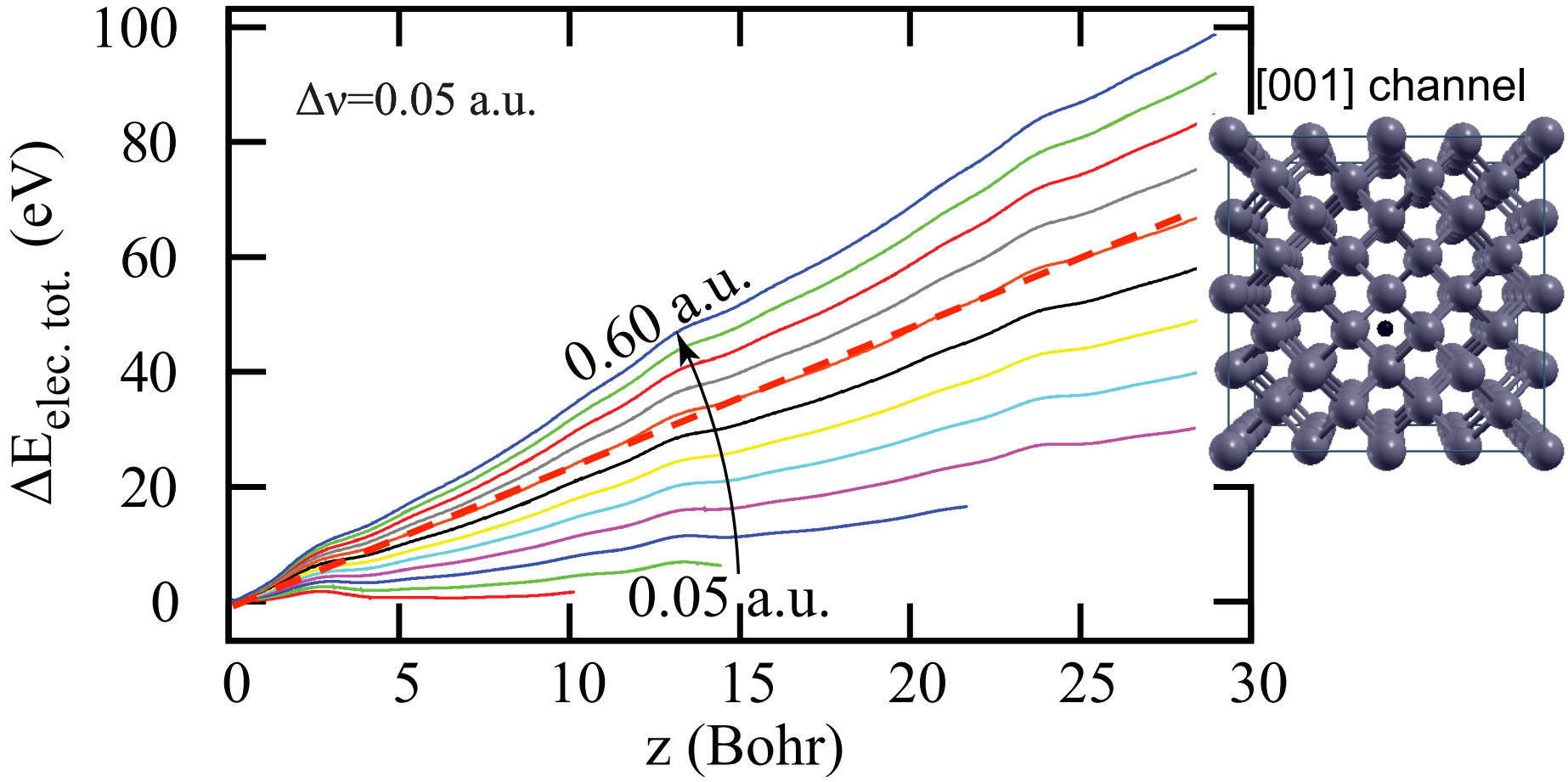
Main result

Real-time TDDFT simulations seem to work to study electronic stopping in solids

- **Periodic boundary conditions/finite size effects do not seems to affect for supercells of reasonable size, at least at low velocities (< 0.5 a.u.)**
- **Very brief transients**
- **Stationary increase of the energy achieved, allowing for the definition of an electronic stopping power**

H in Germanium

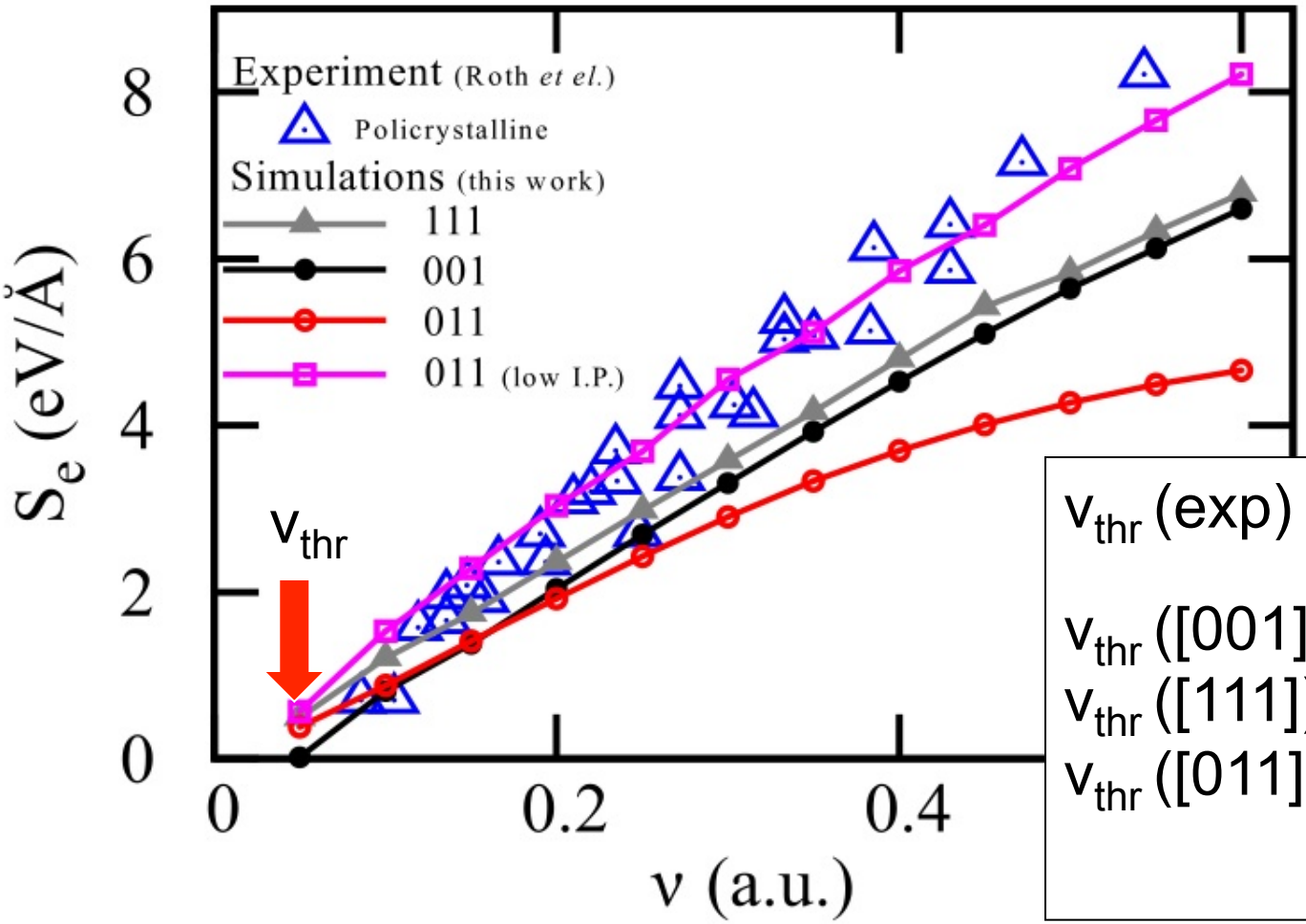
96 atoms supercell (up to 144 in checks)



R Ullah, F Corsetti, D Sanchez-Portal & E Artacho (PRB 2015)

H in Germanium

Experimental data: D. Roth, D. Goebl, D. Primetzhofer, and P. Bauer, (NIMB 2013).



v_{thr} (exp) ~ 0.03 a.u.

v_{thr} ([001]) ~0.05 a.u.
v_{thr} ([111]) ~0.03 a.u.
v_{thr} ([011]) ~0.03 a.u.

Electronic stopping power vs velocity

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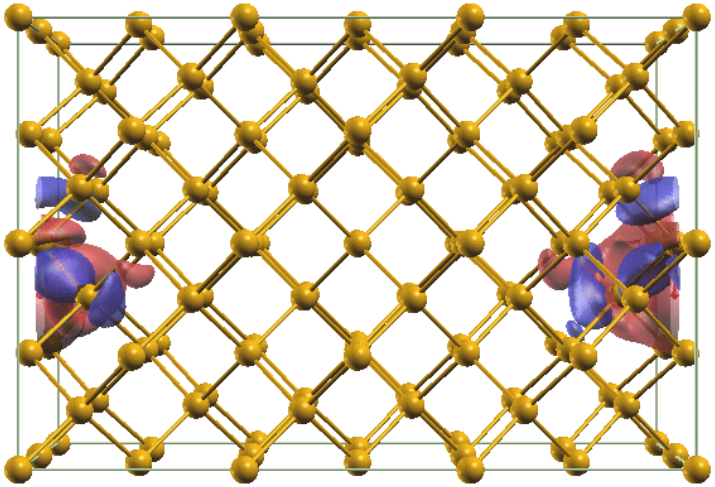
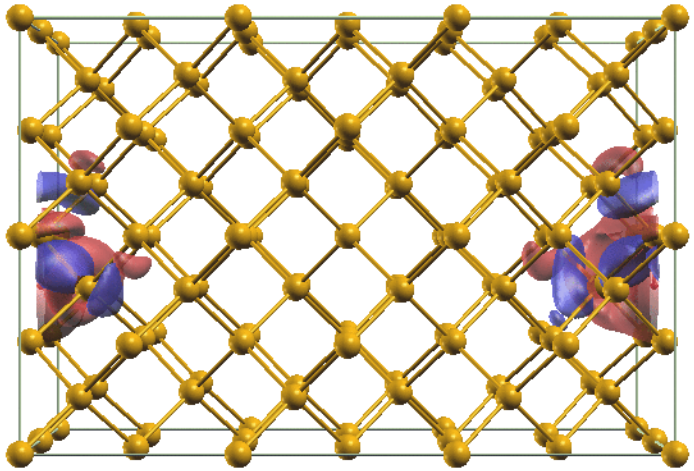
H in germanium: Small-gap semiconductor



Adiabatic screening



Dynamic (v = 0.5 a.u.) screening

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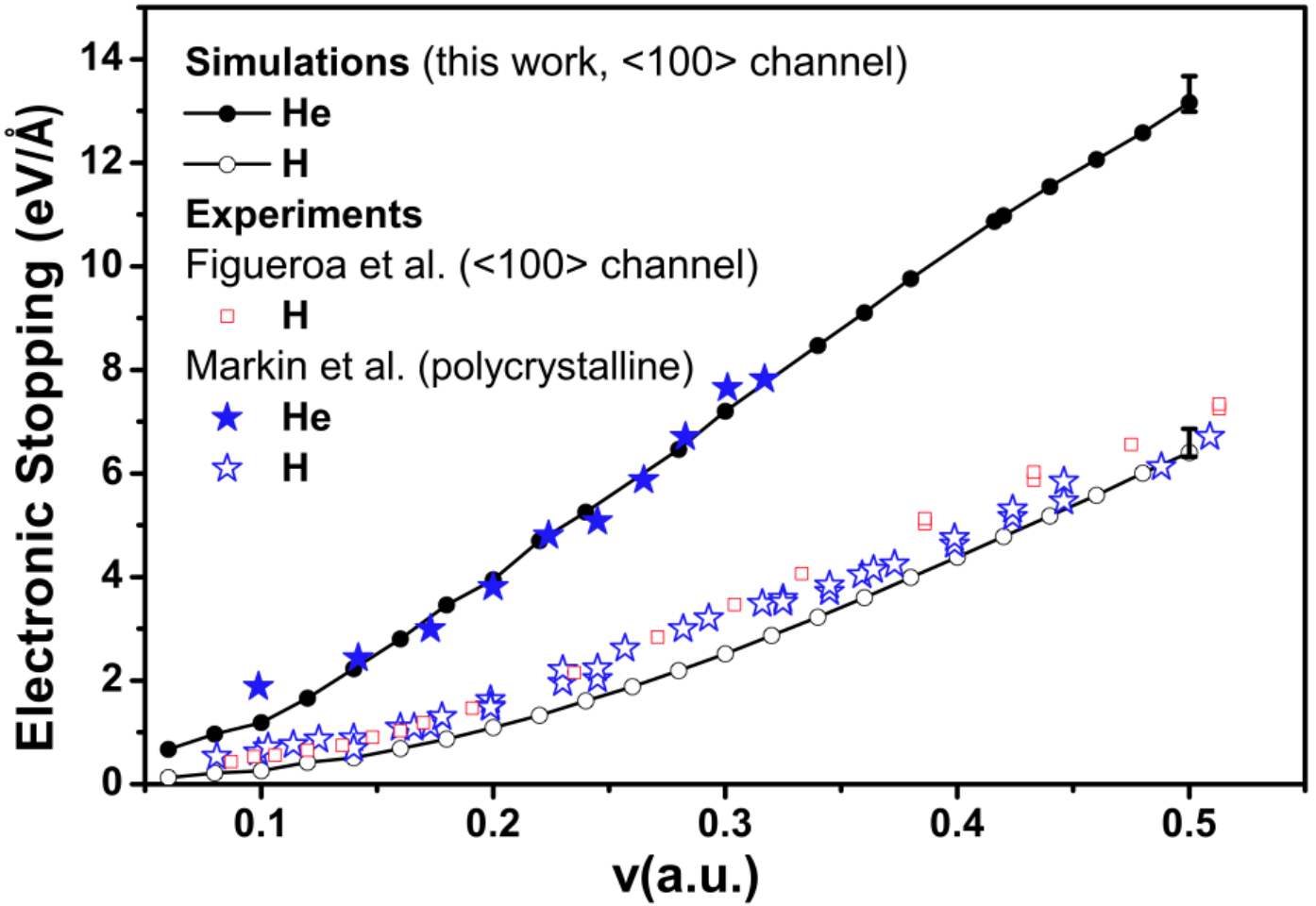
Electronic stopping of H and He in gold

Exp-Th comparison

MA Zeb, J Kohanoff, D Sanchez-Portal, A Arnau, JI Juaristi & E Artacho PRL 2012



Conclusion

- *RT-TDDFT coming soon (next SIESTA release, already in trunk version and available in launchpad)*
- *Although somewhat less optimized than the ground state calculations…*
- *it allows studying the optical properties and the response of the system to perturbations beyond the linear regime for systems containing up to hundreds atoms*
- *So far it has been successfully tested to study the optical properties of nanostructures and the electronic friction in the process of interaction of fast ions with solids.*