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# *Time-evolving TD-DFT for time-dependent electronic problems*


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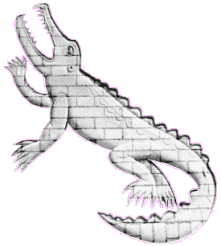
*Nanogune, Ikerbasque & DIPC, San Sebastian, Spain*
*Cavendish Laboratory, University of Cambridge*

*Miguel Pruneda*
*CIN2 - CSIC, Barcelona*

*Ahsan Zeb*
*U Cambridge*

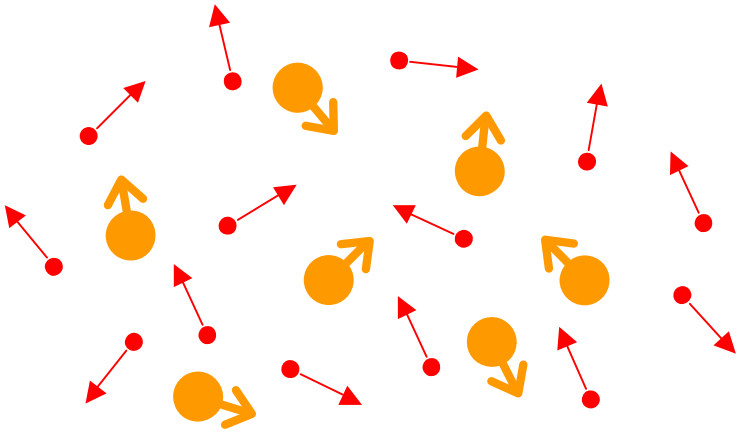
# Collaborators

*Donostia International Physics Centre*
*Daniel Sanchez-Portal (implementation)*
*Andres Arnau*
*Inaki Juaristi*
*Pedro Echenique*
*& Discussions with Txema Pitarke*

*& Thanks to Peter Bauer (Linz, Austria)*

***Jorge Kohanoff (Belfast)***

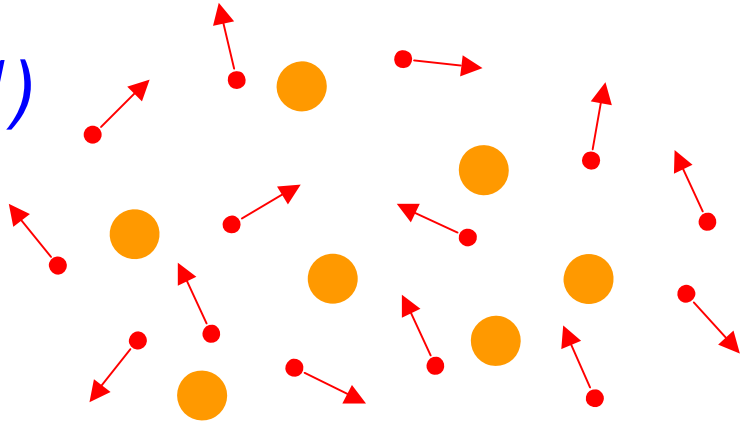
# Adiabatic decoupling



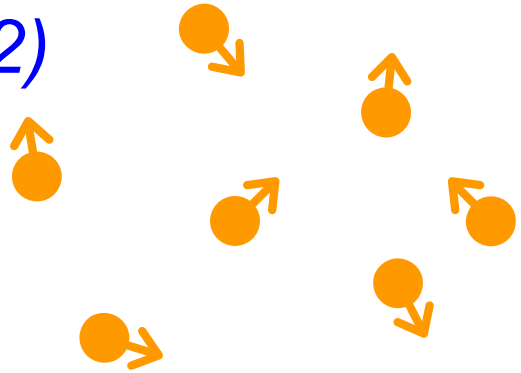
$$\frac{m_n}{m_e} >> 1$$

⇒*Nuclei are much slower than electrons*

*(1)*



*(2)*



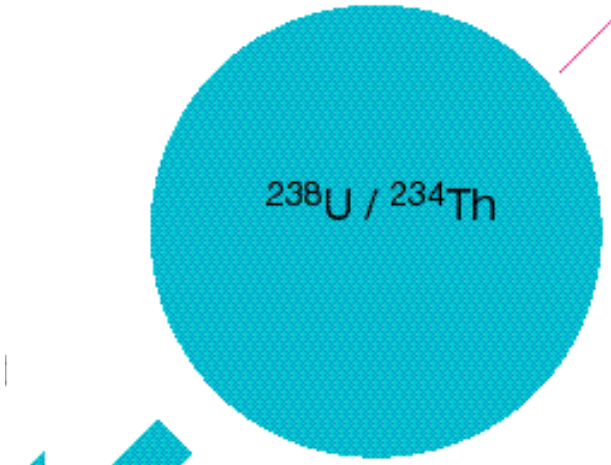
*Quantum mechanics*
*Many electron problem:*
*Density Functional Theory*

F = m a, *evolution in (discretised) time:*
*Molecular dynamics*

# *Radiation damage*

*α-particle*

*α-decay*




*E ~ 5 MeV*

*v ~ 7 a.u.*

*Recoil*

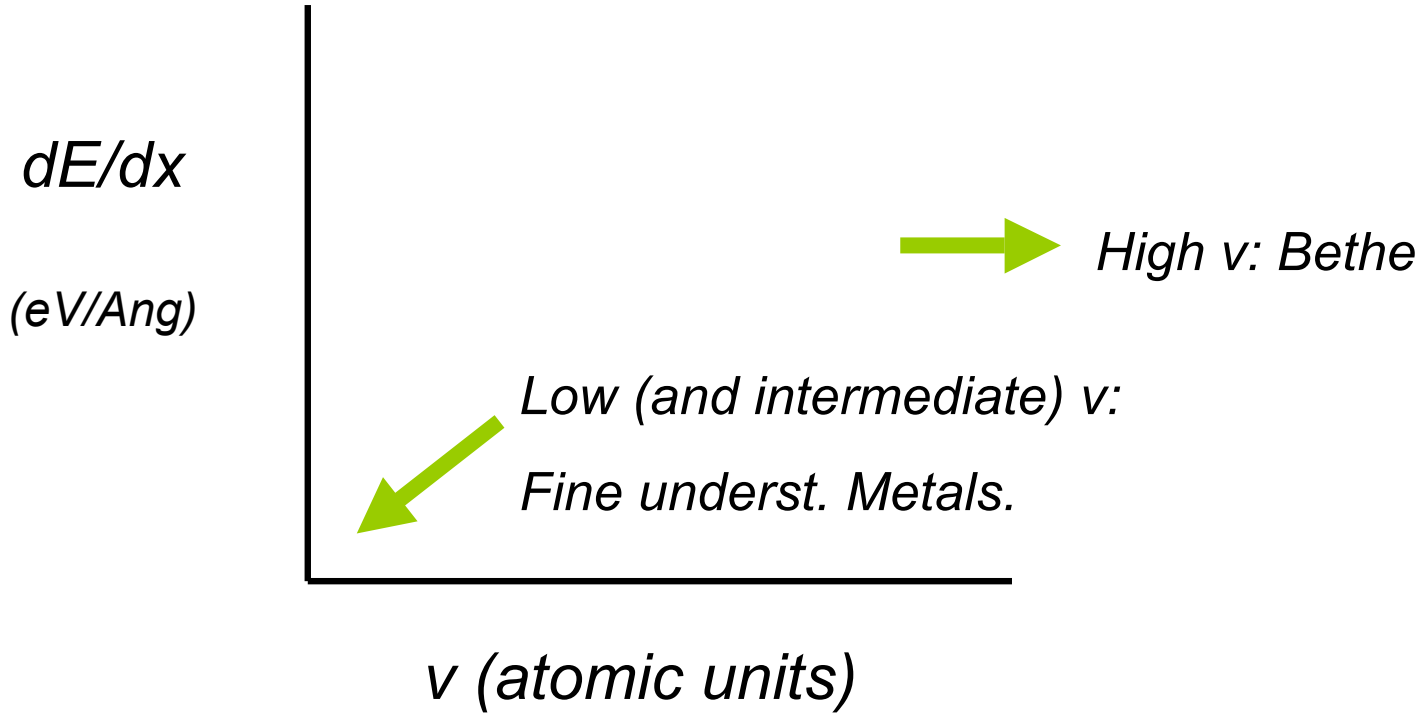
*E ~ 100 keV*

*v ~ 0.1 a.u.*

*Other typical processes*

- *Neutrons, PKA*
- *Cosmic rays: Mostly protons E > 1 GeV*

# *Energy transferred: Measured by stopping power*



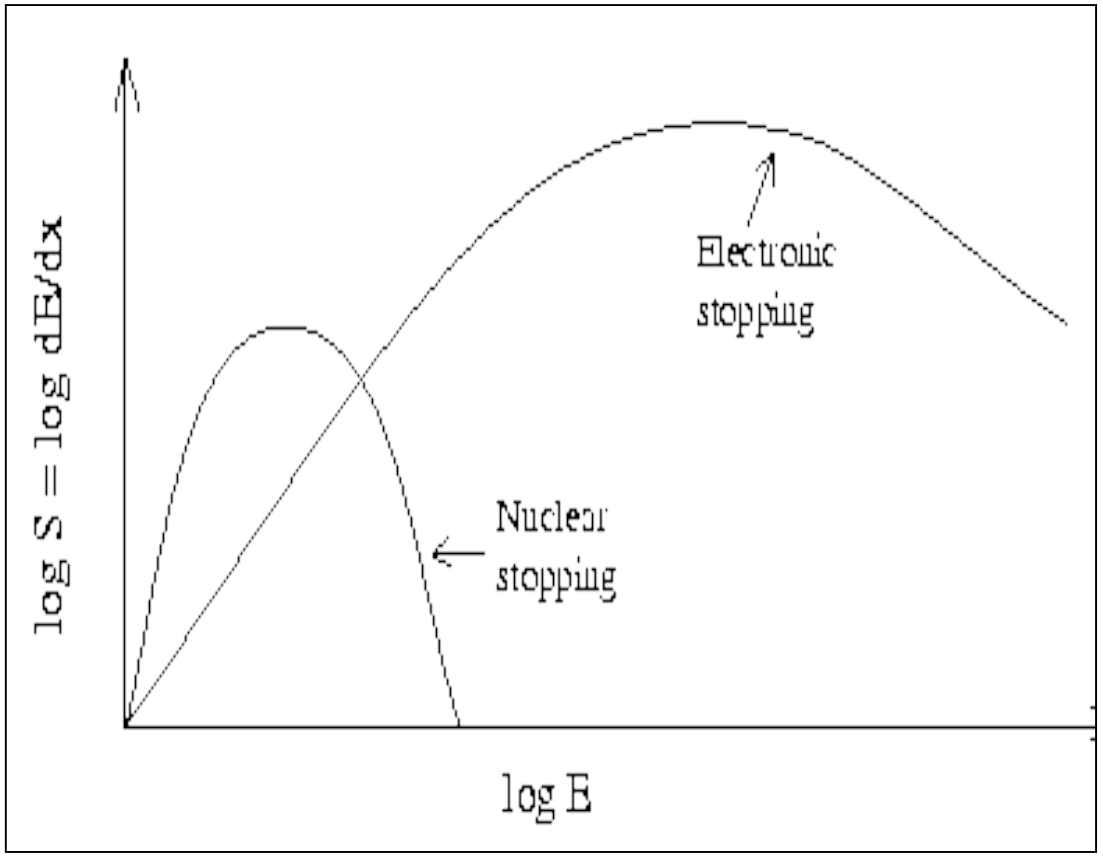

*100 keV Recoiling Th nucleus: v = 0.1 a.u.*

# *Electronic versus nuclear stopping*

*Metals:*

*S ~ v*

*for v -> 0*




*Nuclear stopping dominates at low velocities*

# *Clearly non-adiabatic systems*

*We cannot use the Born-Oppenheimer decoupling*

*Need to solve the coupled system of electrons and nuclei*

*Schroedinger equation for both*

*Dynamical problem (projectile moving) => TD-Schroedinger*

*Classical nuclei?*

*(see discussion of Ehrenfest approximation in Matthew Foulkes's talk)*

*TD-Schroedinger for electrons only*

# Time dependent DFT

*Usual (stationary) DFT:*

$$H\Psi(\{\vec{r}_i\}) = E\Psi(\{\vec{r}_i\}) \quad \rightarrow \quad h^{KS}\psi_n^{KS}(\vec{r}) = \varepsilon_n^{KS}\psi_n^{KS}(\vec{r})$$

*Time-dependent DFT:*

$$H\Psi(\{\vec{r}_i\},t) = i\frac{\partial}{\partial t}\Psi(\{\vec{r}_i\},t) \quad \rightarrow \quad h^{KS}\psi_n^{KS}(\vec{r},t) = i\frac{\partial}{\partial t}\psi_n^{KS}(\vec{r},t)$$

*Neither forces on atoms (no MD), nor moving basis*

# Hohenberg - Kohn

$$\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$$

*For our many-electron problem* $\hat{H} = T + V_{ee} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i)$

1. $E[\rho(\vec{r})] \equiv \int d^3\vec{r}\, V_{ext}(\vec{r})\,\rho(\vec{r}) + F[\rho(\vec{r})] \geq E_{GS}$

*(depends on nuclear positions)*

*(universal functional)*

2. $E[\rho_{GS}(\vec{r})] = E_{GS}$

*Through 1-1 mapping*
*$V_{ext}$ (r) and n(r)*
*Functional unknown!*

# Runge - Gross

PRL 84

$$\Psi(\{\vec{r}_i\},t) \rightarrow \rho(\vec{r},t)$$

*For our many-electron problem* $\hat{H} = T + V_{ee} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i,t)$

1. $V_{ext}(\vec{r},t) \Leftrightarrow \rho(\vec{r},t)$ *up to c(t)*

*1-1 correspondence => Physical properties are functionals of the density*

2. $A\left[\Psi\left(\left\{\vec{r}_i,t\right\}\right)\right] = \int_{t_0}^{t_1} dt \left\langle \Psi(t)\right| i\frac{\partial}{\partial t} - \hat{H}(t)\left|\Psi(t)\right\rangle$

*Variational principle of the action instead of E*

- *Stationary point (not minimum)*
- *Initial value problem: Ψ(t=0) defines*

# Kohn - Sham

*Independent particles in an effective potential*

*They rewrote the functional as:*

$$E[\rho] = T_0[\rho] + \int d^3\vec{r}\,\rho(\vec{r})[V_{ext}(\vec{r}) + \tfrac{1}{2}\Phi(\vec{r})] + E_{xc}[\rho]$$

*Kinetic energy for system with no e-e interactions*

*Hartree potential*

*The rest: exchange correlation*

*Equivalent to independent particles under the potential*

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

# Runge - Gross

*Independent particles in an effective potential*

$$V_{xc} \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \quad \Rightarrow \quad V_{xc} \equiv \frac{\delta A_{xc}[\rho]}{\delta \rho(\vec{r})}$$

*Where $A_{xc}$ is obtained by subtracting the action of known bits (Hartree, Kinetic, etc) from the exact $A$*

$$V_{eff}\left[\vec{r},t,\rho(\vec{r}',t')\right] = V_{ext}(\vec{r},t) + \Phi_{Hartree}(\vec{r},t) + \frac{\delta A_{xc}[\rho(\vec{r}',t')]}{\delta \rho(\vec{r}',t')}$$

$$\text{for} \quad \vec{r}' \in \mathrm{R}^3; \quad t' \le t$$

*Just follow the t-dep of independent particles under $V_{eff}$*

# *Approximations*

*Local Density Approximation (LDA)*

$$V_{xc}[\rho] \approx V_{xc}(\rho(\vec{r}))$$

*(function parameterised for the homogeneous electron liquid as obtained from QMC)*

*Adiabatic Local Density Approximation (ALDA)*

*As above, plus t-dep is local in t*

*No history dependence*

*Same for Generalised Gradient Approximation (GGA)*

$$V_{xc}[\rho] \approx V_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

*(new terms parameterised for heterogeneous electron systems (atoms) as obtained from QC)*

# *Time evolving*

*Although TD-DFT was proposed in t-domain, most use is in frequency domain: DFT for excitations*

*We describe t-dependent processes in t-TD-DFT*

*As implemented by* A Tsolakidis, D Sanchez-Portal and R M Martin, PRB 2002

# *The SIESTA method*

*Linear-scaling DFT based on*
*NAOs (Numerical Atomic Orbitals)*

P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

- *Born-Oppenheimer (relaxations, mol. dynamics)*
- *DFT (LDA, GGA)*
- *Pseudopotentials (norm conserving, factorised)*
- *Numerical atomic orbitals as basis (finite range)*
- *Numerical evaluation of matrix elements (3D grid)*

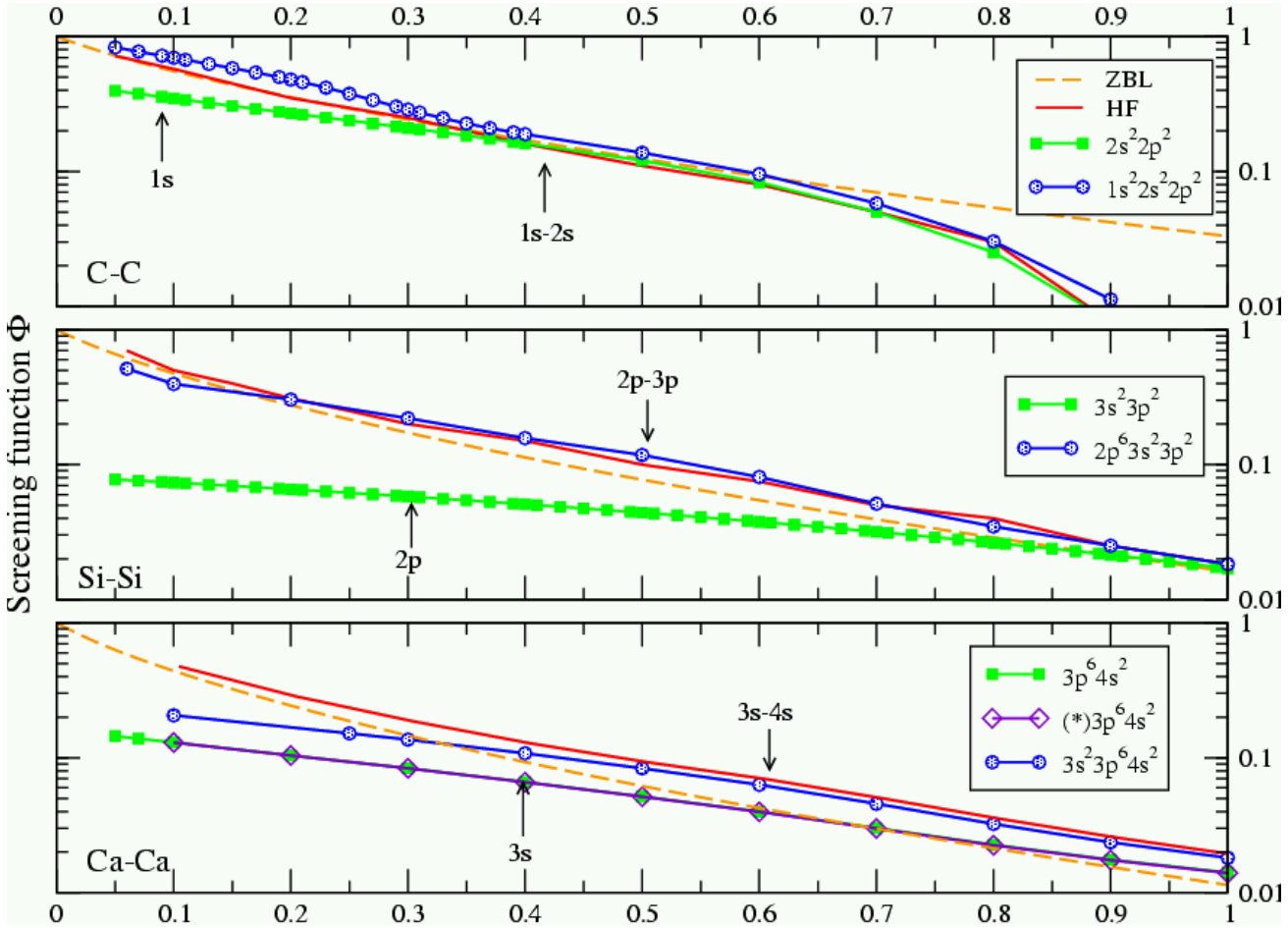
*Implemented in the* ***SIESTA*** *program*

J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon & D. Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002)

# *Performance of pseudopotentials in high-energy collisions*

## *In terms of the screening function*

JM Pruneda & EA, PRB 2004



# *Real time evolution of the density*

- *SIESTA (LCAO)*

$$\psi_i(r,t) = \sum_\mu c_i^\mu(t)\phi_\mu(r)$$

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

- *Evolution of the TD-KS equations:*

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

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

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

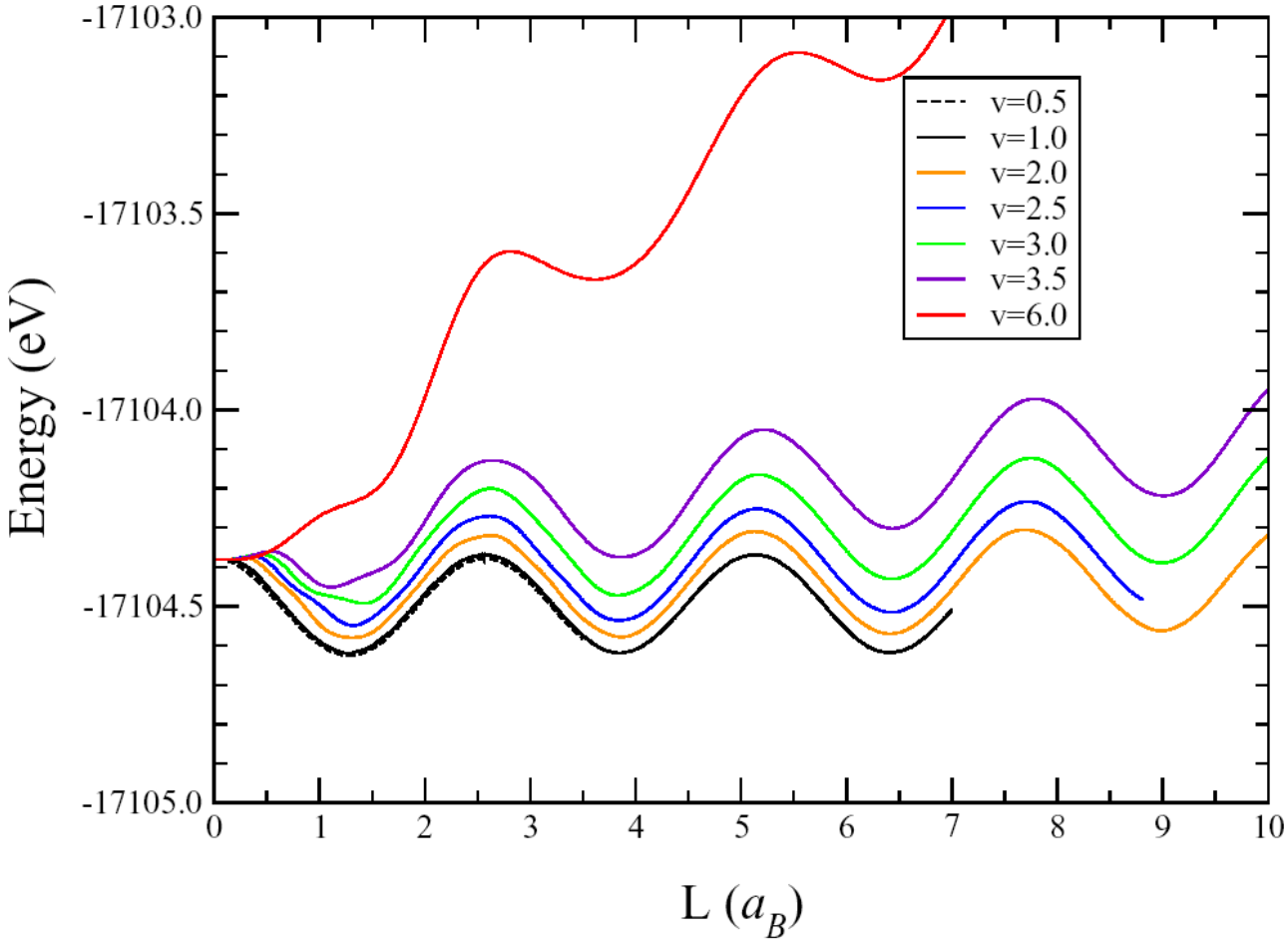
Crank-Nicholson

# *Our approach*

- *Supercell of insulator's bulk*
- *Periodic boundary conditions*
- *Density functional theory*
- *Add external charge (potential)*

- *Move it and follow electron wave-functions with Time-Dependent DFT*

# *Energy as a function of distance: LiF*




***Quite stationary!*** *Short transient, no obvious oscillation*

# *Energy vs t*

*Implies that we take*

$$\left\langle \Psi(t) \middle| \hat{H}(t) \middle| \Psi(t) \right\rangle = E\left[\rho(\vec{r},t')\right]_{t'\le t} \approx E_{KS}^{ALDA}(t)$$

*Goes to the right adiabatic limit, BUT*
*As far as I know, only justified a posteriori*

# *Summary*

- *Need to go beyond adiabatic*
- *Starting with the electrons: A projectile as external potential gives a time-dependent Hamiltonian => TD-Schroedinger eq.*
- *Basics of TD-DFT*
- *Using time-evolving TD-DFT for stopping power of ions in matter*
- *Coupling to classical nuclei: see tomorrow's lecture by Matthew Foulkes*
- *We will see this applied to varied materials tomorrow*

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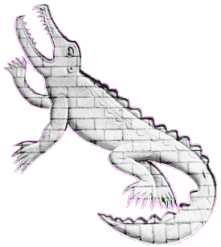
# *Stopping power of projectiles shooting through matter*

## *Predicting the rate of electron heating in radiation damage events*


*Emilio Artacho*

*Nanogune, Ikerbasque & DIPC, San Sebastian, Spain*
*Cavendish Laboratory, University of Cambridge*

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*Pedro Echenique*
*& Discussions with Txema Pitarke*
*& Thanks to Peter Bauer (Linz, Austria)*
*& Nuclear waste project at Cambridge*

***Jorge Kohanoff (Belfast)***

# *What to do with nuclear waste*


**Shoot it at the sun. Send it to Earth's core. What to do with nuclear waste?**

Government advisers consider 14 ways of getting rid of the troublesome legacy

**Paul Brown, environment correspondent**
**Wednesday April 14, 2004**
**The Guardian**

*Now: BNFL (UK) vitrifies it into Borosilicate glass (~20%)*

*Durability ~100 years*

*10ky – 1My needed!*

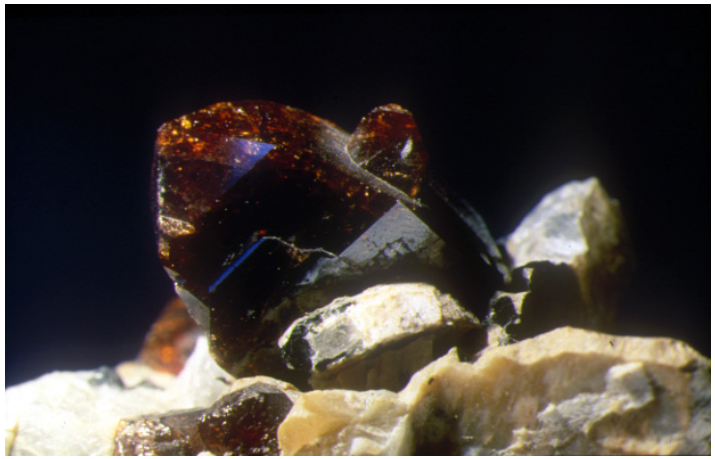
# *What to do with nuclear waste*

## *Immobilisation by dilution in ceramics*

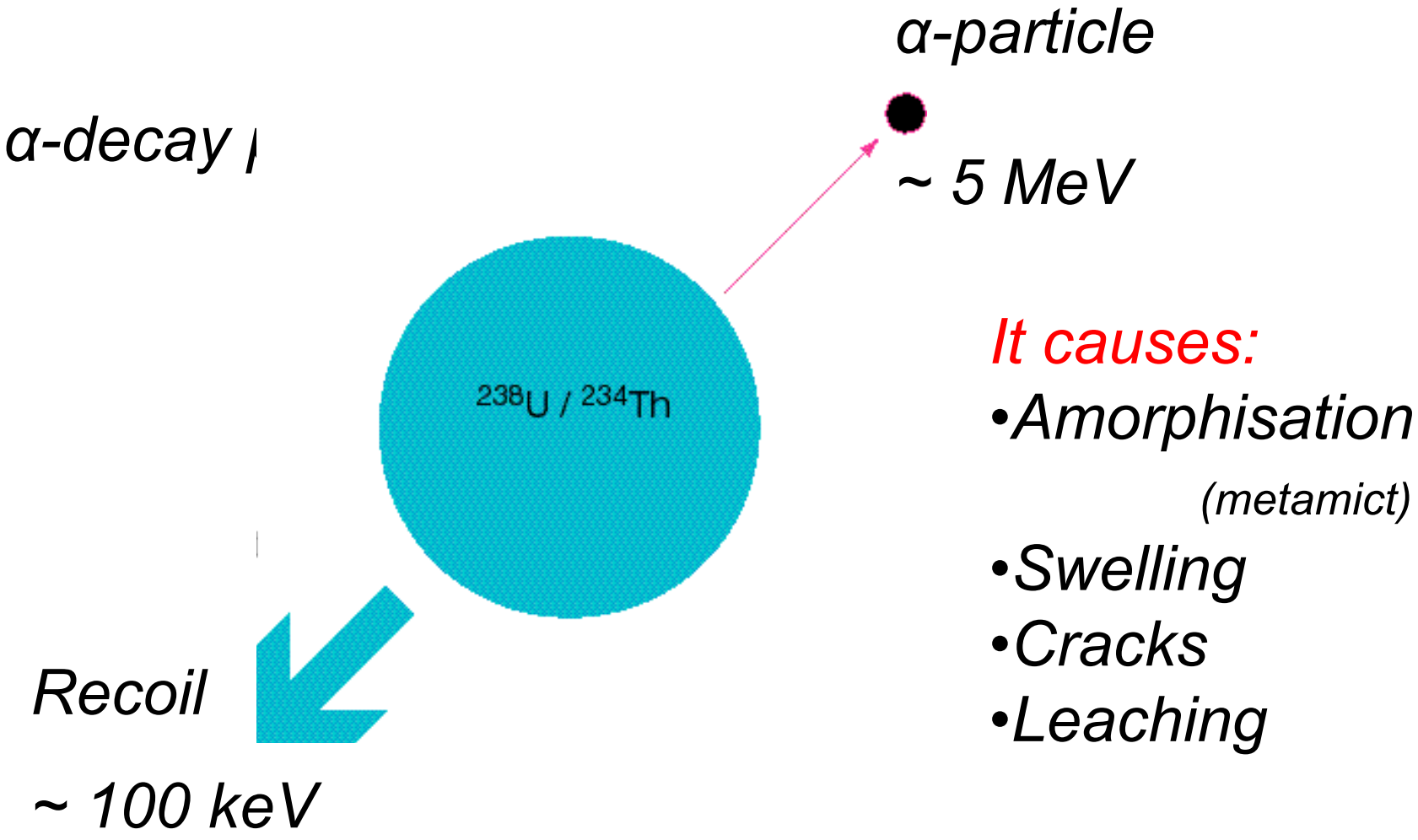
*SYNthetic ROCks with appropriate "minerals" to host high level nuclear waste*

***Research in durability: resistance to radiation damage***

***Zircons have contained uranium for billions of years***



# *Durability: Radiation damage*




*It causes:*

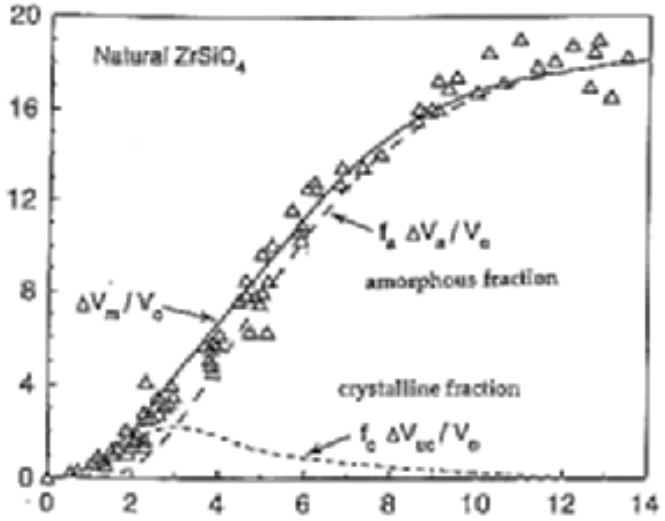
- *Amorphisation*

  *(metamict)*
- *Swelling*
- *Cracks*
- *Leaching*

*Zircon: model study: old natural samples*

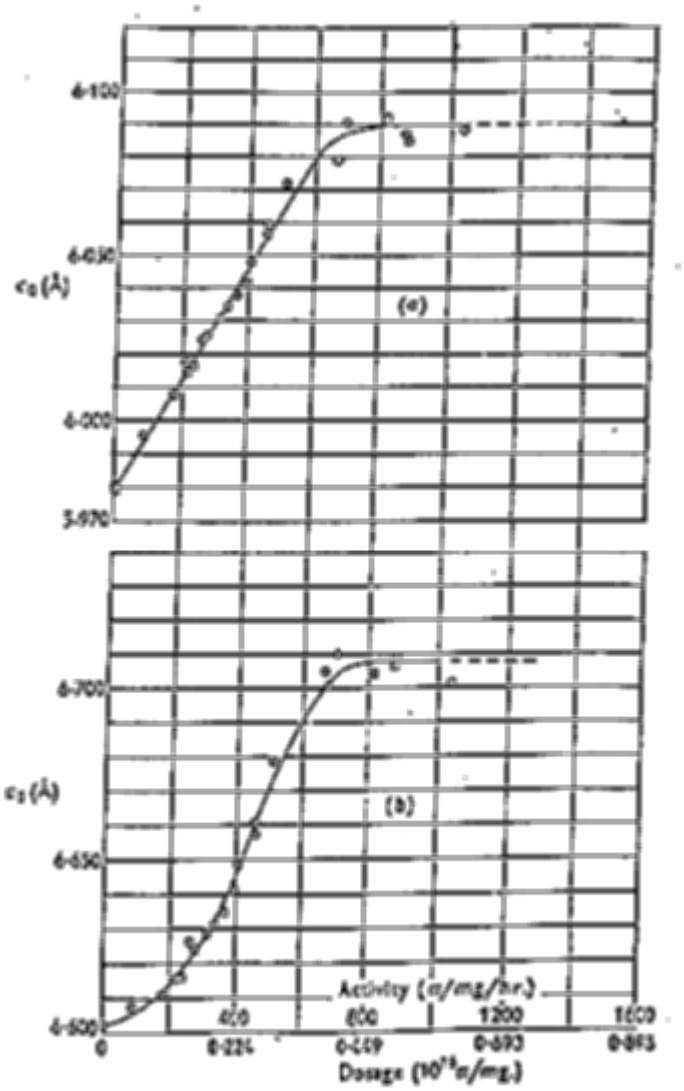
# *Swelling in zircons*

*Volume change (%)*




*Dose ($10^{16}$ decays/g)*

*Crystalline swelling:*
*lattice parameters vs dose*




*Total: ~20%*

*Crystalline: ~5% anisotropic*

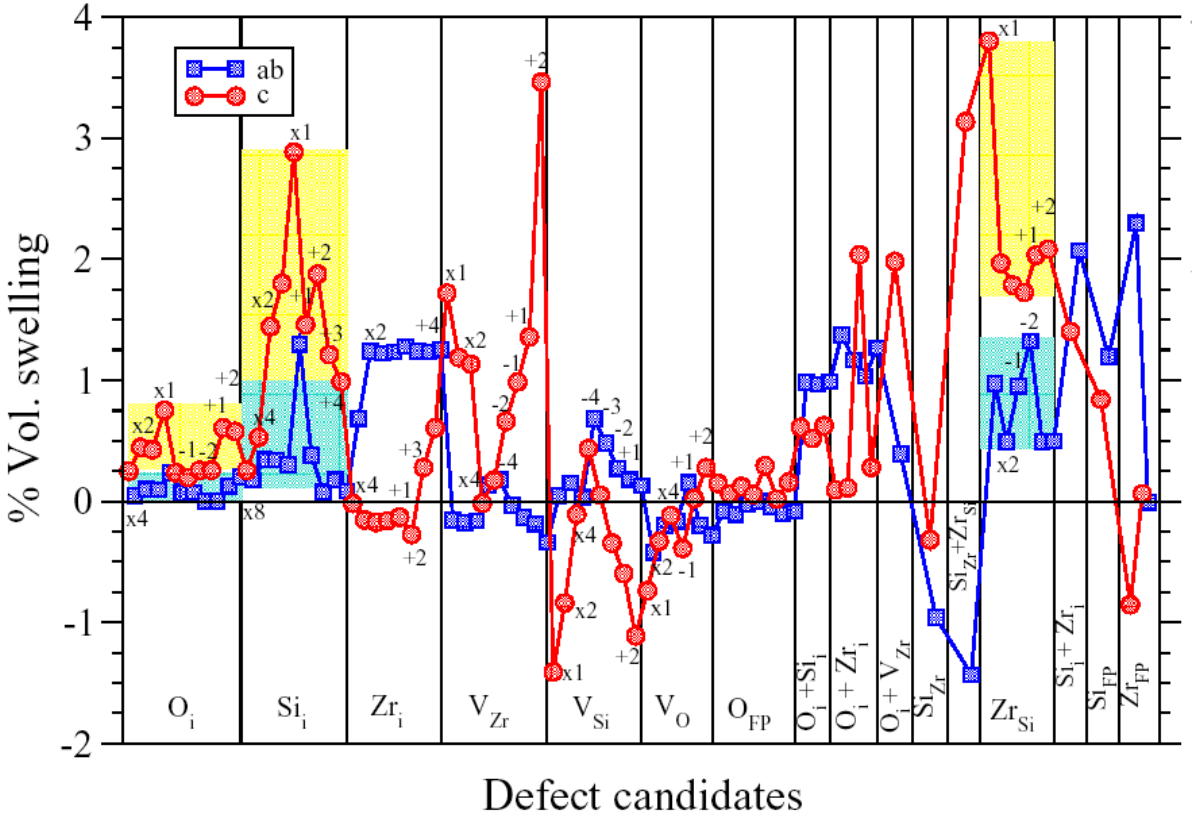
# *Intrinsic point defects and crystalline swelling in ZrSiO4*

- *Radiation cascades & defect accumulation* $\sim 10^{21}$ defects/cm$^3$
- *Anisotropic swelling: ~1.5% in ab-plane*
  *~ 2% in c-axis*
- *IR, Raman & NMR*

*Si …. 0.2% swelling!!*

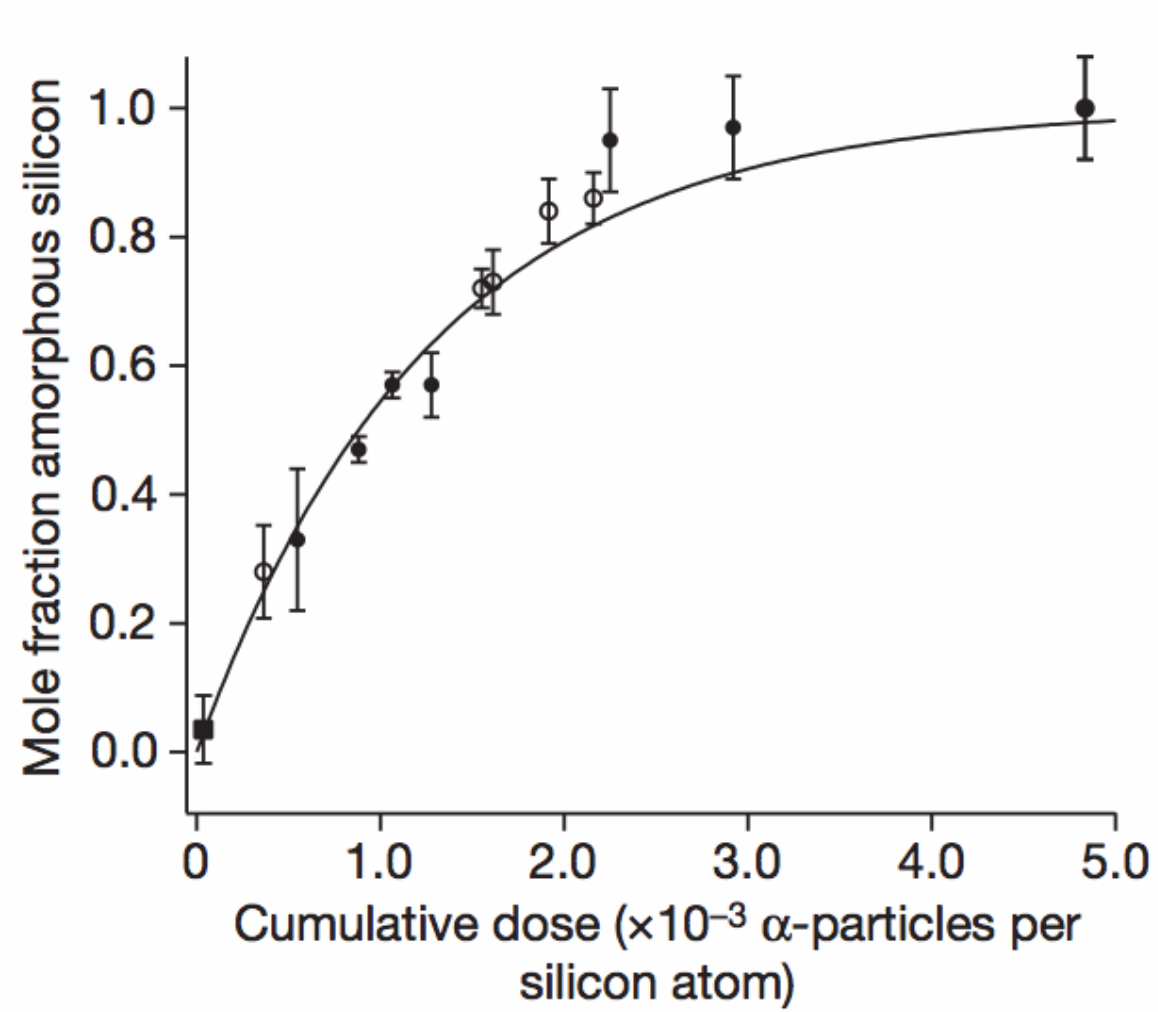
*Possible defects:*

**O & Si interstitials**
**$Zr_{Si}$ anti-site**



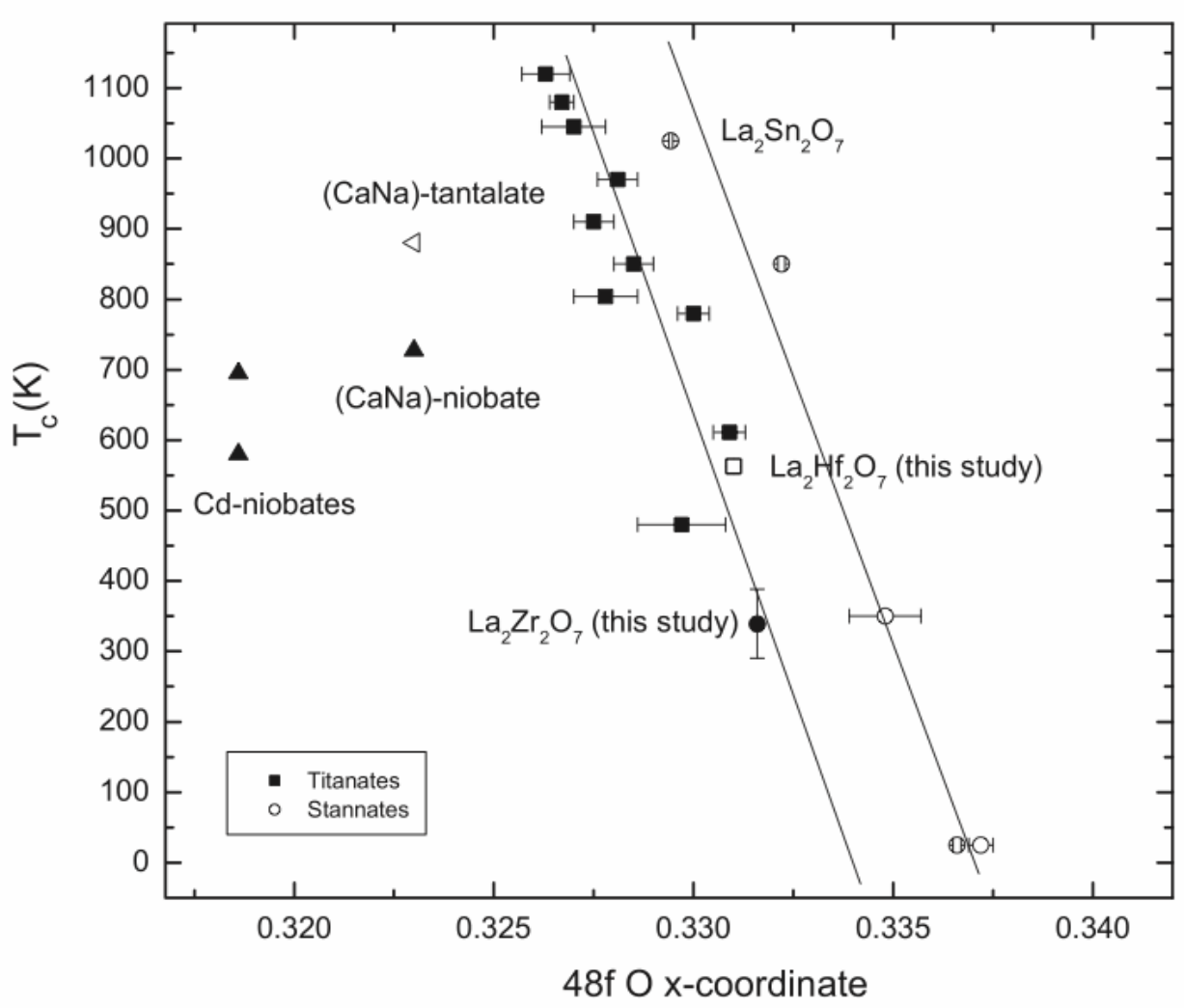
# *Experiments on live samples of Pu containing zircon ($ZrSiO_4$): NMR*

I Farnan *et al*, Nature 2007



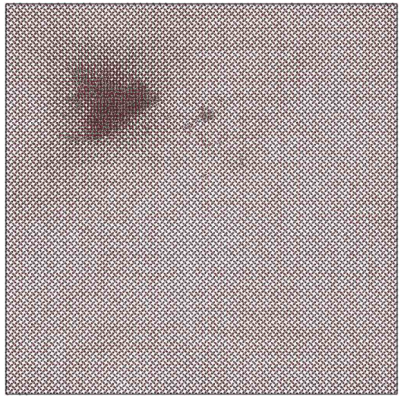
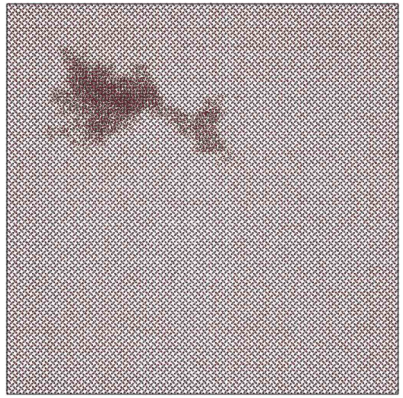
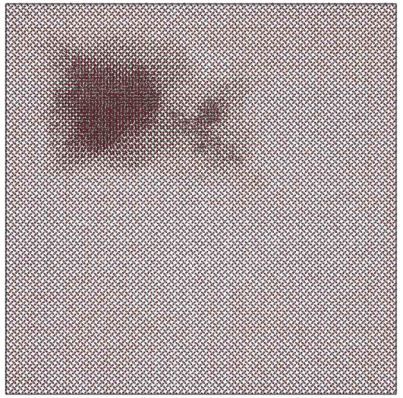
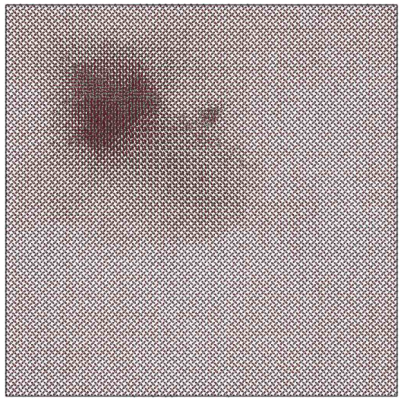
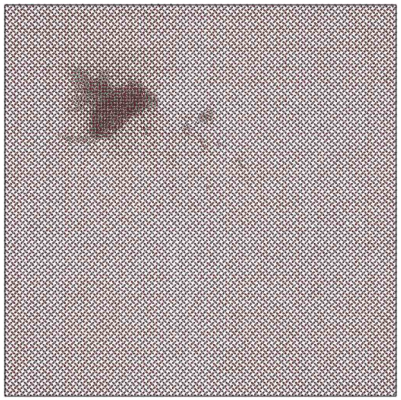
# *Experiments on irradiated samples of pyrochlores*

GR Lumpkin *et al*, JPCM 2004



# *Large scale MD simulations based on empirical force fields*

## *Rutile TiO2*

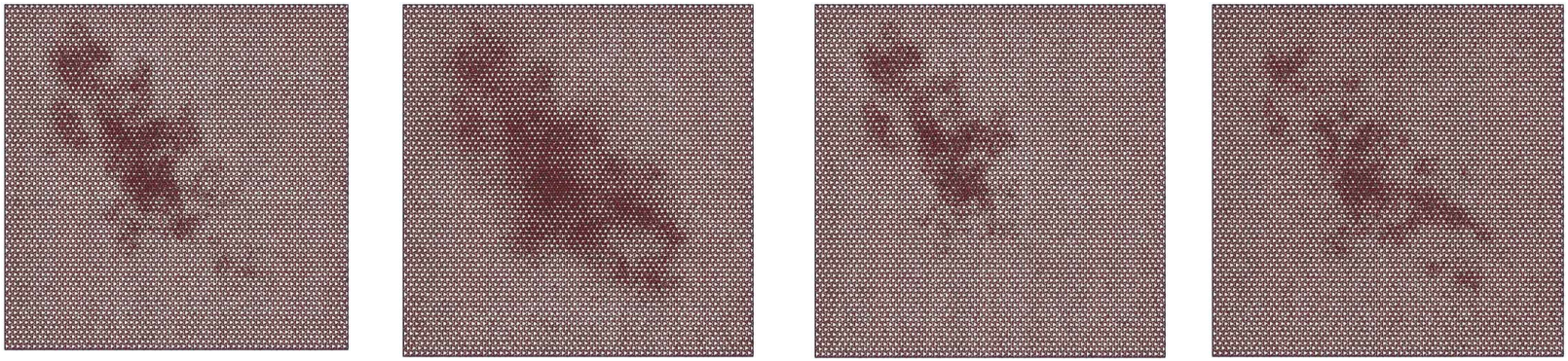
*Kostya Trachenko*

*Martin Dove*

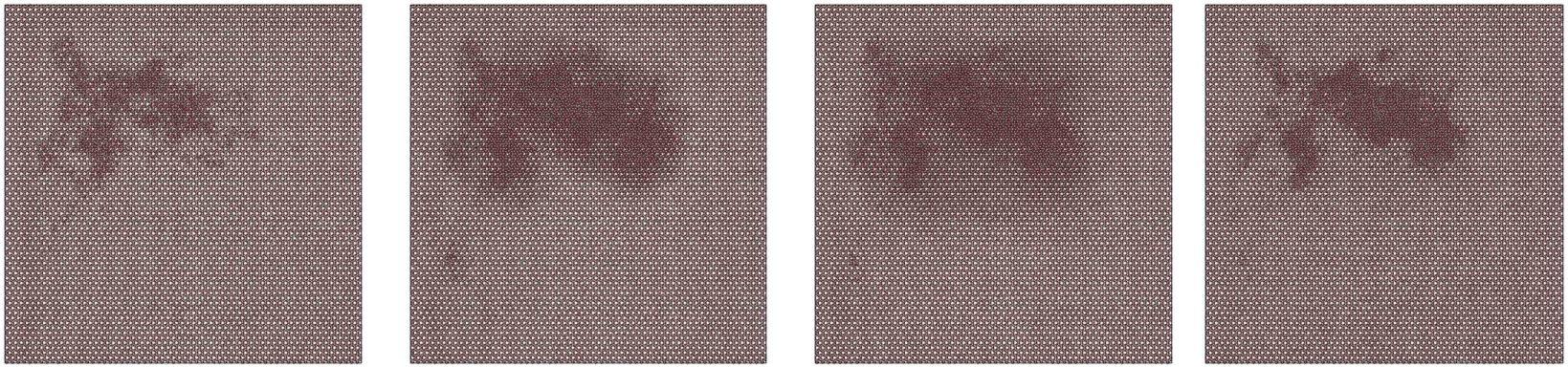
K Trachenko, M T Dove, E Artacho, I T Todorov & W Smith, PRB 2006

# *Large scale MD simulations based on empirical force fields*

## *Quartz SiO2*



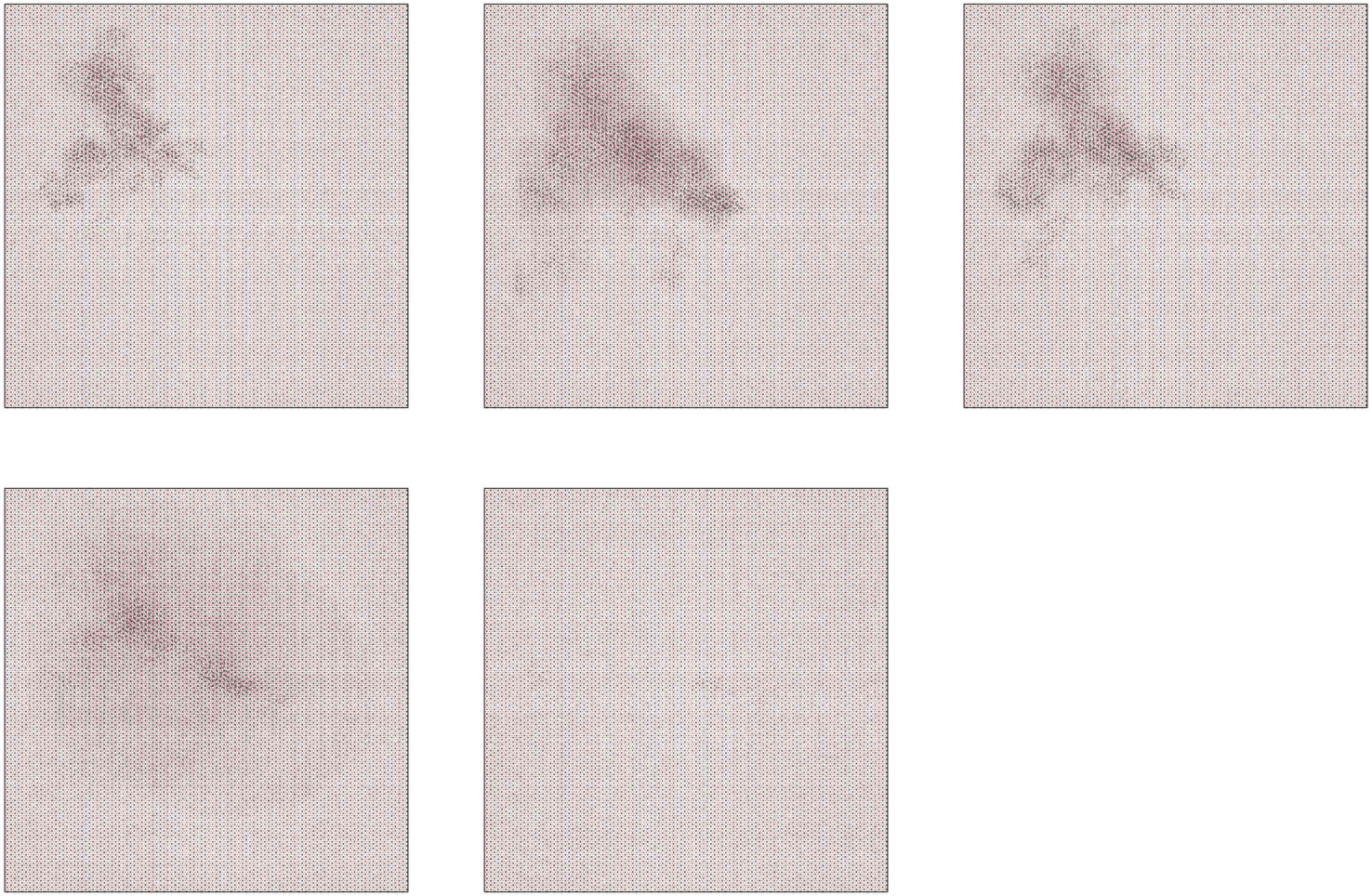
## *Quartz GeO2*



K Trachenko, M T Dove, E Artacho, I T Todorov & W Smith, PRB 2006

# *Large scale MD simulations based on empirical force fields*

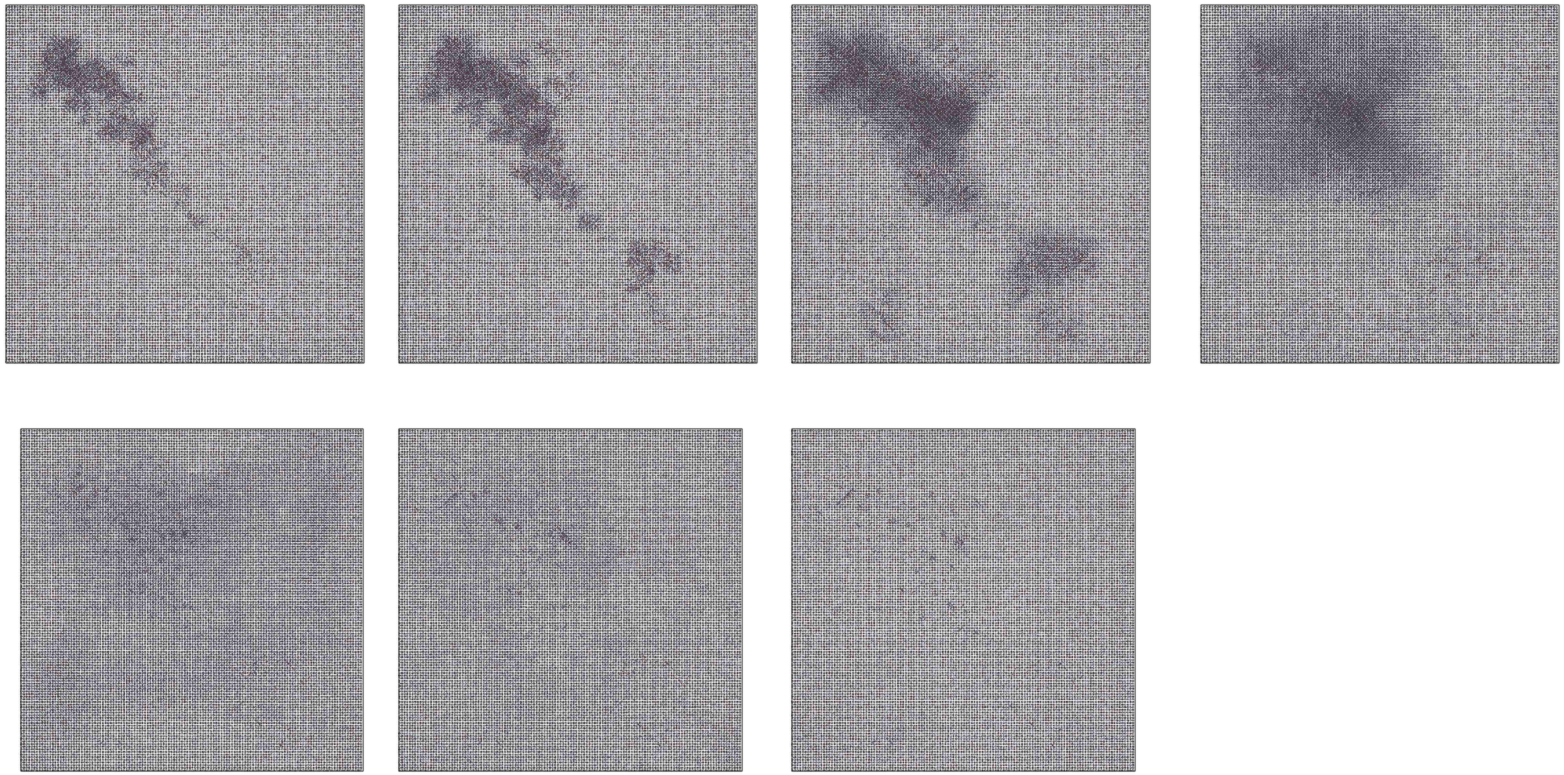
## *Corundum Al2O3*



K Trachenko, M T Dove, E Artacho, I T Todorov & W Smith, PRB 2006

# *Large scale MD simulations based on empirical force fields*

## *MgO*



K Trachenko, M T Dove, E Artacho, I T Todorov & W Smith, PRB 2006

*Electrons heat up: effect on the material?*
*Effect on the simulations?*

*The ion moving in the solid transmits energy to electrons.*
*How much? How? Where? What consequences does it have?*

*Materials soften if electronic subsystem substantially excited*

*Coupled electron-nuclei dynamics*

*FIRST: How much energy goes to electrons?*

*Not trivial either for exp or for th*

## *Coupled dynamics of both electrons & nuclei*

*(realistic simulation demands ~ 2M atoms)*

*Multiscale: Different (decoupled?) timescales*

*Results from*

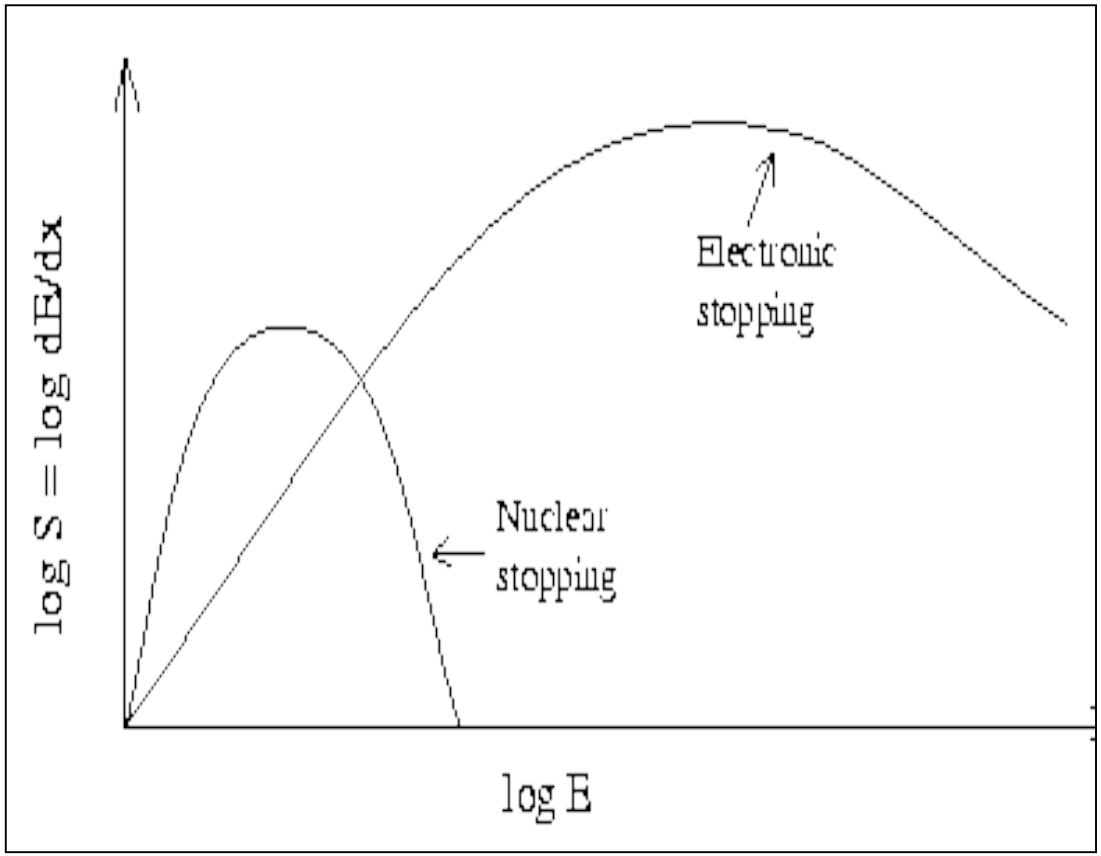
- *this study (electronic excitation)*
- *electron-phonon coupling +*
- *heat conductivities for the electron and phonon subsystems*

$\Rightarrow$*Continuum description of excess energy*

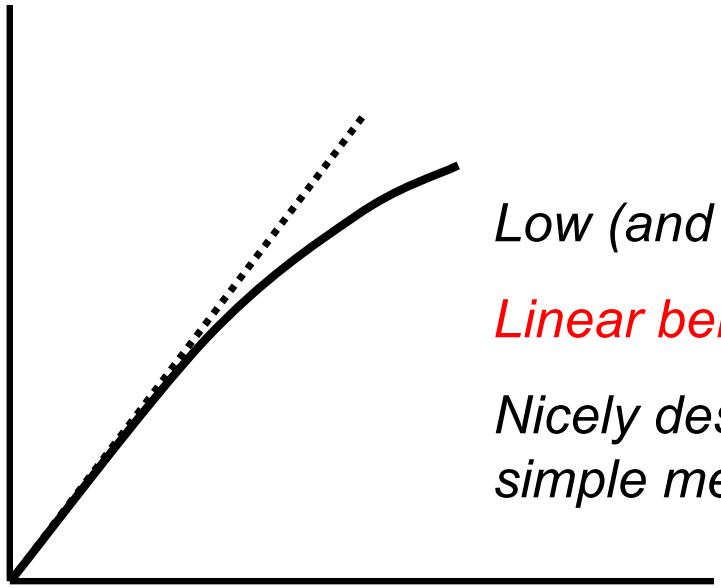
$$\Delta E_{el}(\mathbf{r},t)$$

*First: how much energy is it pumped to the electrons per unit time*

# *Electronic versus nuclear stopping*



# *Electronic stopping power*



*dE/dx*

*(eV/Ang)*

*v (atomic units)*

*Low (and intermediate) v:*

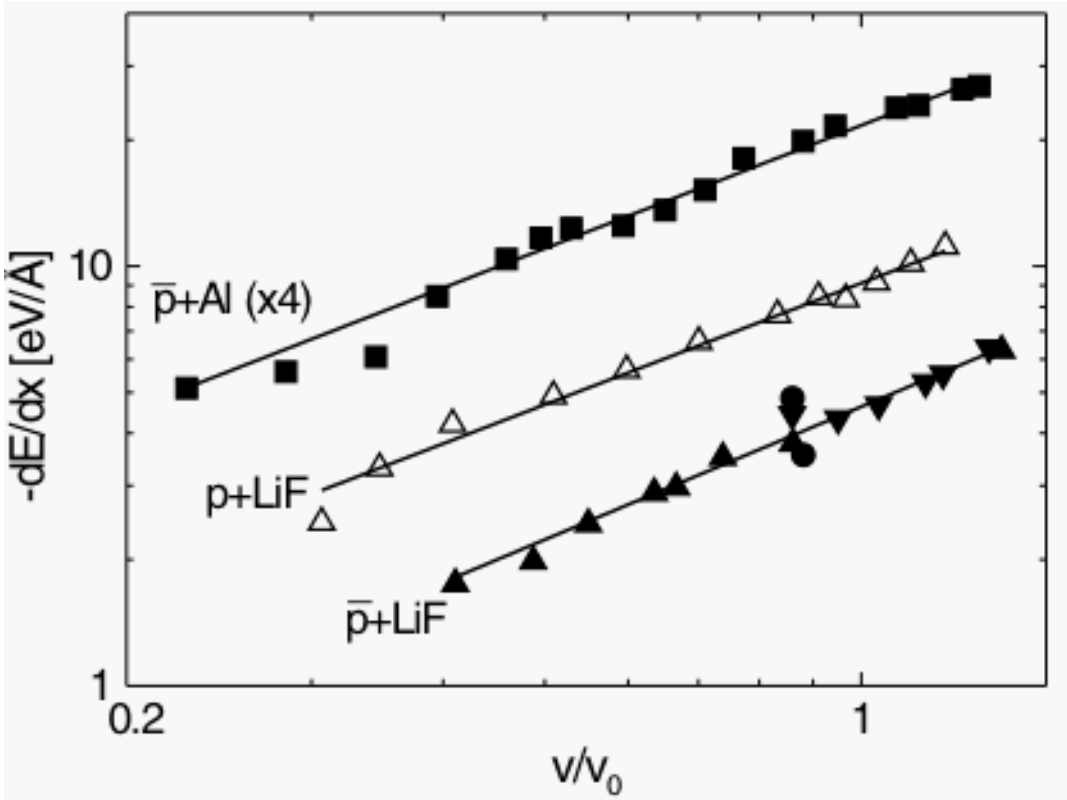
*Linear behaviour simple metals*

*Nicely described for jellium, and simple metals in linear response*

*Scale: few eV/Ang at v = 1 a.u.*

*But what about insulators?*

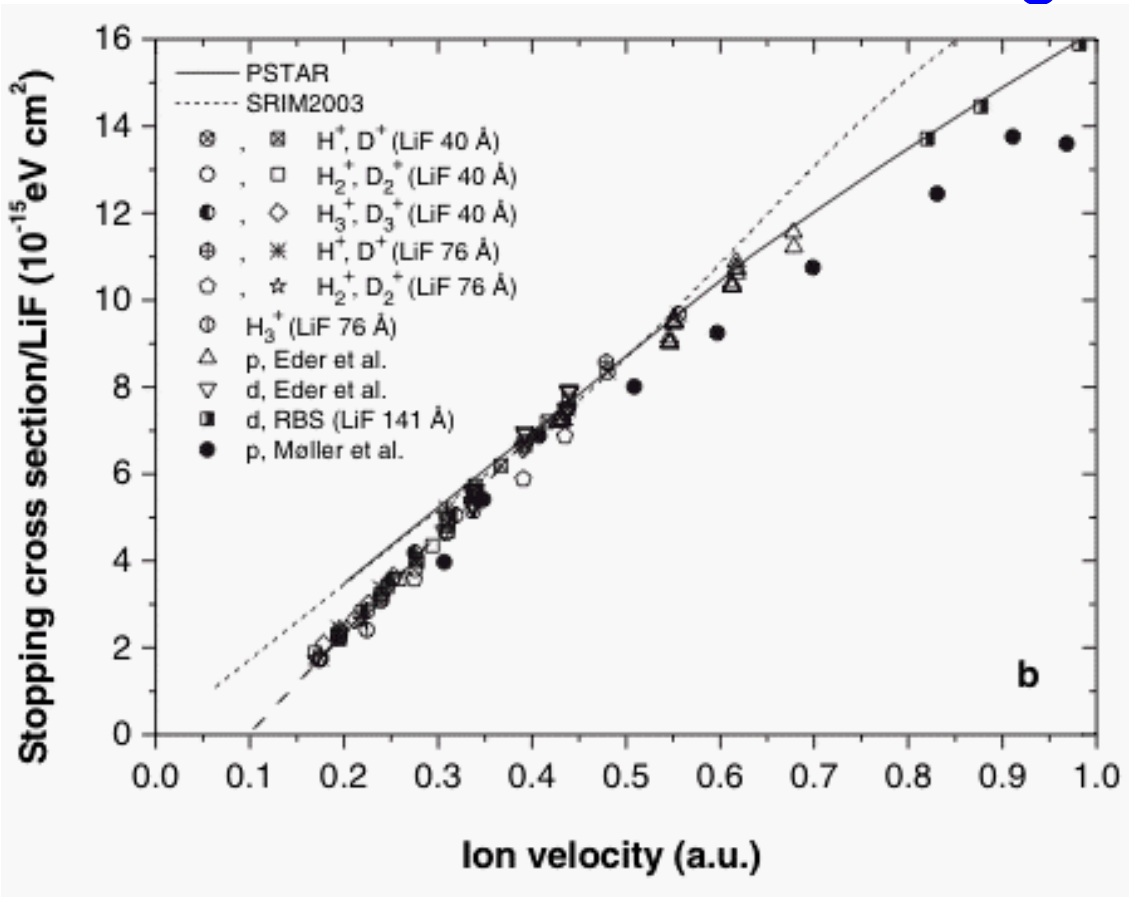
# *Protons and antiprotons into LiF thin films*




"Antiproton Stopping at Low Energies:
Confirmation of Velocity-Proportional Stopping Power"
SP Møller *et al.* PRL **88**, 193201 (2002) & PRL **93**, 042512 **(2004)**

*Perfectly linear, no difference*

# *Protons into LiF thin films again*

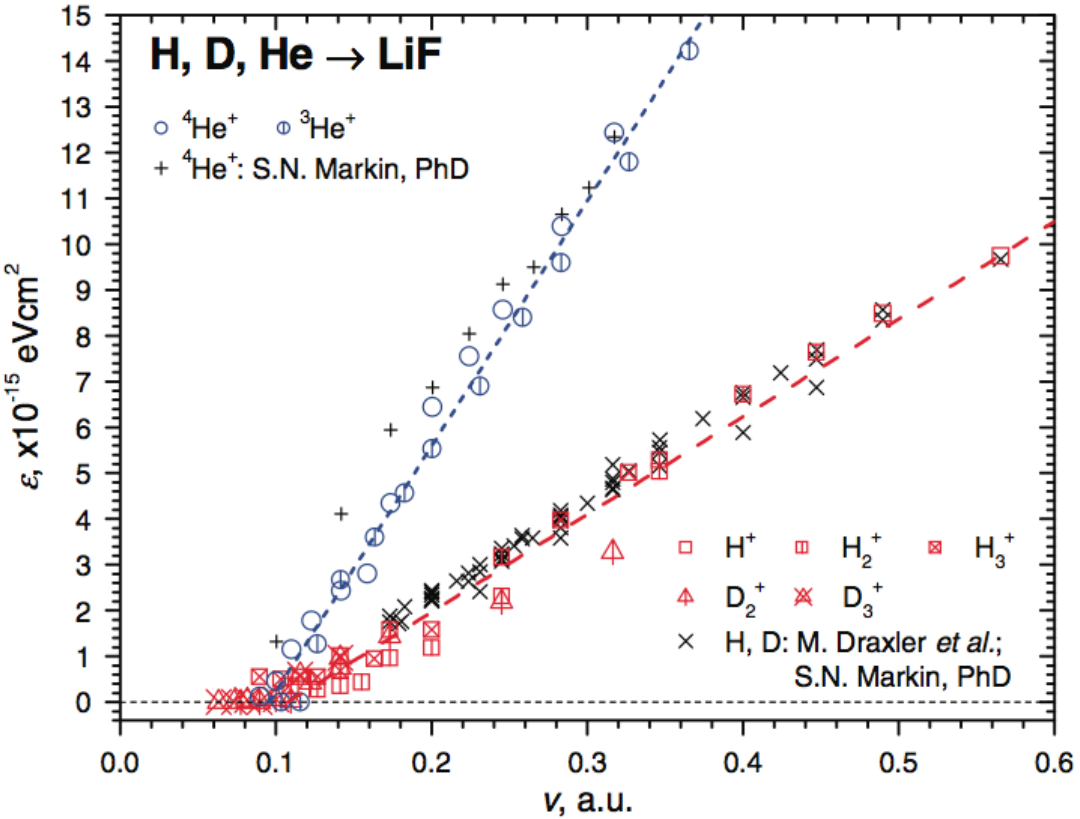



M. Draxler *et al,* PRL **95**, 113201 (2005)

*Scale: v = 0.1 a.u. => Stopping ~ 1 eV/Ang*

*Threshold*

# *Protons into LiF thin films again*




S. Markin *et al,* PRL **103**, 113201 (2009)

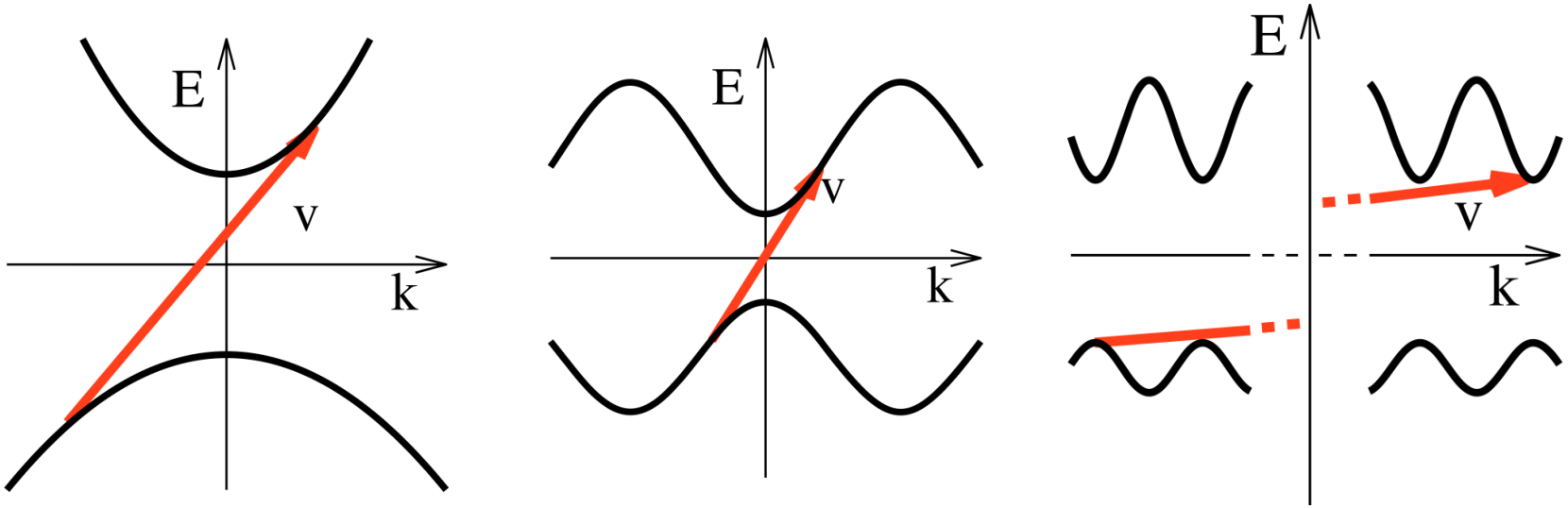
*Scale: v = 0.1 a.u. => Stopping ~ 1 eV/Ang*

*Threshold*

# *Threshold: what to expect?*

*TD Pertub. Th. (weak projectile potential)*
*e-h excitations such that*

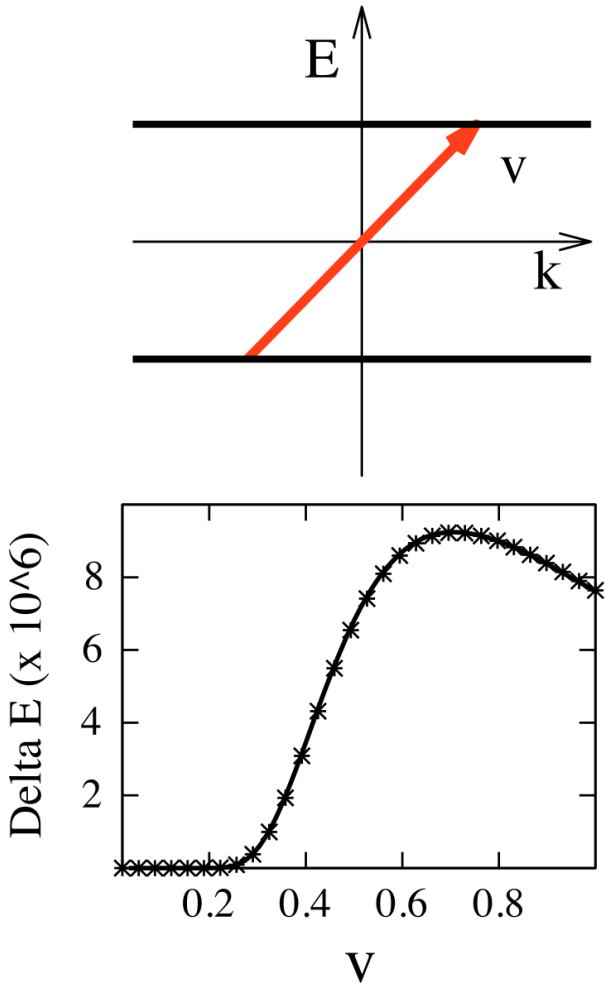
$$\Delta\varepsilon / \Delta k = v$$

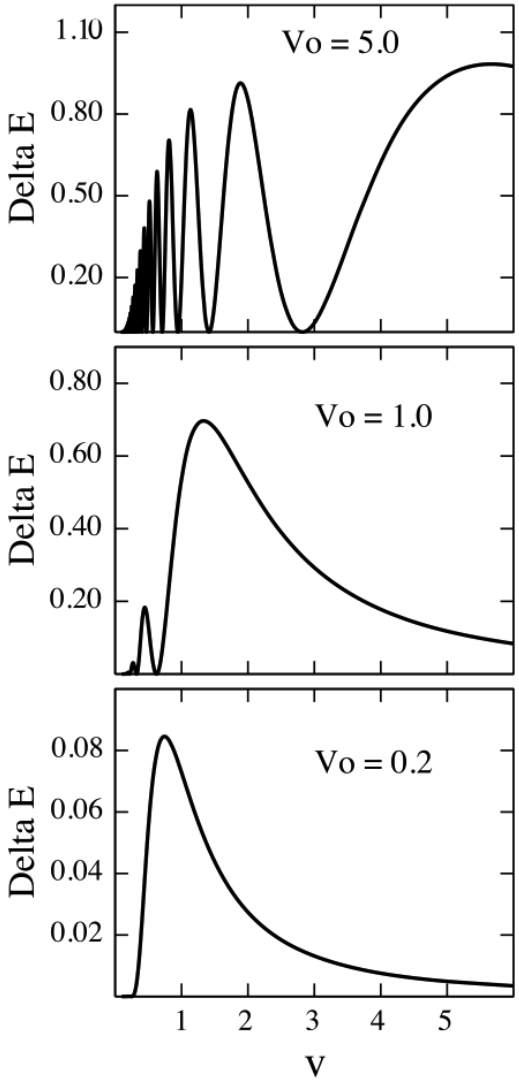



*Excitation amplitude:*
*$V(q=\Delta k)$*

*Strict threshold:* $1/2\,(m_e + m_h)v_c^2 = E_{gap}$

# *Flat-band limit: Simple model*




*Gaussian perturbation scaling as $V_0$*

$$S(\mathrm{v}) \sim e^{-\left(\frac{1}{\mathrm{v}}\right)^{\eta}}; \quad \eta \in \left[\tfrac{3}{2}, 2\right]$$

E Artacho, JPCM 2007

# *Realistic simulations: TD-DFT*

- *Supercell of insulator's bulk*
- *Periodic boundary conditions*
- *Density functional theory*
- *Add external charge (potential)*

- *Move it and follow electron wave-functions with Time-Dependent DFT*

# *The SIESTA method*

*Linear-scaling DFT based on*
*NAOs (Numerical Atomic Orbitals)*

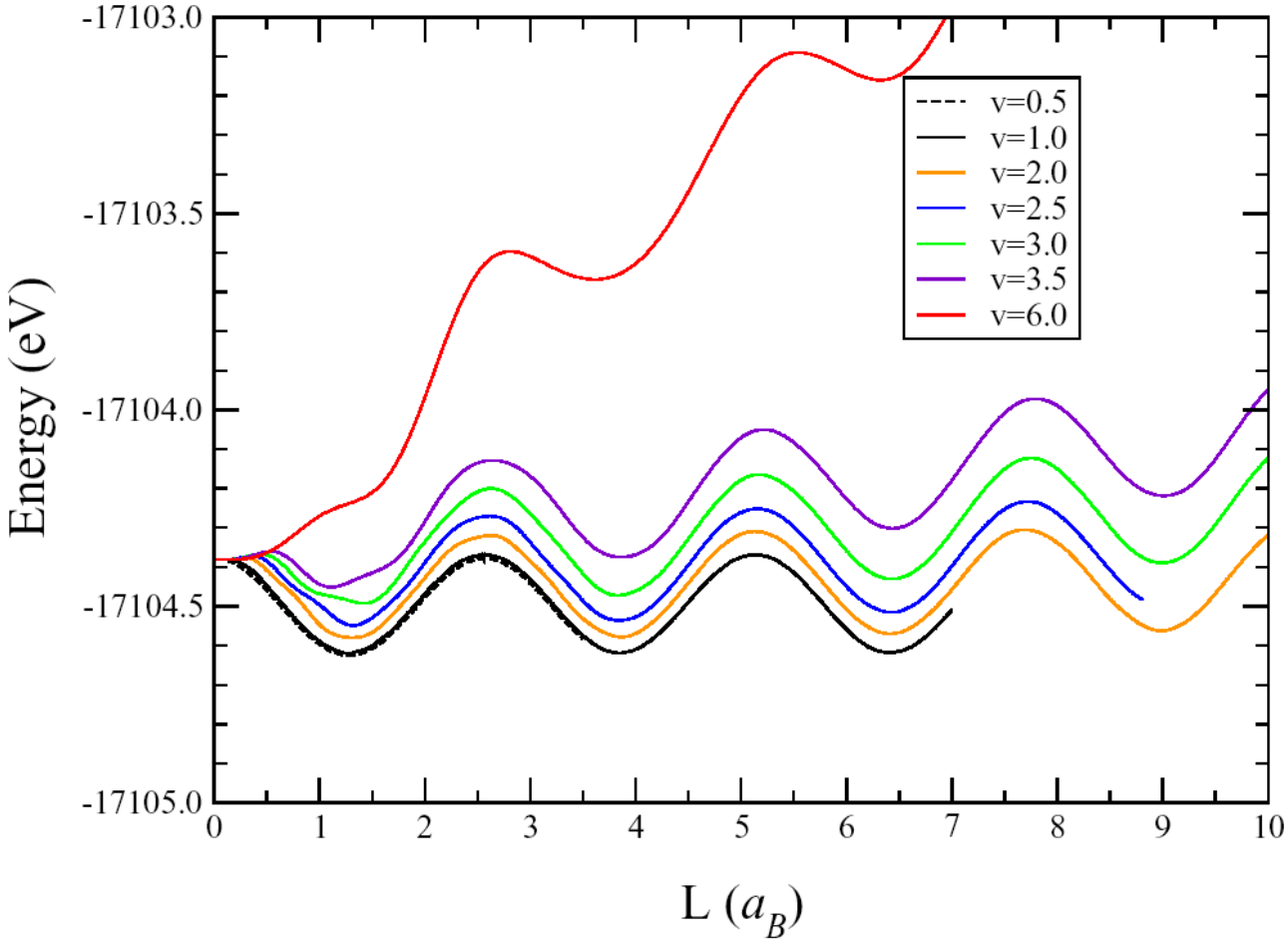
P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

- *Born-Oppenheimer (relaxations, mol. dynamics)*
- *DFT (LDA, GGA)*
- *Pseudopotentials (norm conserving, factorised)*
- *Numerical atomic orbitals as basis (finite range)*
- *Numerical evaluation of matrix elements (3D grid)*

*Implemented in the* ***SIESTA*** *program*

J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon & D. Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002)

# *Energy as a function of distance: LiF*



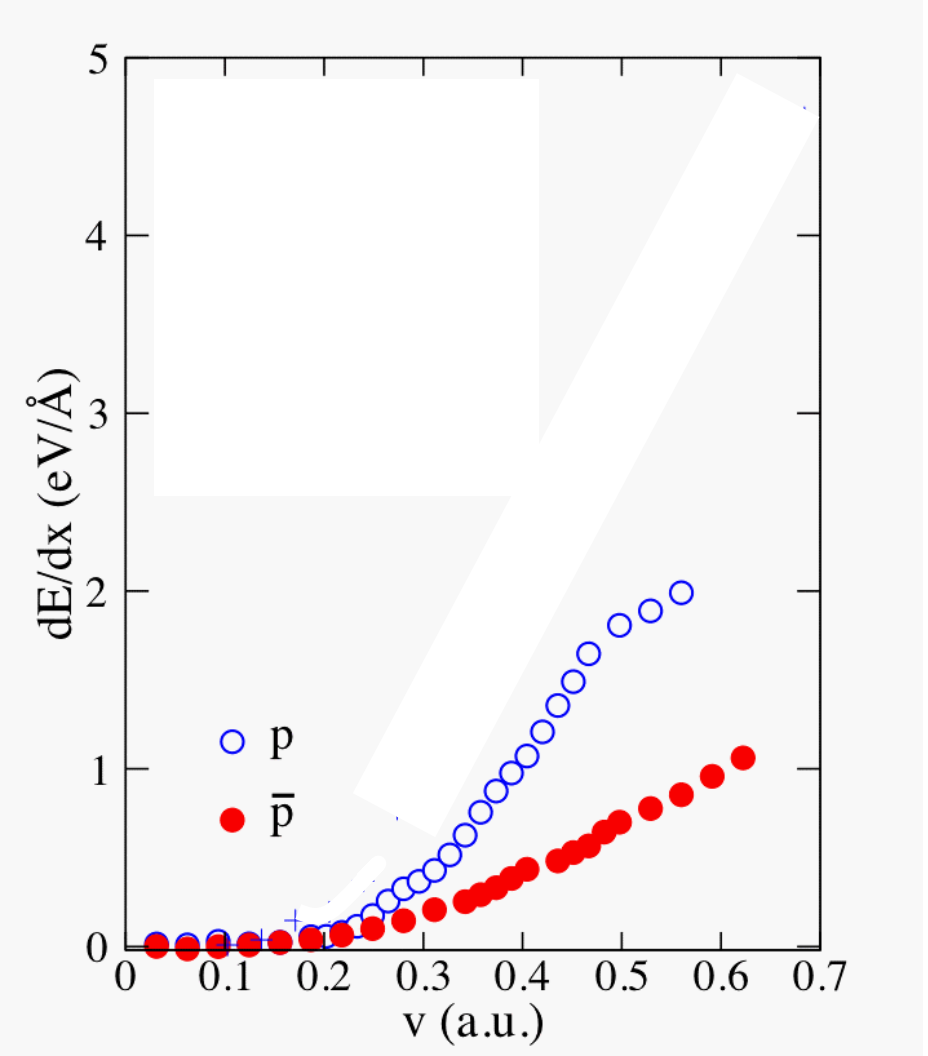

***Quite stationary!*** *Short transient, no obvious oscillation*

# *Rate of energy transfer: electronic stopping power*

*Protons and antiprotons through LiF*

*Threshold ~ 0.2 a.u. (exp ~ 0.1)*

*Ratio $SP_p/SP_a$ ~ 2.4 (exp ~ 2.1)*



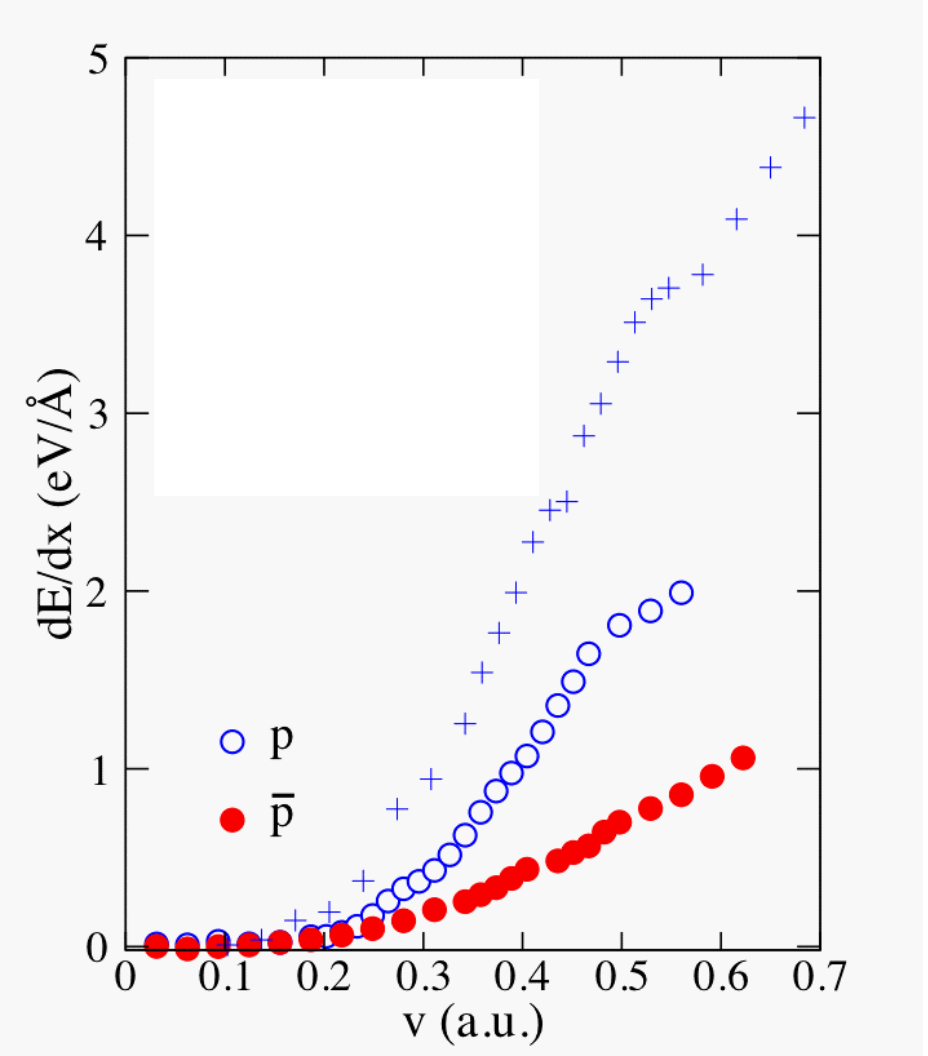
# *Rate of energy transfer: electronic stopping power*

*Protons and antiprotons through LiF*

*Threshold ~ 0.2 a.u. (exp ~ 0.1)*

*Ratio $SP_p/SP_a$ ~ 2.4 (exp ~ 2.1)*

*Absolute value: improve basis; sp basis along trajectory (for p)*



# *Rate of energy transfer: electronic stopping power*

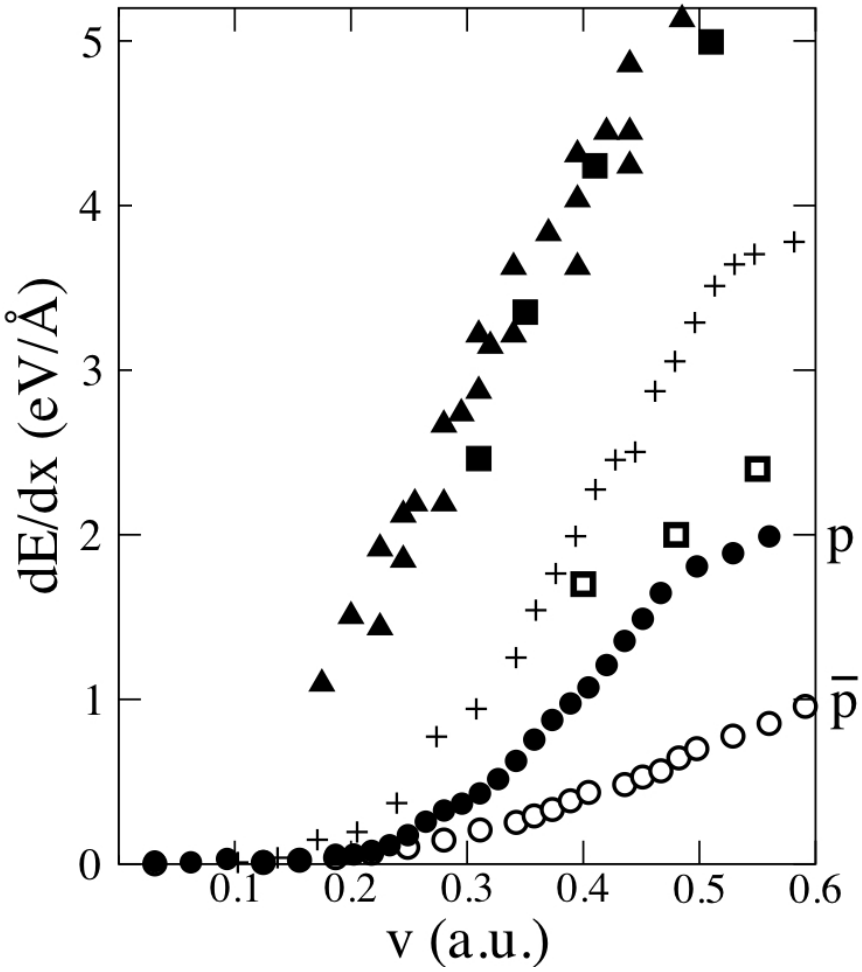
*Protons and antiprotons through LiF*

*Threshold ~ 0.2 a.u. (exp ~ 0.1)*

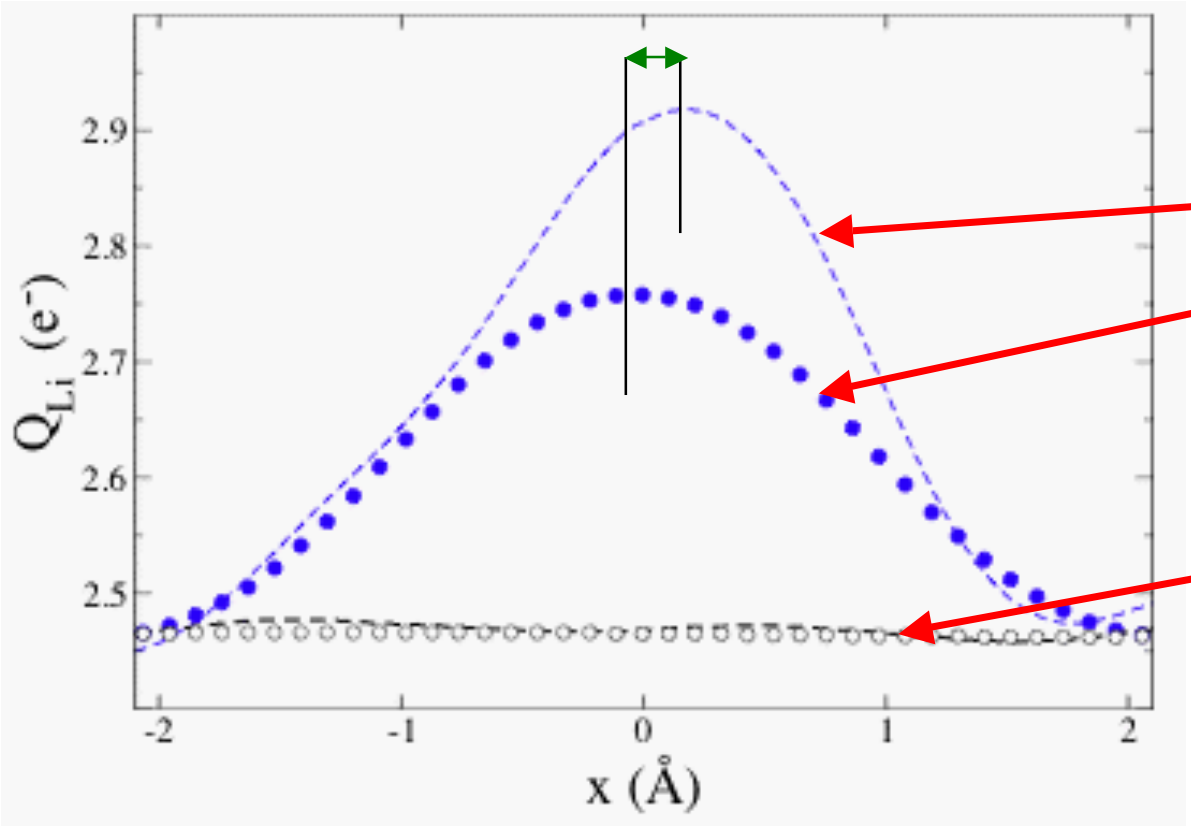
*Ratio $SP_p/SP_a$ ~ 2.4 (exp ~ 2.1)*

*Absolute value ~ 20-50% too small as compared to experiment*

*But: Th is channelling, exp is average*



# *Evolution of the charge on nearby Li atoms*




*v = 1 au*

*v = 0*

*Nearest neighb.*

*2nd nearest neighb.*

*Position of projectile along trajectory (x=0 closest to nearest Li)*

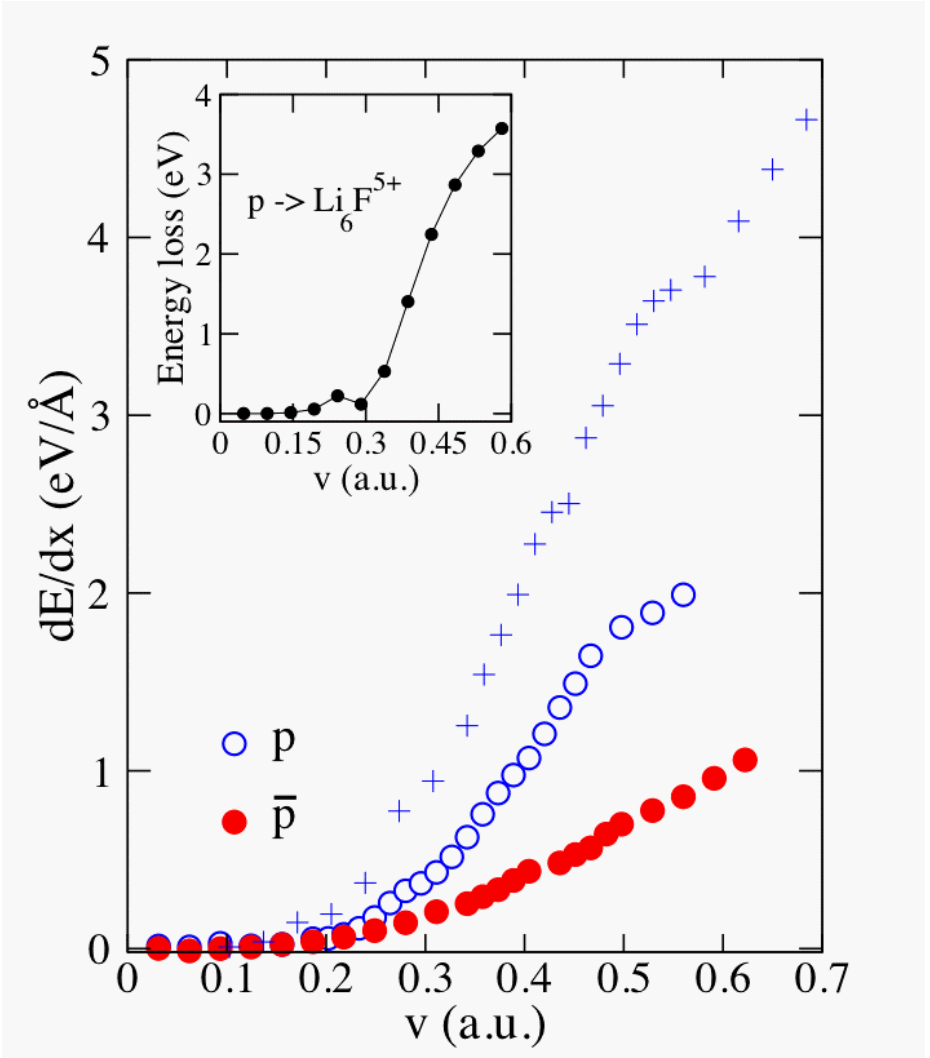
*Screening of charge enhanced at finite v*

*Extremely short-ranged mechanism!* *Why?*

# *Locality in the electronic stopping power*

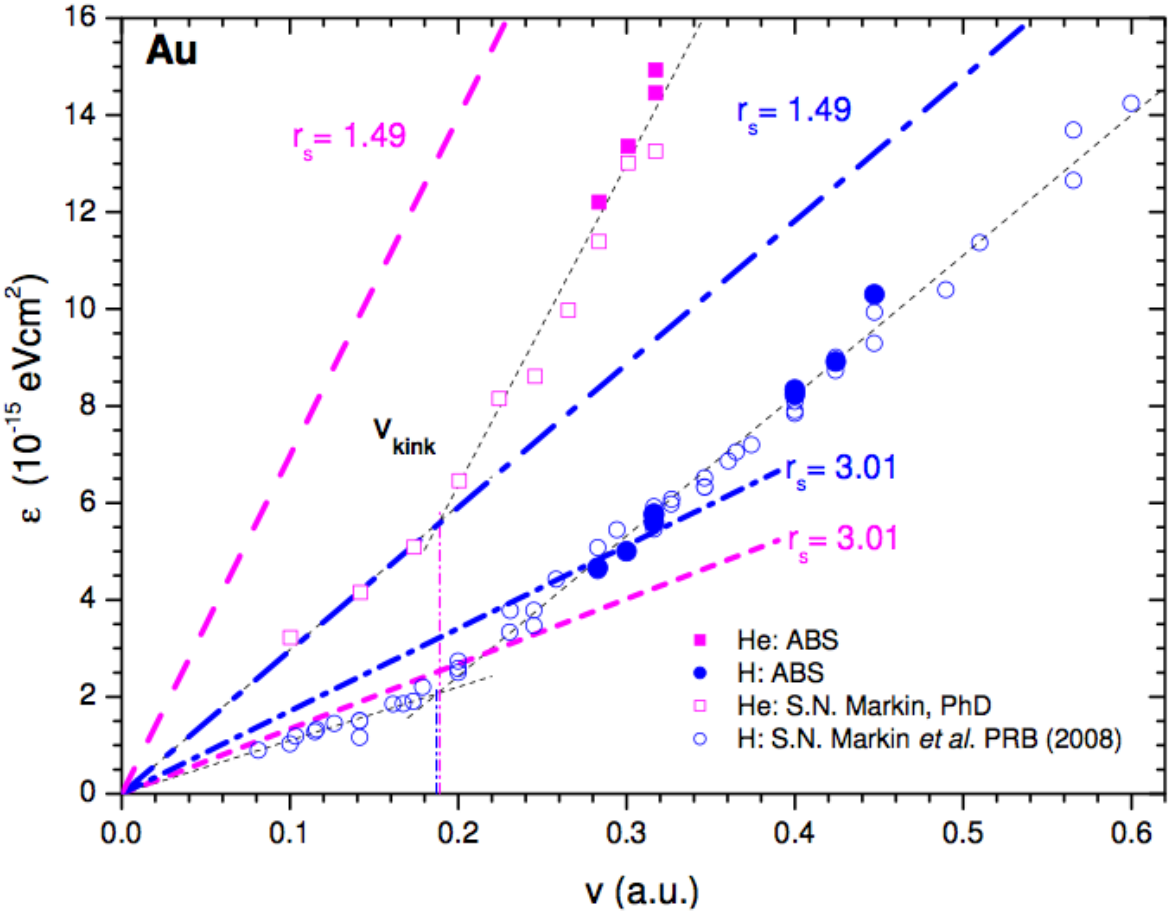
*Protons in LiF*

*Compare bulk with small cluster $Li_6F^{5+}$*



# *What about metals beyond jellium?*

## *Noble and transition metals*




*Electron heating by H and He projectiles in bulk Au*

S. N. Markin, D. Primetzhofer, M. Spitz, and P. Bauer, PRB 2009

# *Summary*

- *Using TD-DFT for obtaining the energy transfer from moving ions to electrons in insulators.*
- *New approach, lots of approximations, but complementary to previous studies*
- *Offers new kinds of information*
- *Need to couple with ion motion*

*Important:*

*Recoiling Th-ion velocity: around threshold!*

*Stopping + Rad Dam + CEID*

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