An Ab-Initio approach to the dynamics of electrons and excitons in solids driven out-of-equilibrium by strong laser pulses

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Yambo©

http://www.yambo-code.org/andrea

Outline

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Motivations and experimental evidences

The AiNEGF approach: solving the Byam-Kadanoff equations in a Kohn-Sham basis

Out-of-equilibrium electron-phonon scattering

Out-of-equilibrium electron-electron scattering

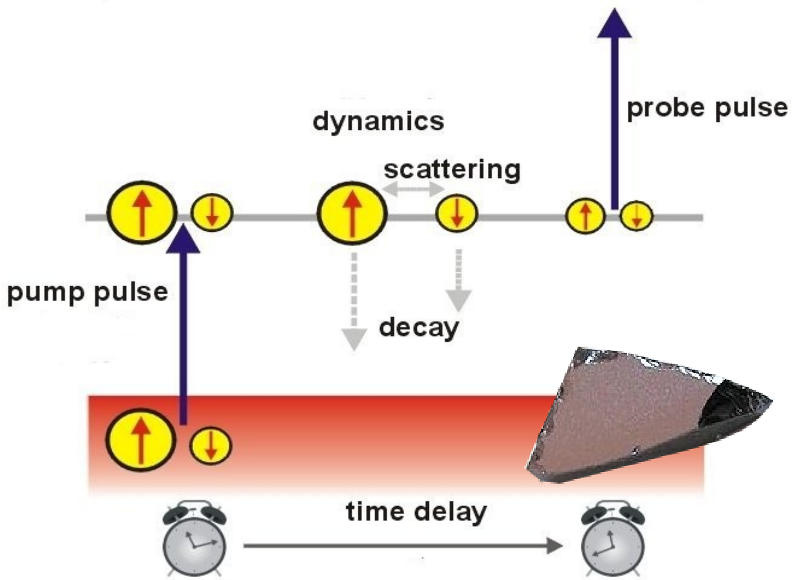
Silicon: intravally scattering of photo-generated electrons

h-BN: photo-induced excitonic collapse

Conclusions...

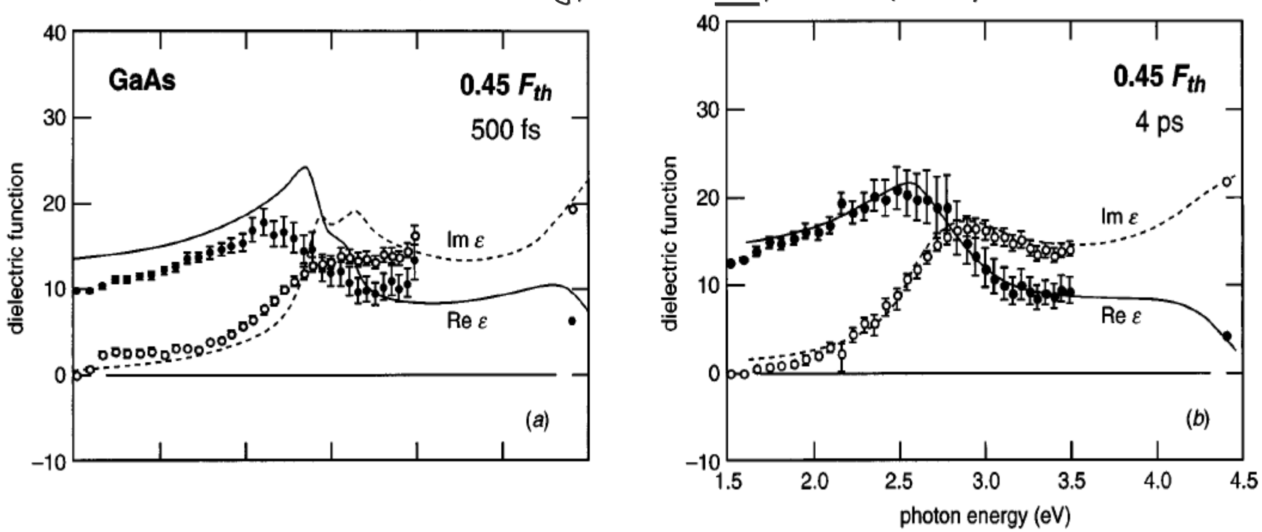
Motivations and experimental evidences

Pump&Probe experiments

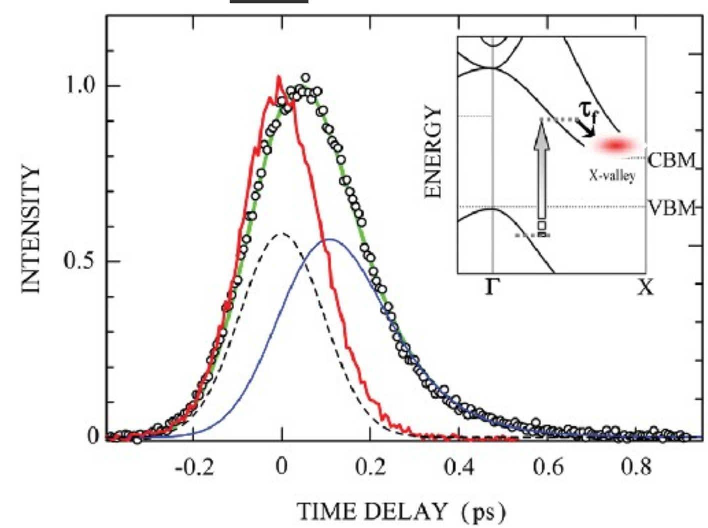


1. An ultra-short laser pulse pumps electrons in the conduction
2. The non-thermal electronic distribution relaxes via e-e and e-ph scatterings
3. The electronic/optical propertiese are probed after varying delays

L. Huang, PRL <u>80</u>, 185 (1997)

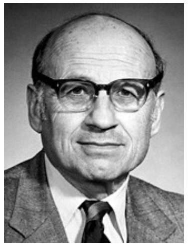


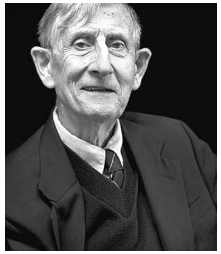
PRL <u>102</u>, 087403 (2009)

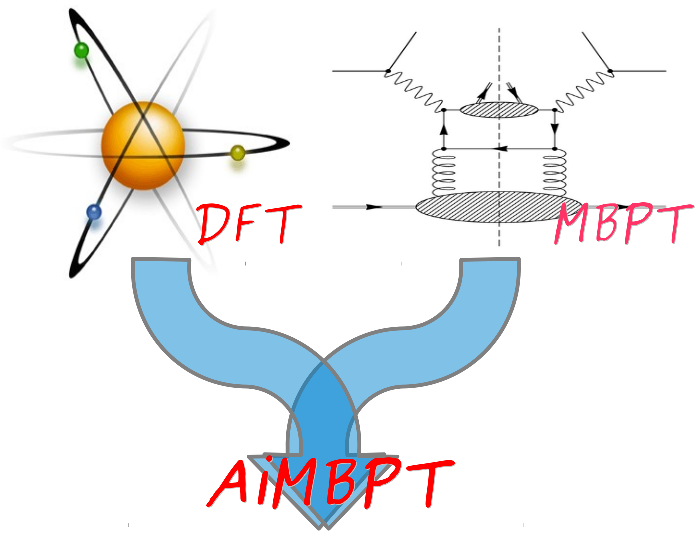


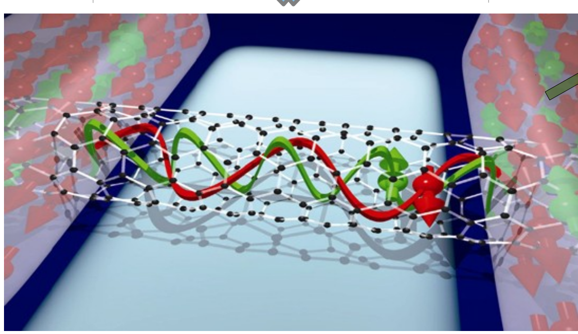
The Ab-Initio non-equilibrium
Green's function approach
(AiNEGF)

The AiMBPT (Ab-Initio Many-Body Perturbation Theory)









G. Onida, Rev. Mod. Phys. 2002

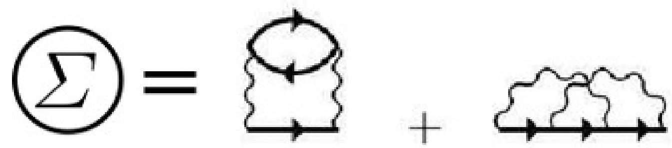
AiMBPT is...

$$\left[\frac{-\nabla^2}{2}+v_s(r)\right]\psi_{nk}(r)=\epsilon_{nk}\psi_{nk}(r)$$

$$v_s(r)=v_{atoms}(r)+V_{Hxc}(r)$$

DFT

+



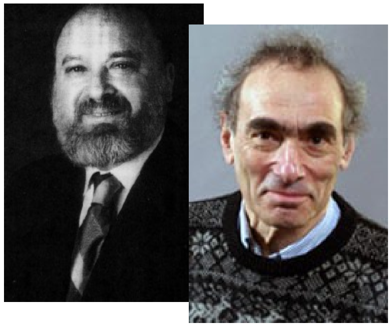
$$G(r_1,r_2;t)\propto\langle T\{\psi(r_1,t)\psi^+(r_2)\}\rangle$$

MBPT

- ✓ Predictive
- ✓ Parameter free
- ✓ Universal
- ✓ Accurate

The Baym–Kadanoff equation in a DFT framework (I)

Any observable is a functional of the Green's functions ($G^{<}$)



Kadanoff & Baym Equations, 1962

DFT (Ab–Initio) Perturbations NEGF theory

$$i\frac{\partial}{\partial t}G^{<}_{nmk}(t)=[H_k+U_k(t),G^{<}_k(t)]_{nm}+S^{<}_{nmk}(t)$$

Kadanoff–Baym "Statistical Mechanics" (1994)

DFT+NEGF → **AiNEGF**

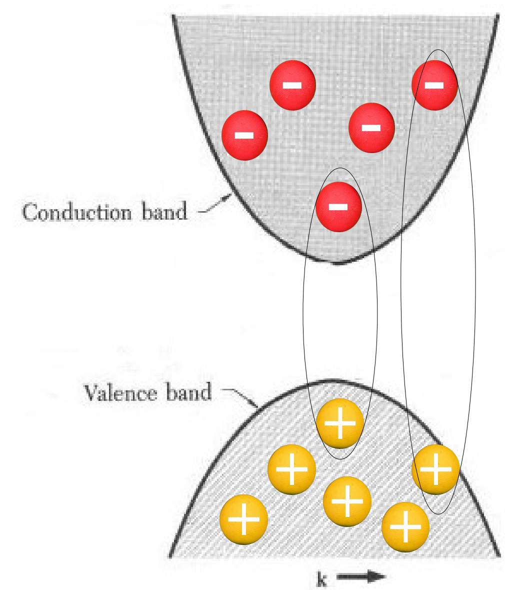
Parameter free, predictive and accurate

$$N_c(t)=-i\sum_{nk\,empty}G^{<}_{nnk}(t)$$

Marker of potential non–perturbative effects

$$P(t)\propto\sum_{mnk}r_{mnk}G^{<}_{mnk}(t)$$

$$\chi(\omega)=\frac{P(\omega)}{E(\omega)}$$



The Baym-Kadanoff equation in a DFT framework (II)

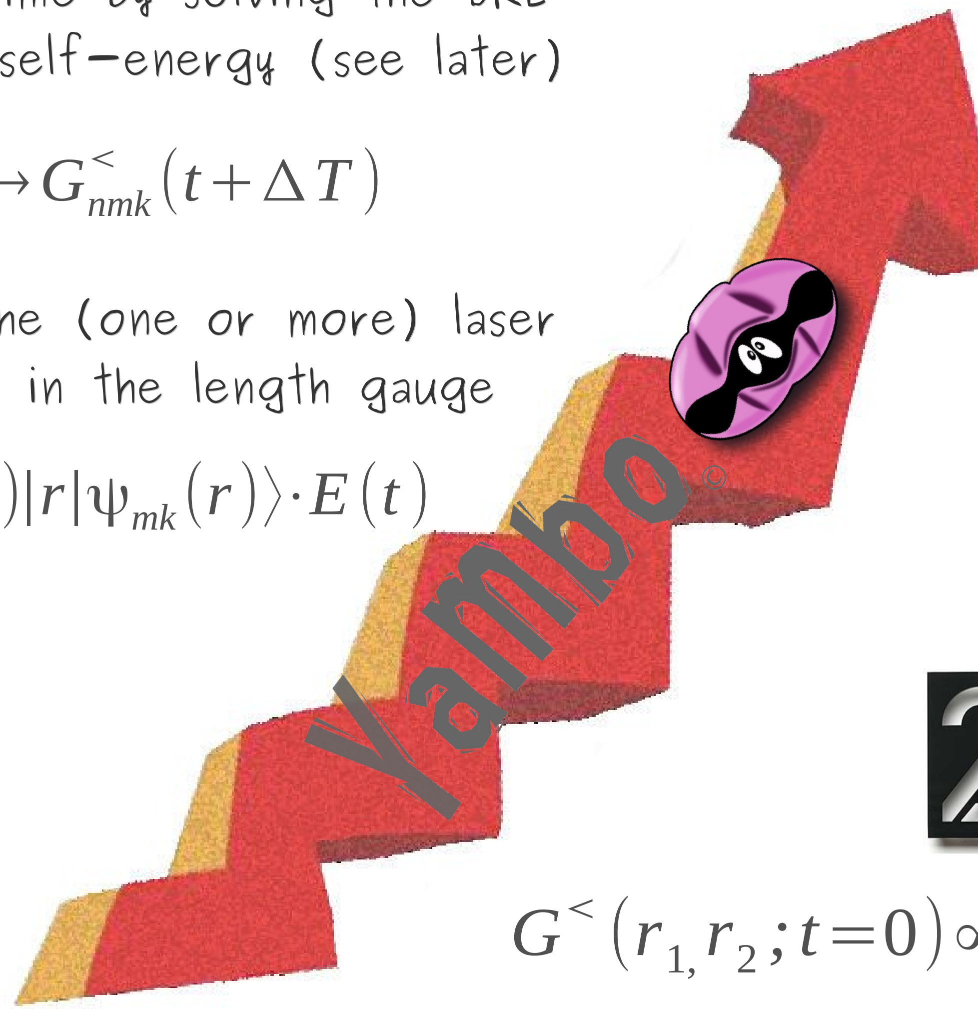
3

The lesser Green's function is evolved in time by solving the BKE for a given self-energy (see later)

$$G^{<}_{nmk}(t) \rightarrow G^{<}_{nmk}(t+\Delta T)$$

The interaction with the (one or more) laser fields is introduced in the length gauge

$$U_k(t) \propto \sum_{nm} \langle \psi_{nk}(r) | r | \psi_{mk}(r) \rangle \cdot E(t)$$



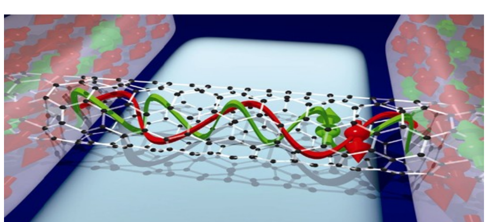
4

Post-Processing

$$G^{<}_{nmk}(t)$$

$$\chi^{n}(\omega) \qquad f_{nk}(t)$$

1

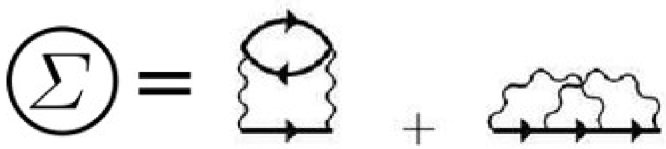


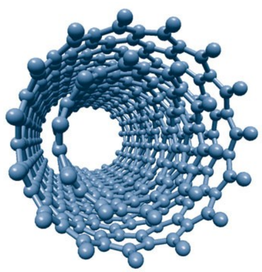
2

$$G^{<}(r_1, r_2; t=0) \propto \langle \psi(r_1, t) \psi^{+}(r_2) \rangle$$

Boundary conditions and lesser and retarded Green's functions are written in the KS basis

The Baym-Kadanoff equation in a DFT framework (III)





AiNEGF

Microscopic details of the system fully and consistently taken into account

$$W(r,r';t,t')$$

$$\psi(r,t)$$

NO ad-hoc parameters

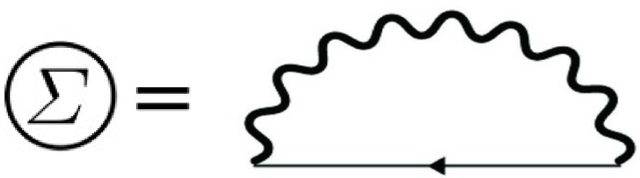
NO use of few-bands models, parabolic (effective mass) dispertion...

The out-of-equilibrium kernel

$$i\frac{\partial}{\partial t}G^{<}_{nmk}(t)=[H_k+U_k(t),G^{<}_k(t)]_{nm}+S^{<}_{nmk}(t)$$

$$S(t)=\int_{-\infty}^{t}d\tau\left[\Sigma^{>}(t,\tau)G^{<}(t,\tau)+G^{<}(t,\tau)\Sigma^{>}(t,\tau)-\Sigma^{<}(t,\tau)G^{>}(t,\tau)-G^{>}(t,\tau)\Sigma^{<}(t,\tau)\right]$$

Phonons



Electron–Phonon scattering

E–h pairs

Electron–Electron scattering

\+ Massive approximations

\+ number–crunching techniques

The NEGF kernel: Electron-phonon and electron-electron scatterings from an Ab-Initio presepective

The electron−phonon out−of−equilibrium kernel (I)

$$i\frac{\partial}{\partial t}G^{<}(t,t)=[h^{DFT}+\Sigma_s(t),G^{<}(t,t)]+S(t)$$

$$S(t)=\int_{-\infty}^{t}d\tau\left[\Sigma^{>}(t,\tau)G^{<}(t,\tau)+G^{<}(t,\tau)\Sigma^{>}(t,\tau)-\Sigma^{<}(t,\tau)G^{>}(t,\tau)-G^{>}(t,\tau)\Sigma^{<}(t,\tau)\right]$$

Kadanoff−Baym "Statistical Mechanics" (1994)

$$\Sigma^{<}_{nn'k}(t,\tau)=\frac{i}{N_q}\sum_{mm'q}\overline{\left(g^{q\lambda}_{nmk}\right)}\,g^{q\lambda}_{n'm'k}\,D^{<}_{q\lambda}(t,\tau)\,G^{<}_{mm'k-q}(t,\tau) \quad +$$

BKE → $$G^{<}(t,\tau)\approx i\left[G^{r}(t-\tau)G^{<}(\tau)-G^{<}(t)G^{r}(t-\tau)\right] \quad +$$

Quasi−equilibrium & Complete Collisions Approx → $$G^{<}_{nmk}(T)\approx\delta_{nm}f_{nk}(T) \quad +$$

G^{r} is polaronic (no short−time correction) → $$G^{r}_{nk}(T)=-i\,e^{-i\varepsilon_{nk}(\beta)t-\Gamma_{nk}(\beta)t}\,\theta(t) \quad =$$

HOLE Lifetime

ELECTRON Lifetime

THERMAL Lifetime

$$\partial_t f_{nk}(T)=\gamma^{(h,e-p)}_{nk}(T)\left(1-f_{nk}(T)\right)-\gamma^{(e,e-p)}_{nk}(T)f_{nk}(T)-\gamma^{(th)}_{nk}(\beta,T)$$

Density Functional Perturbation Theory [S. Baroni, Rev. Mod. Phys. 73, 515 (2001)]

$V_{ion}^{bare}[\{R\}](r)$

$R \to R + \delta R$

$\delta\rho(r)$

$\delta V_{xc}(r)$

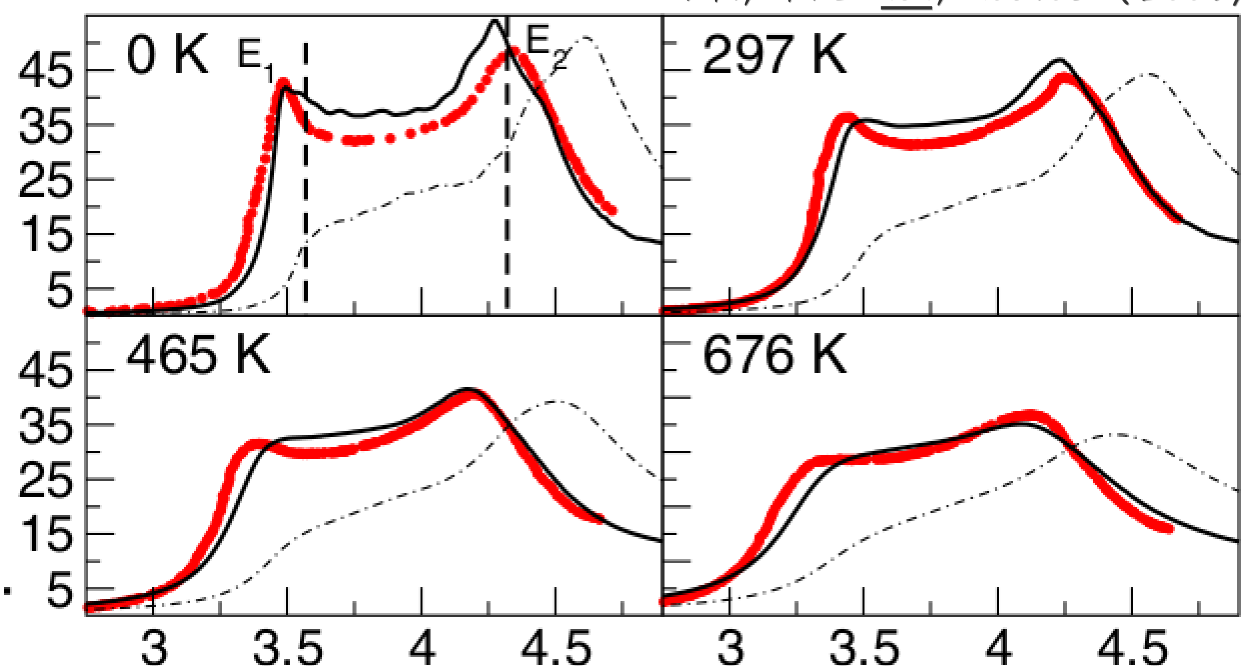
$\chi(r, r')$

$V_{KS}[\{R\}](r)$

$$g_{nn'k}^{q\lambda} \sim (M\omega_{q\lambda})^{-1} \langle nk | \frac{dV_{KS}}{du_{q\lambda}} | n'k-q \rangle$$

- ✓ Off-diagonal m.e. Are naturally included
- ✓ Electron-phonon m.e. And frequencies are calculated Ab-Initio

AM, PRL **101**, 106405 (2008)



The electron–phonon out-of-equilibrium kernel (II)

HOLE Lifetime

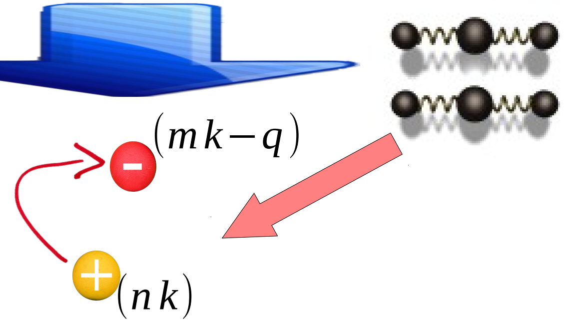
ELECTRON Lifetime

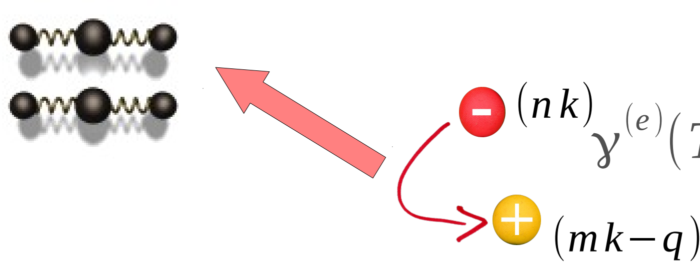
THERMAL Lifetime

$$\partial_t f_{nk}(T) = \gamma_{nk}^{(h,e-p)}(T)\left(1-f_{nk}(T)\right) - \gamma_{nk}^{(e,e-p)}(T)\, f_{nk}(T) - \gamma_{nk}^{(th)}(\beta,T)$$

$$P_{ph-emit} \equiv \frac{\Gamma_{nk}+\Gamma_{mk-q}}{(\Gamma_{nk}+\Gamma_{mk-q})^2+(\varepsilon_{mk-q}-\varepsilon_{nk}+\omega_{q\lambda})^2} \qquad P_{ph-ab} \equiv \frac{\Gamma_{nk}+\Gamma_{mk-q}}{(\Gamma_{nk}+\Gamma_{mk-q})^2+(\varepsilon_{mk-q}-\varepsilon_{nk}-\omega_{q\lambda})^2}$$

$$\gamma^{(h)}(T) = \frac{\sum_{q\lambda m} |g_{nmk}^{q\lambda}|^2}{N_q} P_{ph-ab} f_{mk-q}(T)$$





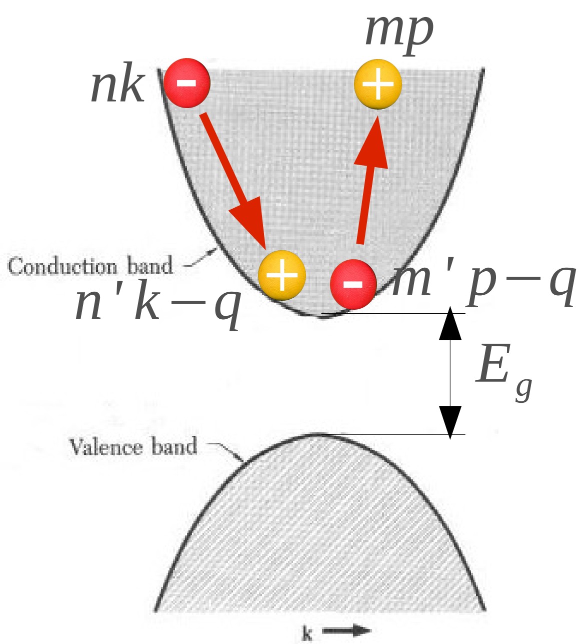
$$\gamma^{(e)}(T) = \frac{\sum_{q\lambda m} |g_{nmk}^{q\lambda}|^2}{N_q} P_{ph-emit}\left(1-f_{mk-q}(T)\right)$$

The thermal lifetime includes both kinds of scatterings weighted by the phonon occupation. It is vanishing at zero temperature

Electron–Electron scattering in the GW approximation

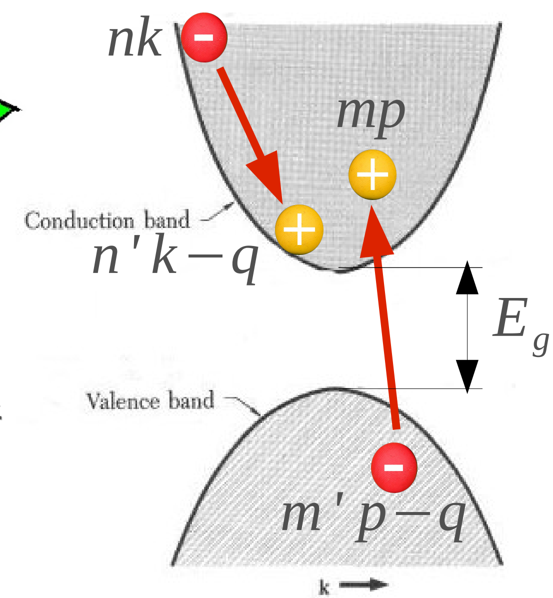
$$\partial_t f_{nk}(T) = \left(\gamma_{nk}^{(h,e-p)}(T) + \gamma_{nk}^{(e,e-e)}\right)\left(1 - f_{nk}(T)\right) - \gamma_{nk}^{(e,e-p)} + \gamma_{nk}^{(e,e-e)}(T) f_{nk}(T) - \gamma_{nk}^{(th)}(\beta, T)$$

$$\gamma_{nk}^{(e,e-e)}(T) \propto \sum_{qp} \sum_{n'mm'} \left|W^{q}_{nn'k,mm'p}\right|^2 \left[\frac{4\Gamma}{\left(\epsilon_{n'k-q} + \epsilon_{mp} - \epsilon_{m'p-q} - \epsilon_{nk}\right)^2 + 16\Gamma^2}\right] \left(1 - f_{n'k-q}(T)\right)\left(1 - f_{mp}(T)\right) f_{m'p-q}(T)$$



Intraband scattering. It takes contributions ONLY from the photo-excited electrons. Its strength goes with the carrier density.

In the e-p case this process is ALWAYS non zero as the Debye energy is much smaller than the gap



Dominant process in the low carriers density. It takes contributions also from the unperturbed electrons. But it is zero whenever

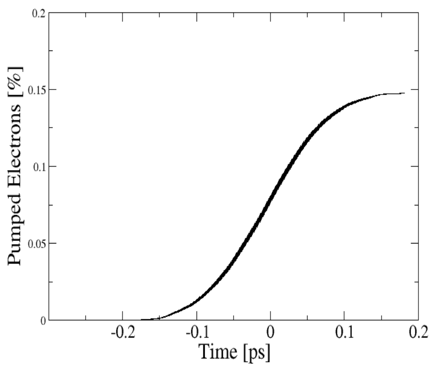
$$\epsilon_{nk} \leq 2E_g$$

Ultrafast Carrier Relaxation in Si: Intravalley Scattering and Energy Relaxation of photoexcited Electrons

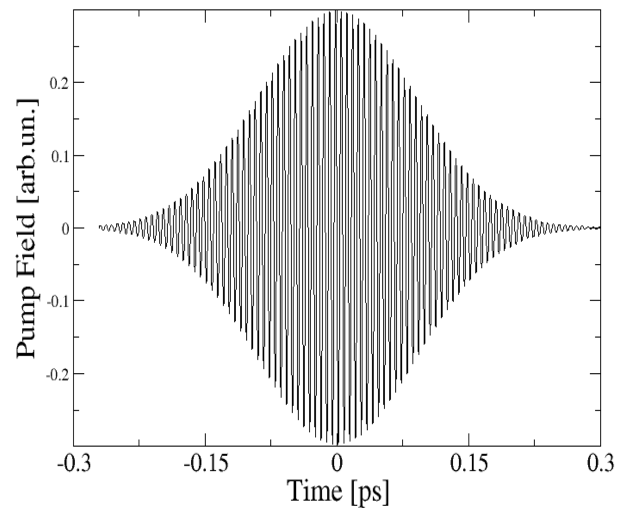
Phonon induced electronic decay in Bulk Silicon [A. Marini, in preparation]

$$\partial_t f_{nk}(T) = \gamma^{(h)}(1 - f_{nk}(T)) - \gamma^{(e)}(T) f_{nk}(T) - \gamma^{(th)}(\beta, T)$$

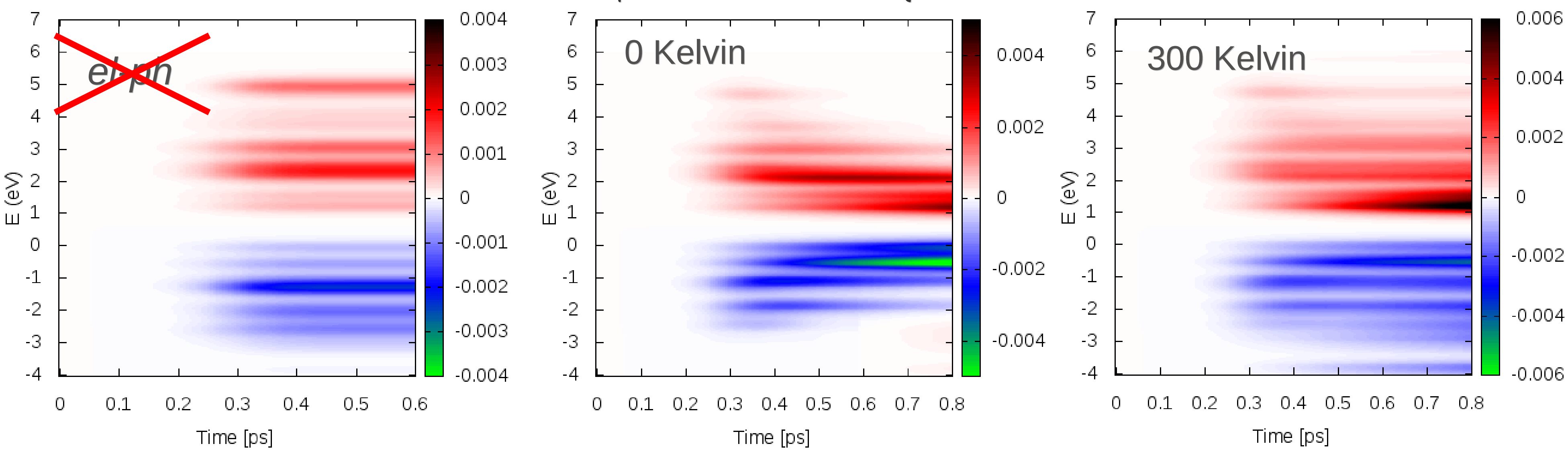
Pump field is "quasi harmonic" with frequency 2.03 eV and fluence 0.004 $\frac{J}{cm^2}$



Pumped electrons

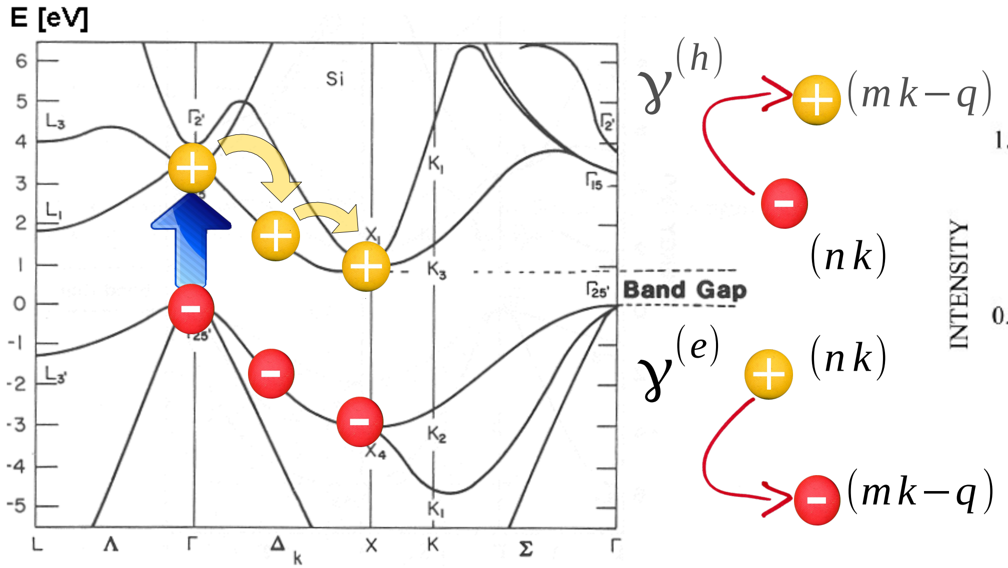


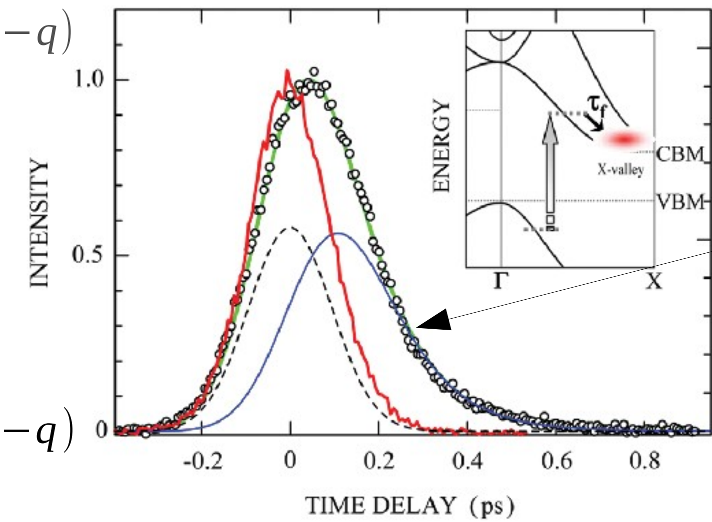
Time-dependent Density-of-states



Intra-valley scattering in Bulk Silicon

$$\partial_t f_{nk}(T) = \gamma^{(h)}(1 - f_{nk}(T)) - \gamma^{(e)}(T) f_{nk}(T) - \gamma^{(th)}(\beta, T)$$

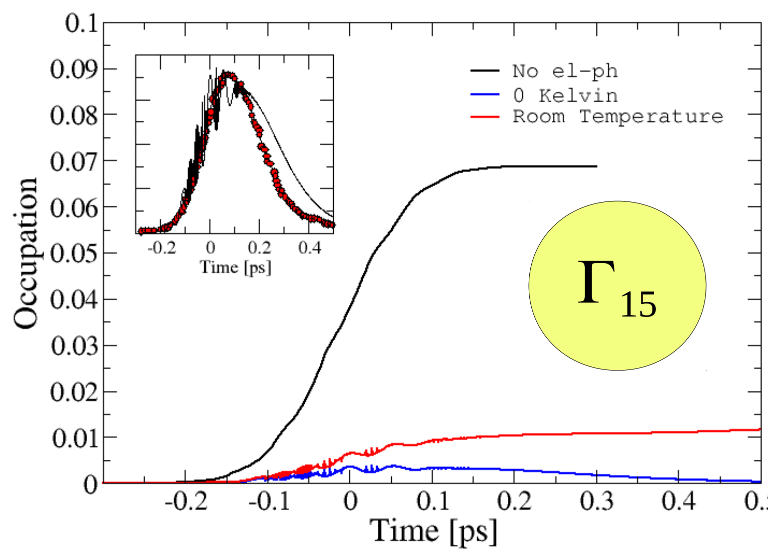


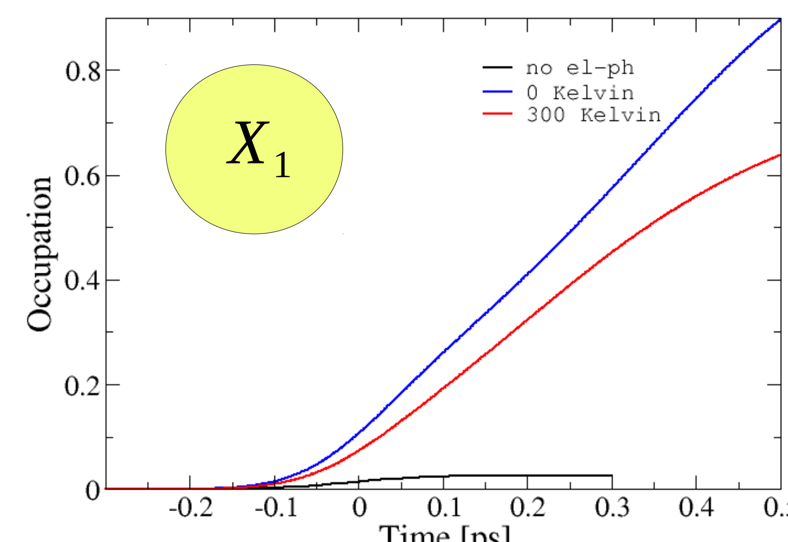


$\tau_f^{exp} = 40 \pm 10\,fs$

$\tau_f^{MBPT} = 18\,fs$

Relaxation is a
CASCADE process.
Standard MBPT
does not apply!





h-BN: photo-induced
excitonic collapse

The Method

The TD-BSE

$$f_{nk}(t) = -iG^{<}_{nnk}(t)$$

L.X. Benedict PRB 63, 075202 (2001)
F.X. Camescasse PRL 77, 5429(1996)

K. F. Berggren
PRB 24, 1971 (1981)

Standard BSE
(at each time)

Standard GW
(at each time)

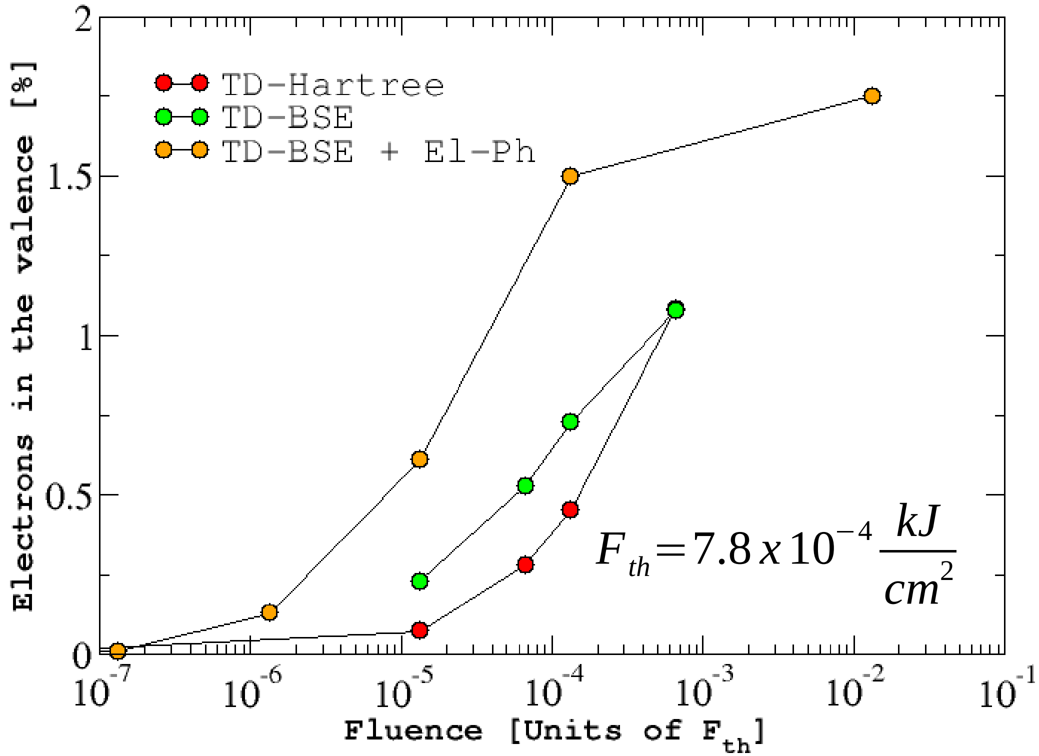
$$H^{BSE}_{IJ}(t) = E_I \delta_{IJ} + f^{eh}_I(t)\left(2V_{IJ} - W_{IJ}(t)\right)$$

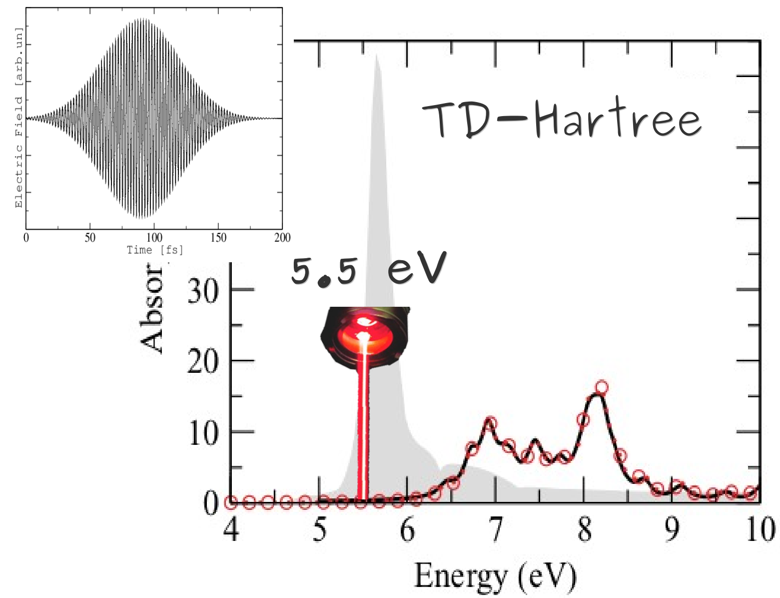
$$\Sigma(t) = iG(t)W(t)$$

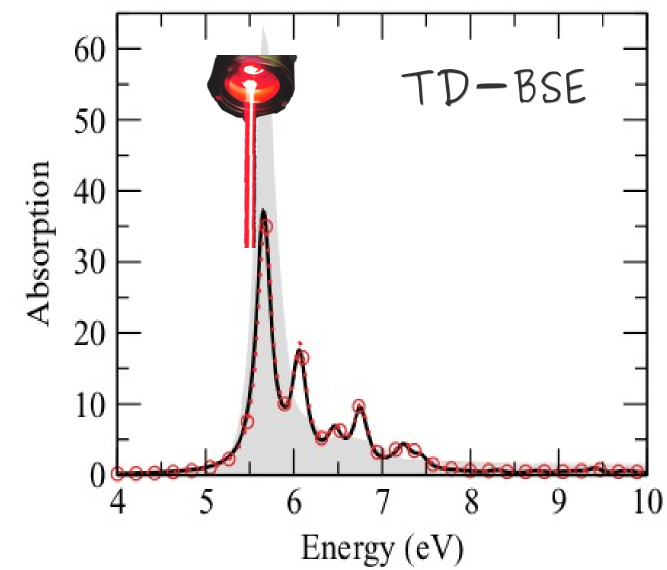
Time-resolved
Probe Absorption

Band-gap
renormalization

Exciton collapse by Pauli blocking + intra-band screening in h-BN (I)





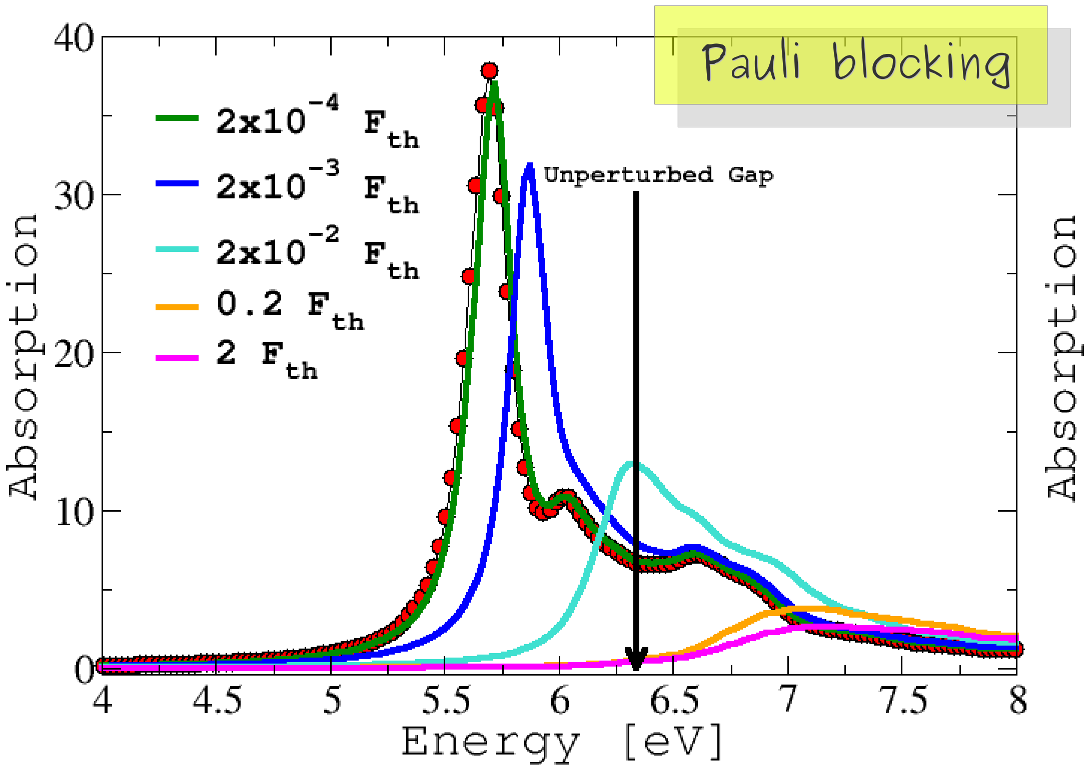


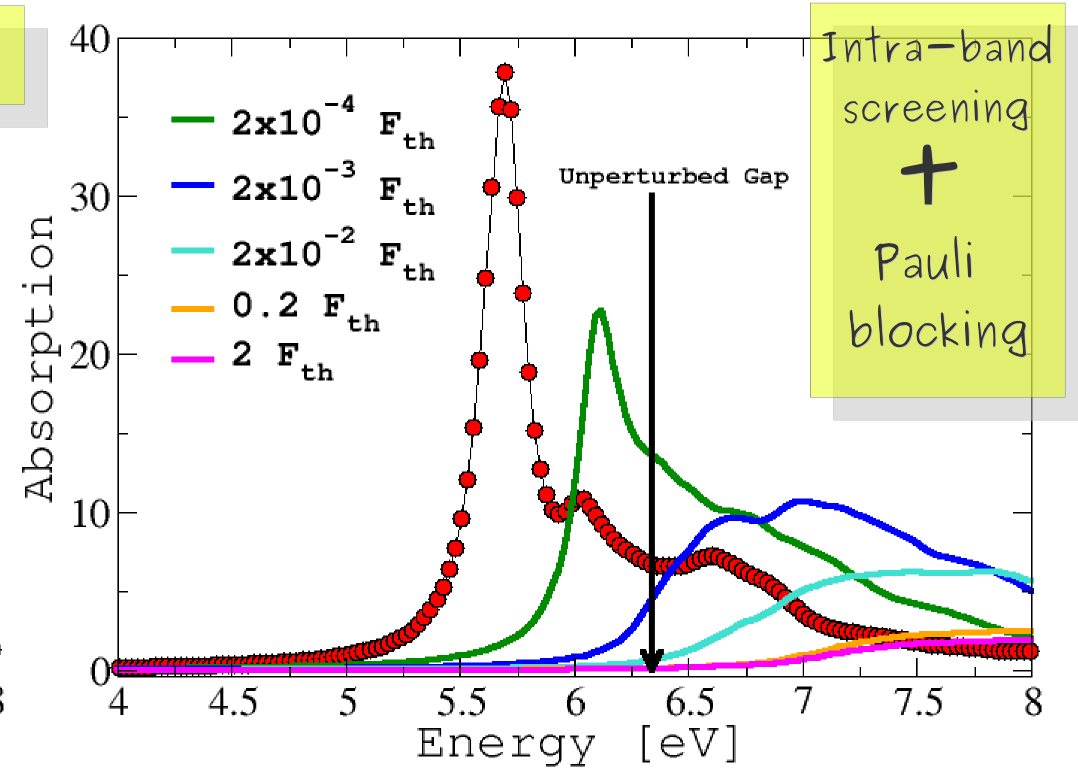
Crucial use of ab-initio polaronic dephasing for a correct pumping dynamics

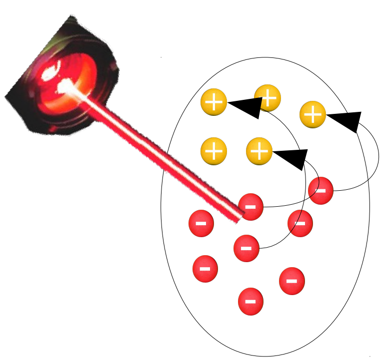
The TD-BSE enhances the carriers excitation when the pulse is resonant with the exciton

The El-Ph interaction empties on-the-fly the pumped states

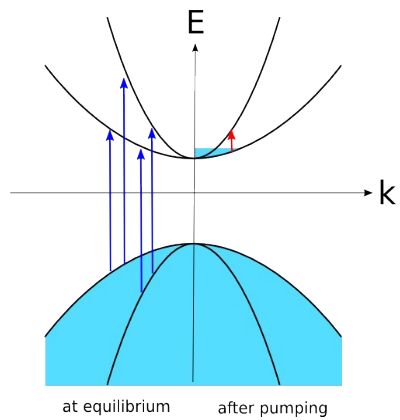
Exciton collapse by Pauli blocking + intra-band screening in h-BN (II)



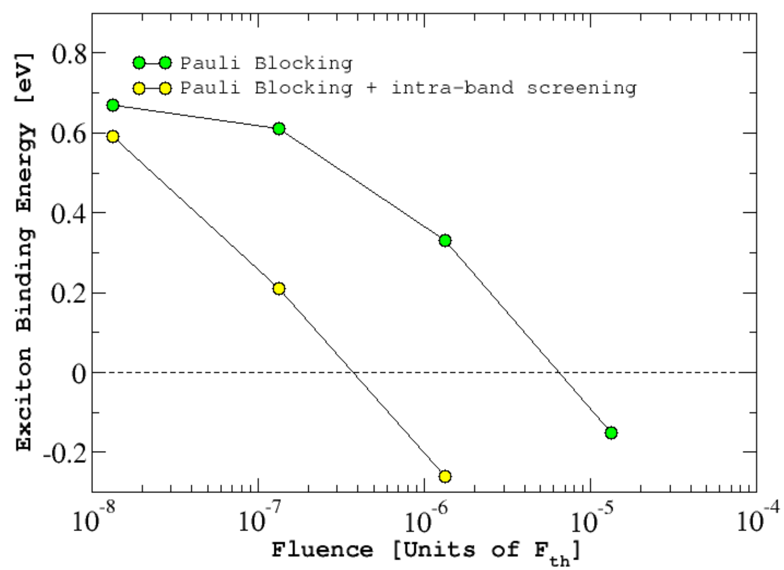




Pauli blocking

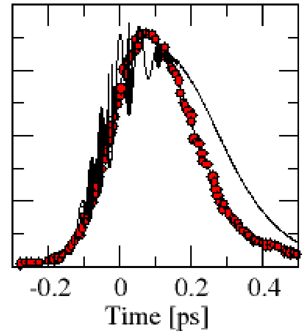


Intra-band screening

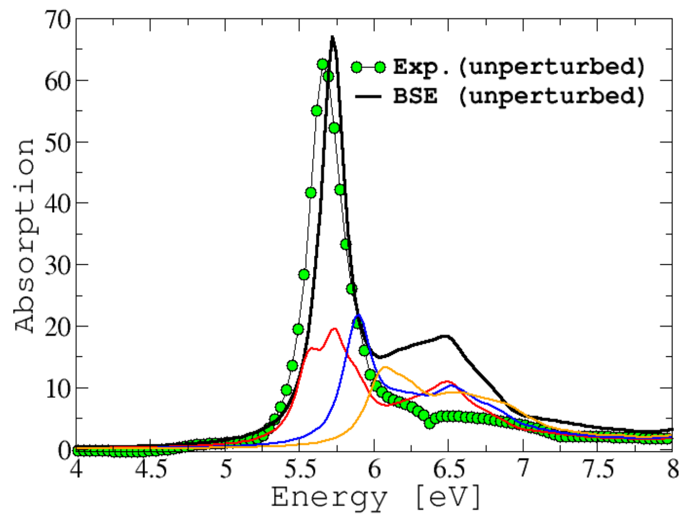


Conclusions...

Time-dependent Density-of-states in excellent agreement with experimental results

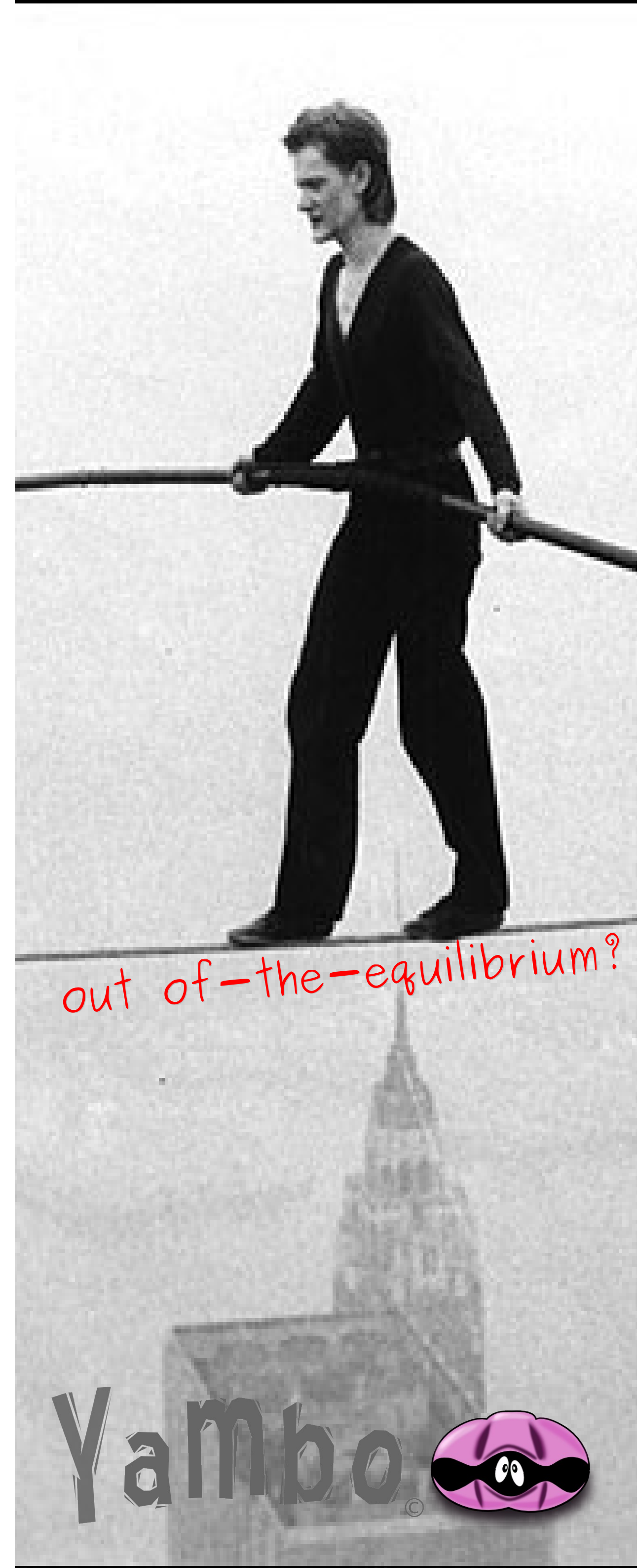


The modifications induced by the pump in the probe absorption can be moderate (GaAs) or even so strong to collapse the excitonic state (hBN)



AiNEGF → Several potential applications...

Yambo: an ab initio tool for excited state calculations, A. Marini, C. Hogan, M. Grüning, D. Varsano, Comp. Phys. Comm. 180, 1392 (2009).



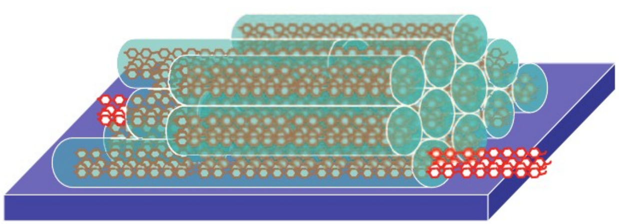
Potential AiNEGF applications...

AiNEGF

Saturation Phenomena

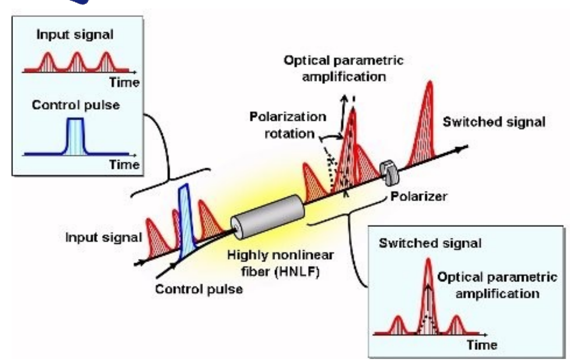
X-ray induced transparency in Al (Nagler. Nature, 2009)

FLASH II.



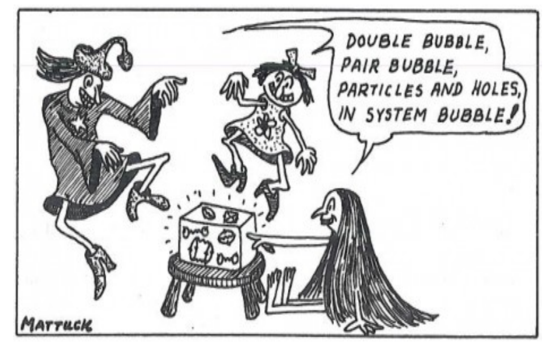
High-gain materials

Amplified light emission in aligned polymers (I.B. Martini. Nature, 2007)



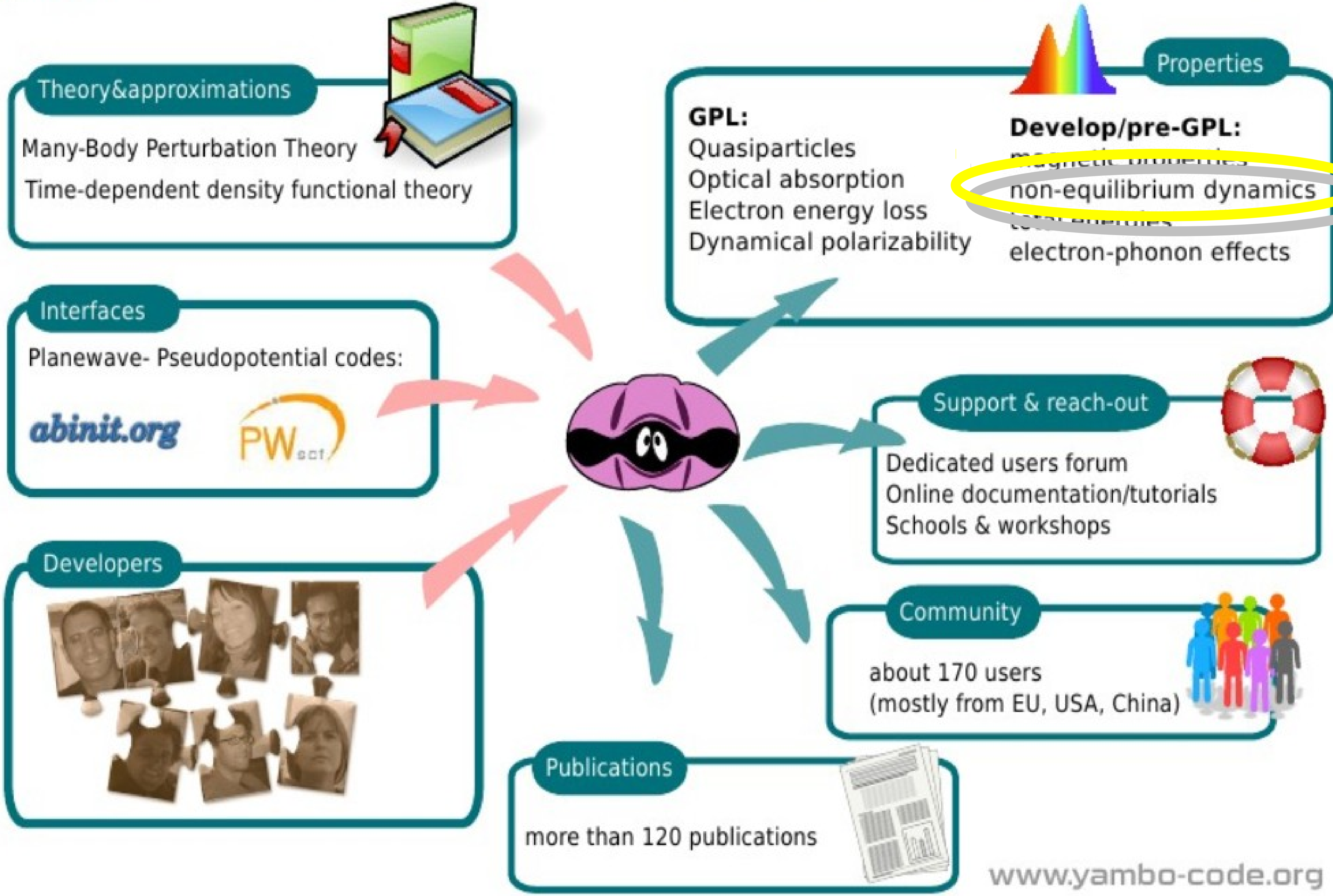
Nano optical devices

Single-molecule (Hwang. Nature, 2009) and Carbon Nanotube (Tans, Nature, 1998) optical transistors



Severe testing-ground for Many-Body theories

Yambo: an ab-initio tool for excited state calculations



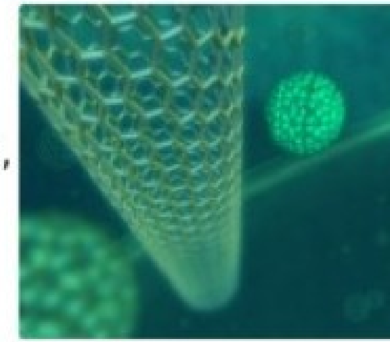
Yambo: an ab-initio tool for R&D

Material Science

applications to
e.g. photovoltaics,
lithium batteries,
microelectronics

Nano Science

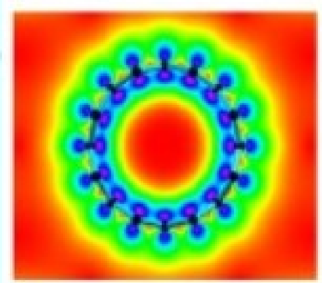
applications to
e.g. nanophotonics,
nanoelectronics



Biology

studies of
photoactive
molecules
and molecular
complexes

Physics



fundamental
understanding
of physical
processes

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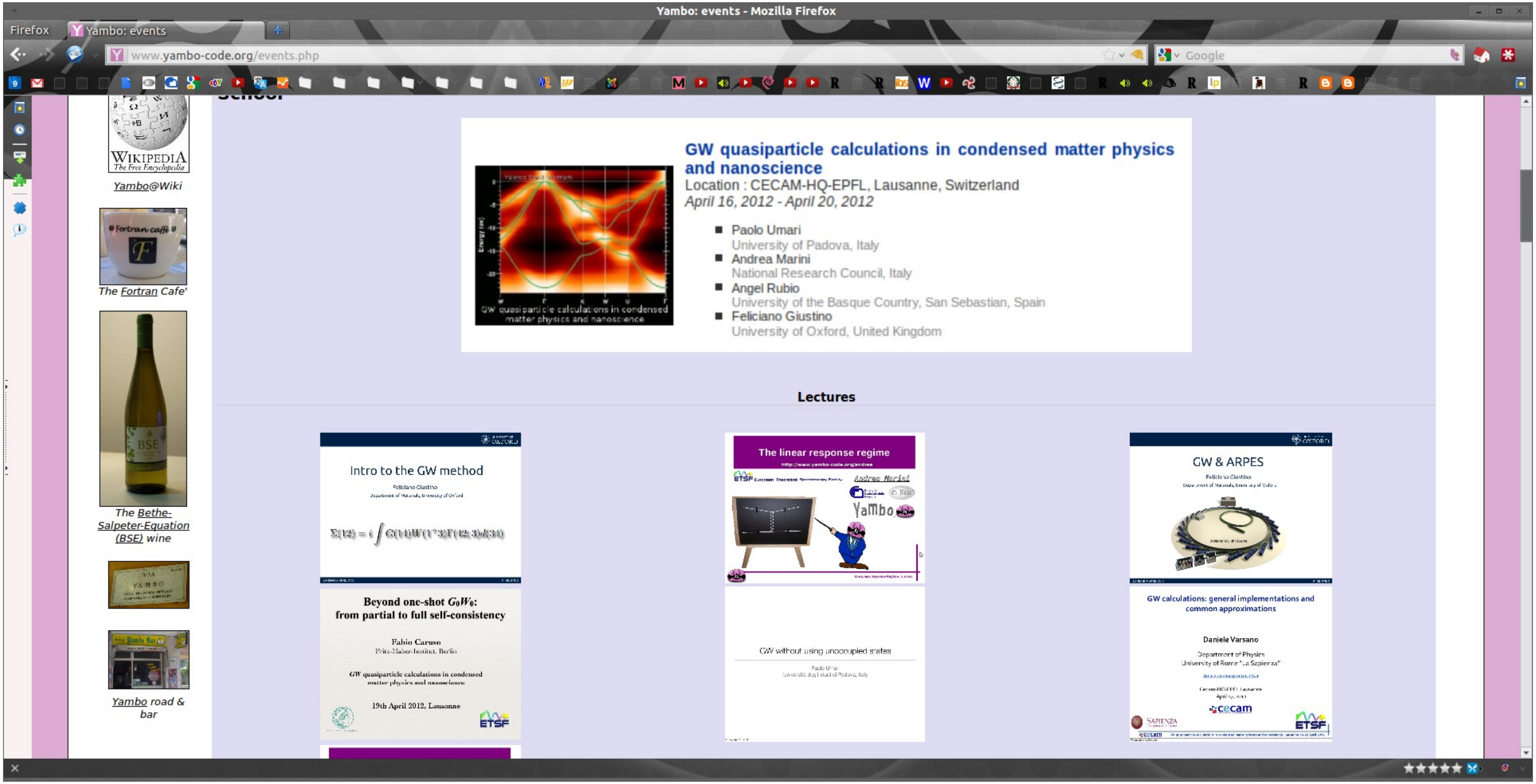

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