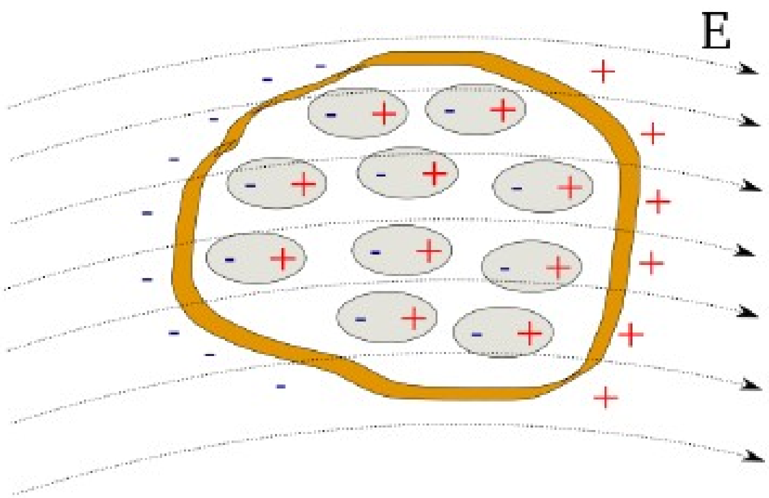
Real Time spectroscopy

the Yambo team

Absorption



Materials equations:

$$D(r,t)=E(r,t)+P(r,t)$$

Electric Displacement — Electric Field — Polarization

In general:

$$\Delta P(r,t)=\int \alpha(t-t',r,r')E(t'r')dt'dr'+\int dt^1 dt^2 \alpha^2(\ldots)E(t^1)E(t^2)+O(E^3)$$

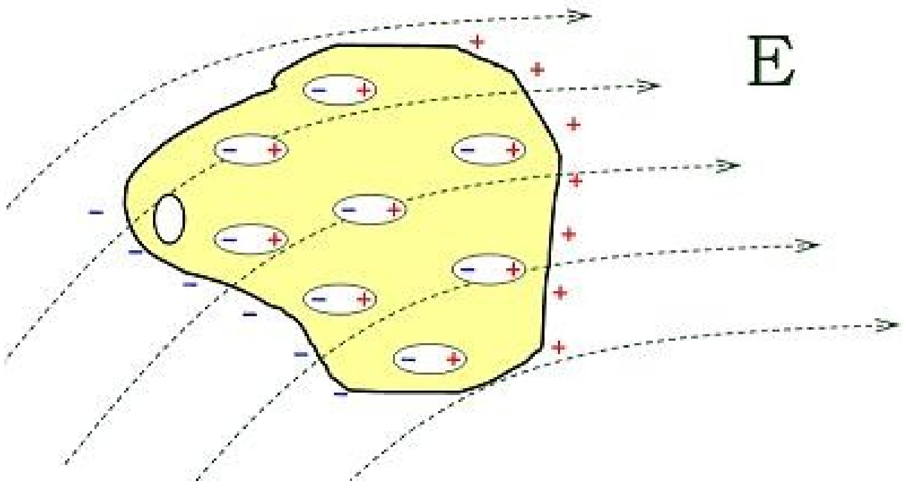
Theory of Absorption

small perturbation → **first term in the expansion,**
the linear response regime

$$\Delta P(r,t)=\int \alpha(t-t',r,r')E(t'r')dt'dr'+O(E^2)$$

$$\Delta P(\omega)=\alpha(\omega)E(\omega)$$

$$P(\omega)=D(\omega)-E(\omega)$$
$$=(\epsilon(\omega)-1)E(\omega)$$



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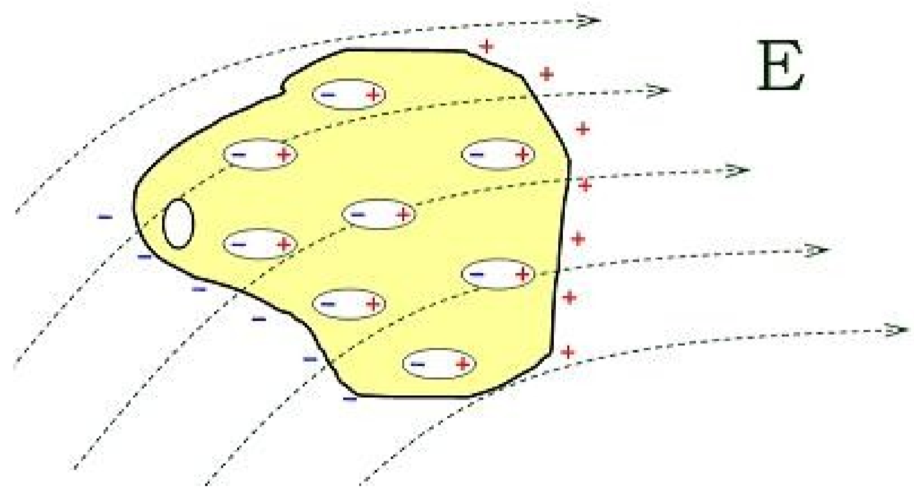
Frequency space spectroscopy

$$\epsilon(\omega)=1+\alpha(\omega)$$



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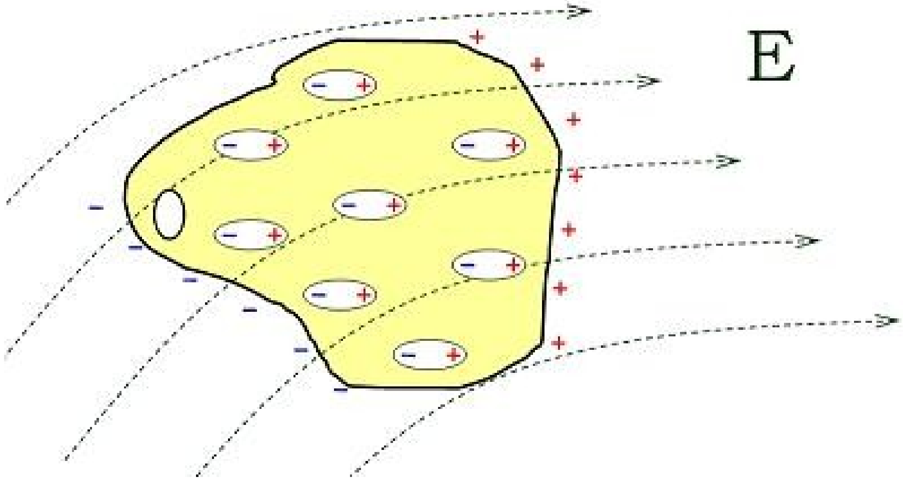
Frequency space spectroscopy

$$\epsilon(\omega)=1+\alpha(\omega)$$

Real time spectroscopy

$$\epsilon(\omega)=1+\frac{\Delta P(\omega)}{E(\omega)}$$



Frequency space spectroscopy

Solve a Dyson equation for the response function

$$L(\omega)=L^0(\omega)+L^0(\omega)(v+K_{xc})L(\omega)$$

$$\alpha(\omega)=\sum_{ij,hk} d_{ij} L_{ij,hk}(\omega) d_{hk}$$

Only equilibrium quantities are needed

$\psi_{nk}^{KS}(x)$ ϵ_{nk}^{KS}

Real Time spectroscopy

excitation

perturbation

response

Real Time spectroscopy

1) Choose an **external small perturbation E(t)**

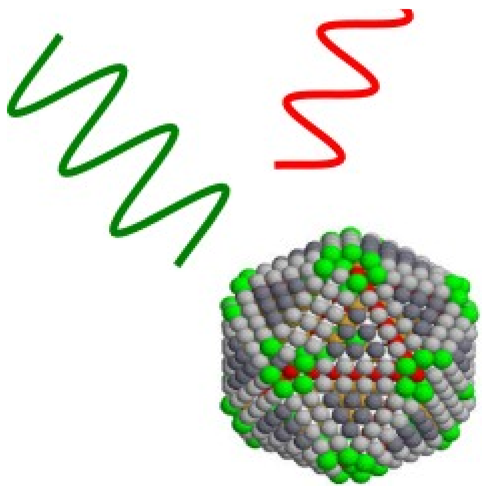
2) Evolve some (?) **equation**

3) Calculate the **P(t) from such equation**

Fourier transform P(t) and E(t) → $\alpha(\omega) \approx \frac{\Delta P(\omega)}{E(\omega)}$

Real Time spectroscopy with Yambo

Perturbation:
Remove symm. with
ypp_rt / ypp_nl



$$E(t)=\delta(t-t_0)\,E_0$$

$$E(t)=\sin(\omega t)\,E_0$$

Real Time spectroscopy with Yambo

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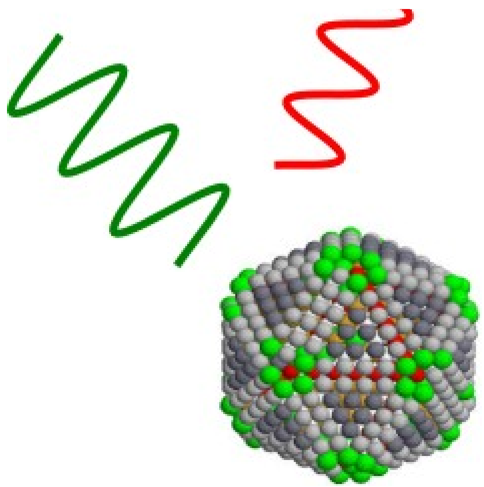

$$E(t)=\delta(t-t_0)E_0$$

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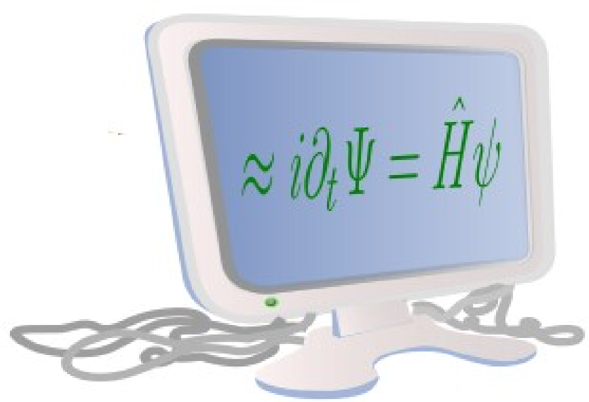
Time propagation
with yambo_rt
or yambo_nl



$$\rho(t+dt)=\rho(t)-i\Delta t[H,\rho(t)]$$

$$\Psi(t+\Delta t)=\Psi(t)-i\Delta t H\Psi(t)$$

Real Time spectroscopy with Yambo

Perturbation:
Remove symm. with
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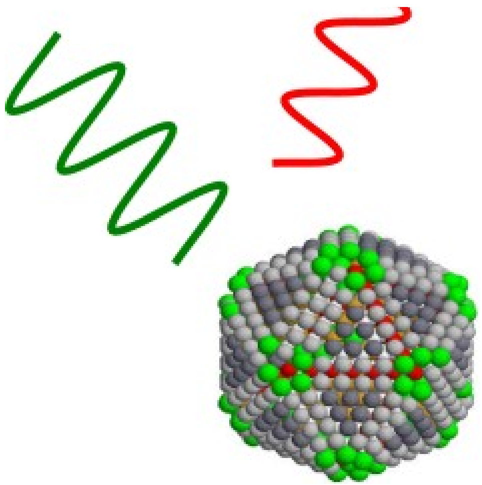

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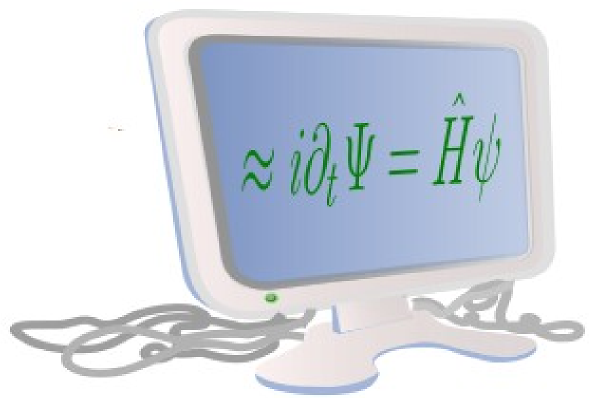
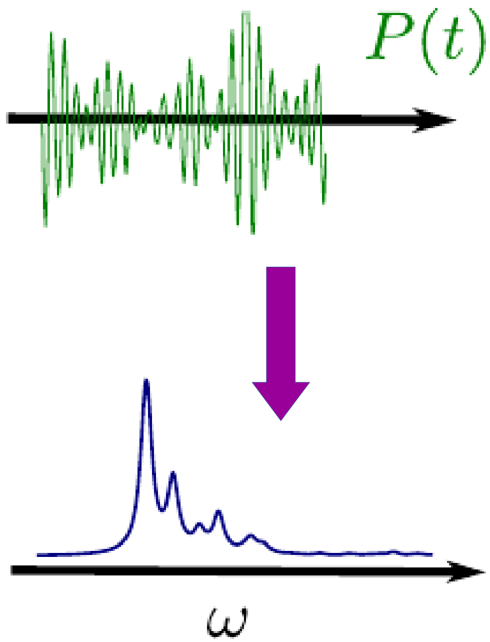


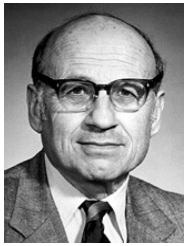
$$\rho(t+dt)=\rho(t)-i\Delta t[H,\rho(t)]$$

$$\Psi(t+\Delta t)=\Psi(t)-i\Delta t H\Psi(t)$$

Analise the
results with
ypp_rt or ypp_nl



ab initio Many Body Pert. Theory



DFT

AiMBPT

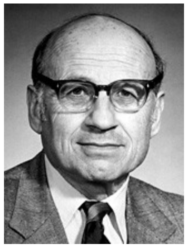
G. Onida, L. Reining, and A. Rubio,
Rev. Mod. Phys. **74**, 601 (2002)

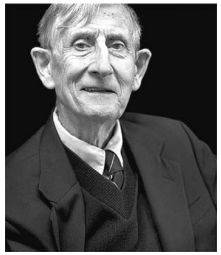
DFT

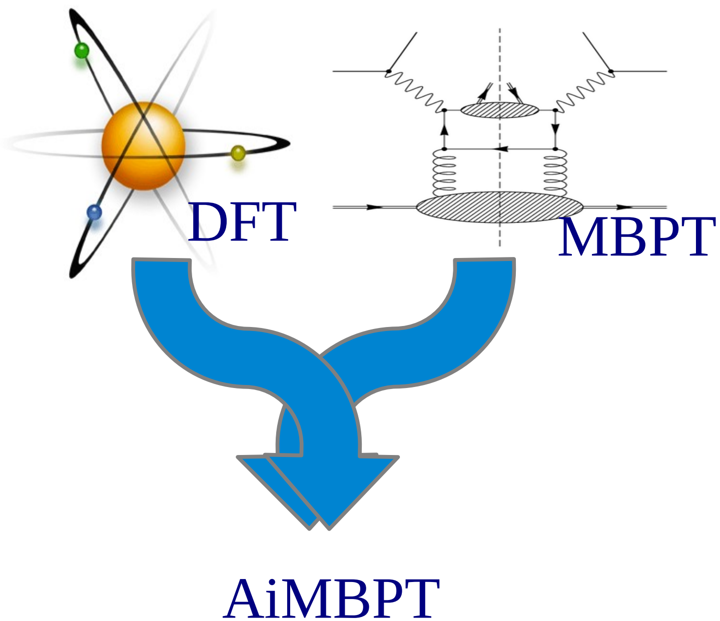
$$\left[\frac{-\nabla^2}{2} + v_s(r)\right]\psi_{nk}(r) = \epsilon_{nk}\,\psi_{nk}(r)$$

$$v_s(r) = v_{ions}(r) + v_{Hxc}[n](r)$$

ab initio Many Body Pert. Theory







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$$v_s(r)=v_{ions}(r)+v_{Hxc}[n](r)$$

+

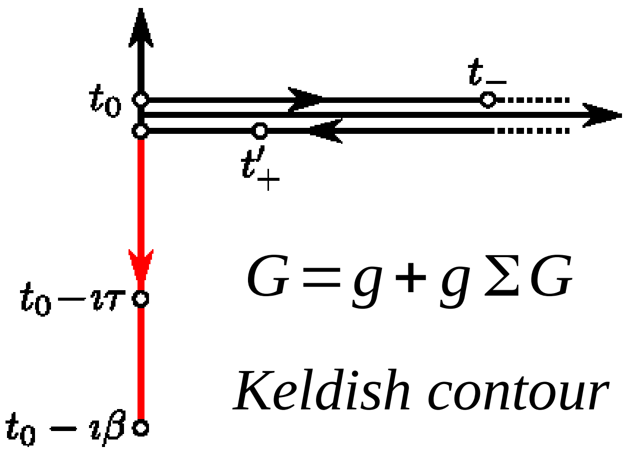
MBPT

$$G_{KS}^{(r)}(r,r',\omega)=\sum_{nk}\frac{\psi_{nk}^{*}(r)\,\psi_{nk}(r')}{\omega-\epsilon_{nk}^{KS}+i\eta}$$

Σ =

$$\epsilon_{nk}^{QP}=\epsilon_{nk}^{KS}+\langle\Sigma(\epsilon^{QP})-V_{Hxc}\rangle$$

Non-Equilibrium Green Function



$$G = g + g\,\Sigma\, G$$

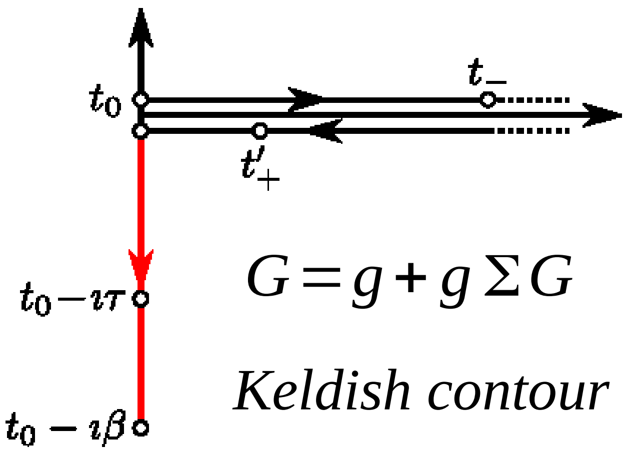
Keldish contour

$$G^{<}(t,t') \qquad G^{>}(t,t')$$

$$G^{(r)}(t,t') \qquad G^{(a)}(t,t')$$

back on the real axis

Non-Equilibrium Green Function



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Keldish contour

→

$$G^{<}(t,t') \qquad G^{>}(t,t')$$

$$G^{(r)}(t,t') \qquad G^{(a)}(t,t')$$

back on the real axis

Kadanoff-Baym equation

$$\begin{cases} \left[i\dfrac{d}{dt} - h_{\mathrm{HF}}(t)\right] G^{<}(t,t') = I^{<}(t,t') \\ G^{>}(t,t')\left[-i\dfrac{d}{dt'} - h_{\mathrm{HF}}(t')\right] = I^{>}(t,t') \end{cases}$$

I collision integral

Equation of motion for rho

$$\rho(t) = -iG^{<}(t,t)$$

Equation of motion for rho

$$\rho(t) = -iG^{<}(t,t)$$

$$\frac{d}{dt}\rho(t) + i\left[h_{\mathrm{HF}}(t), \rho(t)\right] = -\left(I^{<}(t,t) + \mathrm{h.c}\right)$$

With the collision integral the equation is closed only within the Generalized Kadanoff Baym Ansatz

Equation of motion for rho

$$\rho(t) = -iG^{<}(t,t)$$

$$\frac{d}{dt}\rho(t) + i[h_{HF}(t), \rho(t)] = 0$$

Neglecting the collision integral the equation is closed

Any hamiltonian containg a static self-energy can be used

$$h_{HF}(t) = h_0 + \Sigma_{HF}[\rho(t)] + U^{ext}(t)$$

$$h_{HSEX}(t) = h_0 + \Sigma_{HSEX}[\rho(t)] + U^{ext}(t)$$

ab initio NEGF

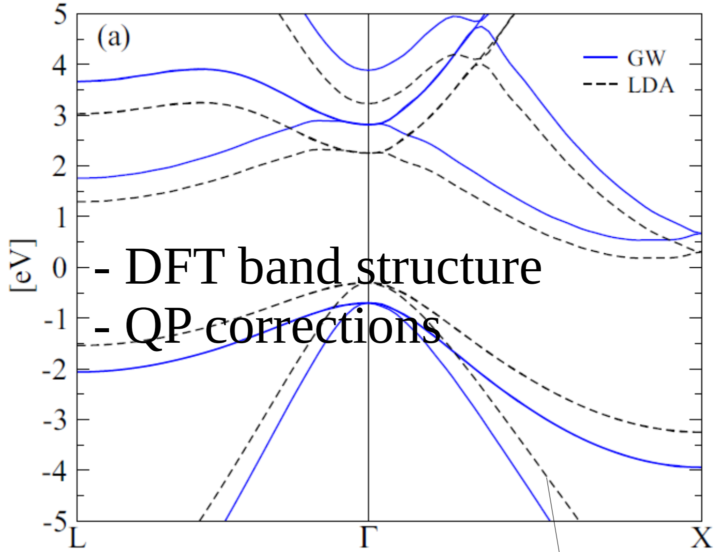
$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta V_H + \Delta\Sigma_{xc}^{static} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = 0$$

$$\rho_{nm\mathbf{k}}(t) = \langle\psi_{n\mathbf{k}}^{KS}|\rho(r,r';t)|\psi_{m\mathbf{k}}^{KS}\rangle$$

$$\rho_{nm\mathbf{k}}^{eq} = \delta_{n,m} f_{n\mathbf{k}}^{eq}$$

Density matrix

ab initio NEGF



- DFT band structure
- QP corrections

Many body effects

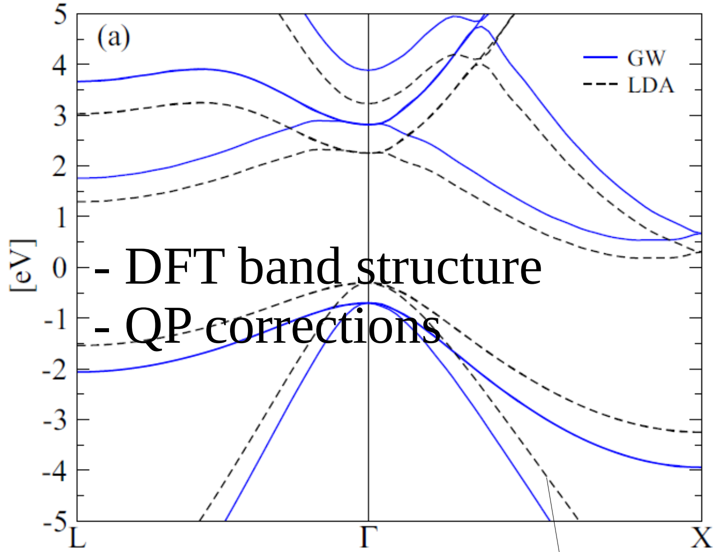
Pump laser pulse

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta V_H + \Delta\Sigma_{xc}^{static} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = 0$$

$$\rho_{nm\mathbf{k}}(t) = \langle\psi_{n\mathbf{k}}^{KS}|\rho(r,r';t)|\psi_{m\mathbf{k}}^{KS}\rangle \qquad \rho_{nm\mathbf{k}}^{eq} = \delta_{n,m} f_{n\mathbf{k}}^{eq}$$

Density matrix

ab initio NEGF



- DFT band structure
- QP corrections

Many body effects

<u>Comparison with TDDFT:</u>

- Mean field effects can be non local in space
- Dynamical effects can be introduced in a controlled manner

Pump laser pulse

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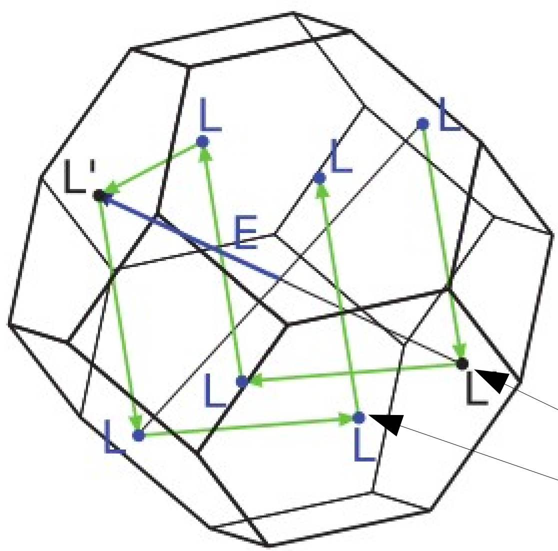
Density matrix

Remove symmetries

$$U^{ext}(t) = -e \sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk} \circ \boldsymbol{E}(t)$$



Simmetry breaking !

Before performing real-time propagation symmetries need to be removed

$$\rho_{nm\mathbf{k}}(t) = \langle \psi^{KS}_{n\mathbf{k}} | \rho(r, r'; t) | \psi^{KS}_{m\mathbf{k}} \rangle$$

The Equation of motion

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta V_H + \Delta\Sigma_{xc}^{static} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = 0$$

QP energies

$$H_{nmk}^{eq} = \delta_{nm}\epsilon_{nk}^{QP}$$

All correlations from
the ground state are here

C. Attaccalite, M. Gruning, and A. Marini,
Phys. Rev. B **84**, 245110 (2011)

The Equation of motion

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Classical field

$$\Delta V_H$$

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$$\Delta V_H$$

xc-correlation

$$\Delta\Sigma_s = v_{xc}^{adiabatic}$$
$$= \Delta\Sigma^{SEX} \approx W_s^{eq}\Delta\rho$$

C. Attaccalite, M. Gruning, and A. Marini, Phys. Rev. B **84**, 245110 (2011)

The Equation of motion

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

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$$H^{eq}_{nmk} = \delta_{nm}\epsilon^{QP}_{nk}$$

Classical field

$$\Delta V_H$$

xc-correlation

$$\Delta\Sigma_s = v^{adiabatic}_{xc}$$

$$= \Delta\Sigma^{SEX} \approx W^{eq}_s \Delta\rho$$

Constant dephasing

$$I_{nmk}(t) = -\eta\rho_{nmk}(t)$$

QP dephasing

$$I_{nmk}(t) = -\gamma^{eq}_{nmk}\rho_{nmk}(t)$$

$$\gamma^{eq}_{nmk} = \Im[\Sigma_{nk}] + \Im[\Sigma_{mk}]$$

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The Hartree term

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

Classical field

$$\Delta V_H[\rho]$$

Macroscopic part

Microscopic part

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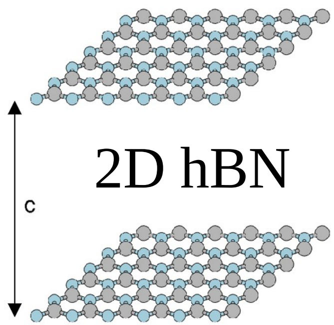

Classical field

$$\Delta V_H[\rho]$$

Macroscopic part

This is the average over the cell → it is zero for any system with dimensionality D < 3

Microscopic part

“Local fields”

C. Attaccalite, M. Gruning, and A. Marini, Phys. Rev. B **84**, 245110 (2011)

The Hartree term: 3D systems

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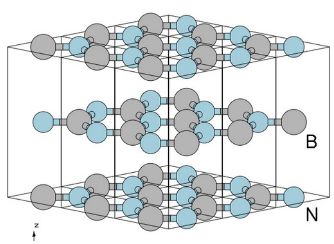
3D hBN



Classical field

$\Delta V_H[\rho]$

Macroscopic part

Non analytical in ρ,
L-T splitting

Not included in V_H,
but absorbed in U^{ext}

Microscopic part

“Local fields”

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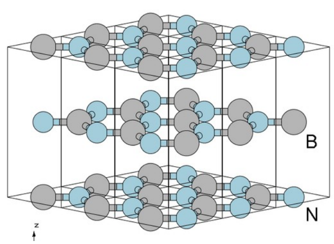
The Hartree term: 3D systems

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{tot}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

3D hBN



Classical field

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Microscopic part

“Local fields”

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The xc term

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{tot}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

$$\Delta\Sigma_{Hxc} \approx \frac{\delta\Sigma^{static}_{Hxc}}{\delta\rho}[\rho^{eq}]\Delta\rho$$

Exact for functionals linear in ρ

The xc term

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{tot}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

BSE kernel or real-time collisions

$$\Delta\Sigma_{Hxc} \approx K^{static}_{Hxc}[\rho^{eq}]\Delta\rho$$

Exact for functionals linear in ρ

$$\partial_t \rho^{(1)}_{nmk}(t) - i\left[\Delta\epsilon_{nmk}\delta_{n,i}\delta_{m,j}\delta(k-p) + \Delta f_{nmk} K_{nmk,ijp}\right]\Delta\rho^{(1)}_{ijp} + \dots$$

Bethe-Salpeter equation (for $\overline{L}$ since we use U^{tot})

The xc term

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{tot}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

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Bethe-Salpeter equation (for $\bar{L}$ since we use U^{tot})

$$\partial_t \rho^{(1)}_{\lambda}(t) - i E_\lambda \Delta\rho^{(1)}_{\lambda} + \dots$$

$$\partial_t \rho^{(1)}_{\lambda}(t) \approx e^{-iE_\lambda t}$$

Post-processing: real-time vs chi

$$P(t) \xrightarrow{\textbf{Fourier transform}} \epsilon(\omega) = 1 + \frac{P(\omega)}{E(\omega)}$$

Post-processing: real-time vs chi

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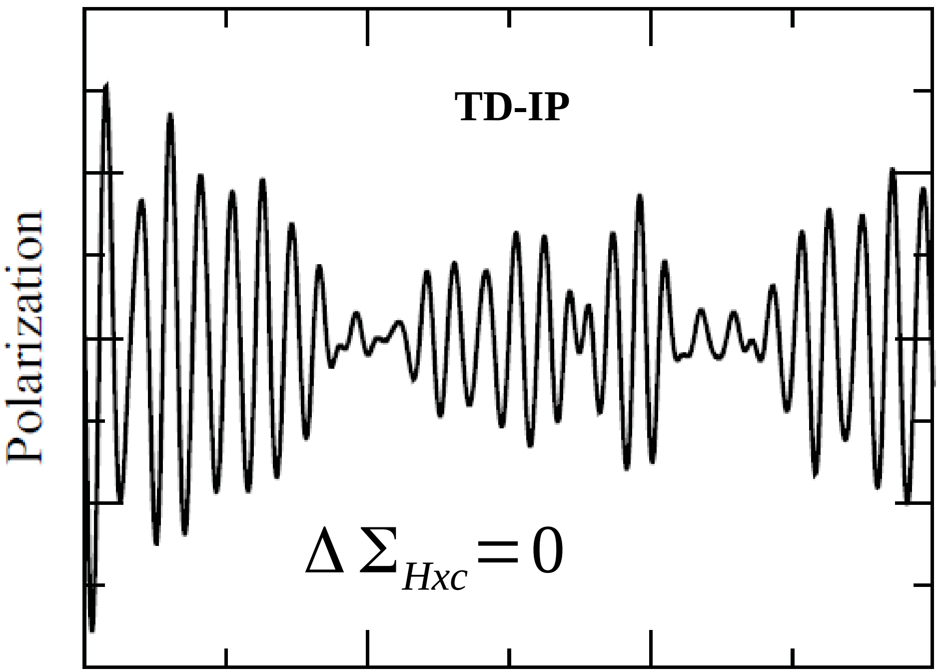
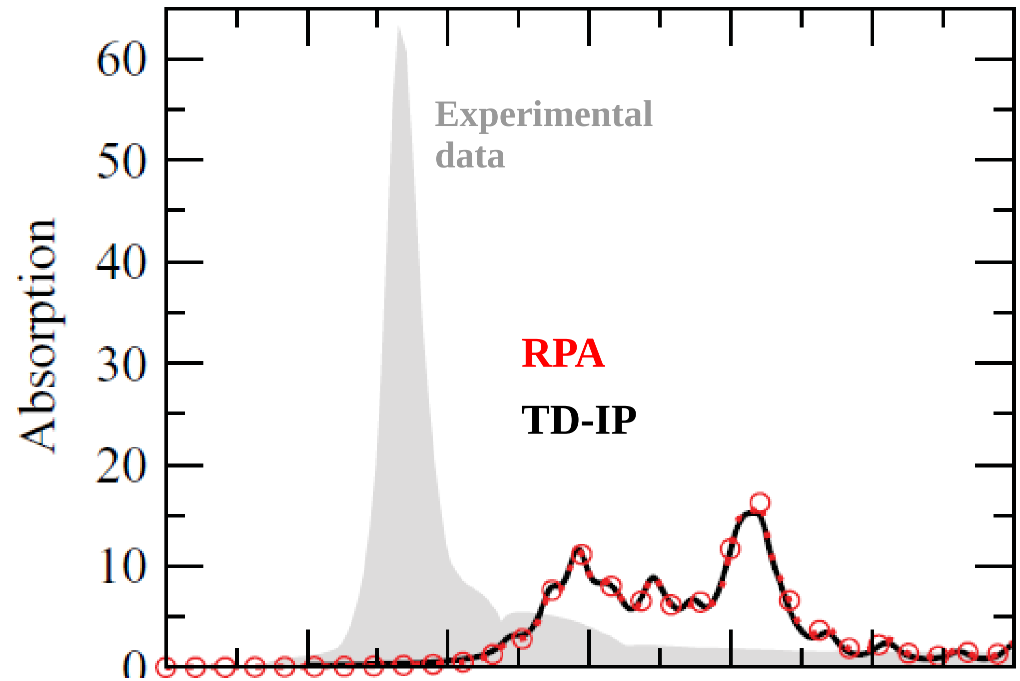
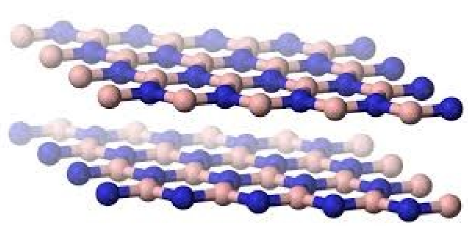




Hexagonal Boron Nitrite



C. Attaccalite, M. Gruning, and A. Marini, Phys. Rev. B **84**, 245110 (2011)

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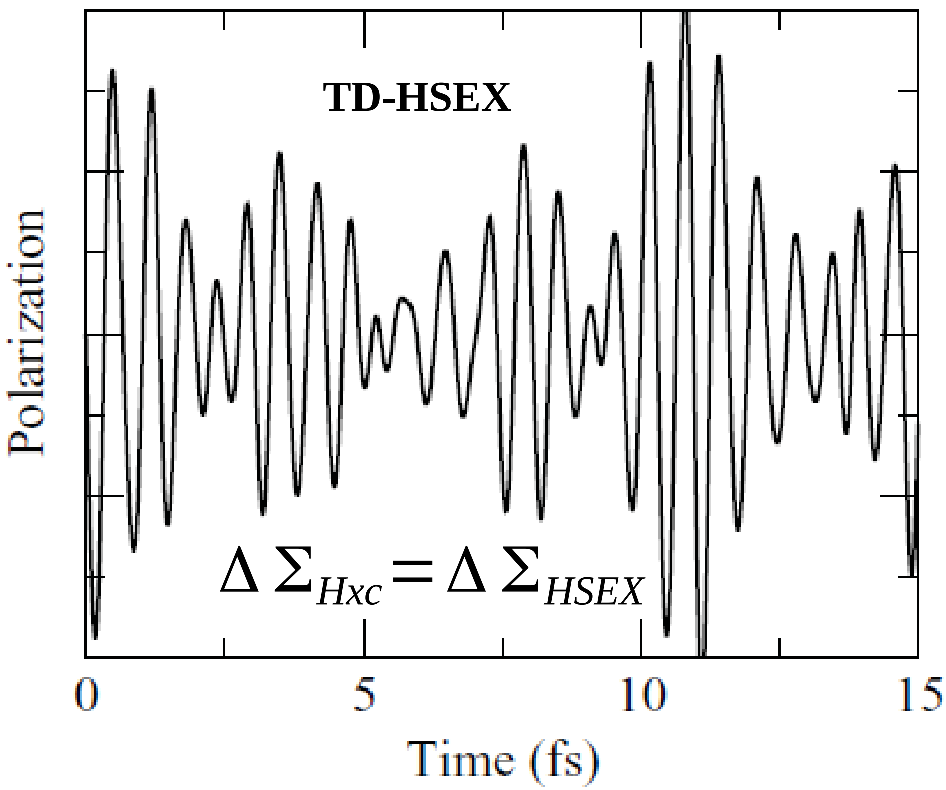
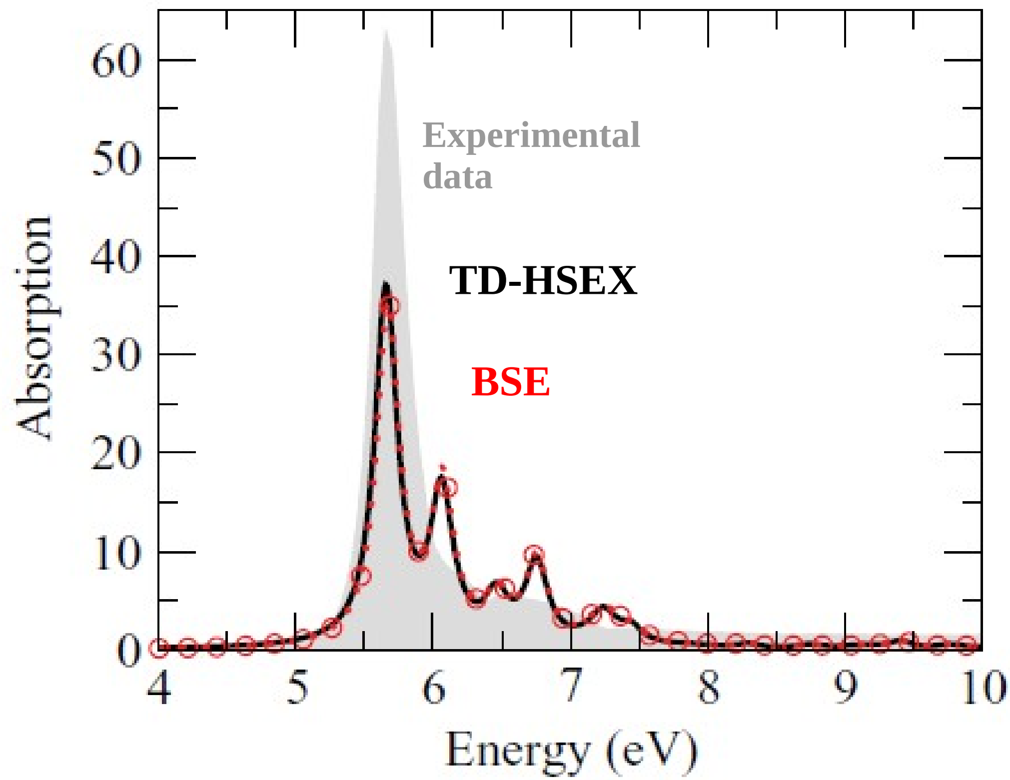
Post-processing: real-time vs chi

$$P(t) \xrightarrow{\text{Fourier transform}} \epsilon(\omega) = 1 + \frac{P(\omega)}{E(\omega)}$$





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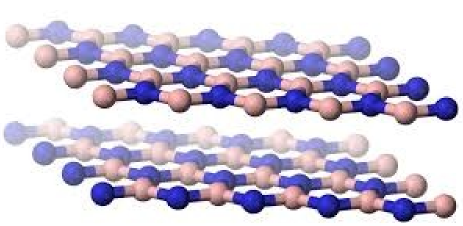

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Propagation scheme

Single step: $$\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)$$

Propagation scheme

Single step: $\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)$

Eulero $\rho(t+dt)=\rho(t)+i[H(t),\rho(t)]dt$

Exponential $\rho(t+dt)=\rho(t)+e^{iH(t)dt}\rho(t)e^{-iH(t)dt}$

Inversion (implicit) $\rho(t+dt)=\rho(t)+\frac{1+iH(t)dt/2}{1-iH(t)dt/2}\rho(t)\frac{1-iH(t)dt/2}{1+iH(t)dt/2}$

Propagation scheme

Single step: $$\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)$$

Eulero $$\rho(t+dt)=\rho(t)+i[H(t),\rho(t)]\,dt$$

Exponential $$\rho(t+dt)=\rho(t)+e^{iH(t)dt}\rho(t)e^{-iH(t)dt}$$

Inversion (implicit) $$\rho(t+dt)=\rho(t)+\frac{1+iH(t)dt/2}{1-iH(t)dt/2}\rho(t)\frac{1-iH(t)dt/2}{1+iH(t)dt/2}$$

Multi-step (2 steps)

Runge Kutta 2nd order $$\rho(t+dt)=\rho(t)+F(t+dt/2,\rho(t+dt/2),dt)$$

Heun $$\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)+F_{TMP}(t+dt,\rho_{TMP}(t+dt),dt)$$

Propagation scheme

Single step: $\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)$

Eulero $\rho(t+dt)=\rho(t)+i[H(t),\rho(t)]dt$

Exponential $\rho(t+dt)=\rho(t)+e^{iH(t)dt}\rho(t)e^{-iH(t)dt}$

Inversion (implicit) $\rho(t+dt)=\rho(t)+\dfrac{1+iH(t)dt/2}{1-iH(t)dt/2}\rho(t)\dfrac{1-iH(t)dt/2}{1+iH(t)dt/2}$

Multi-step (2 steps)

Runge Kutta 2nd order $\rho(t+dt)=\rho(t)+F(t+dt/2,\rho(t+dt/2),dt)$

Heun $\rho(t+dt)=\rho(t)+F(t,\rho(t),dt)+F_{TMP}(t+dt,\rho_{TMP}(t+dt),dt)$

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Time step “dt” needs to be carefully chosen

Gauges

Length gauge E*P: $$U^{ext}(t)=-e\sum_{nmk}\rho_{nmk}(t)\boldsymbol{x}_{nmk}\circ\boldsymbol{E}(t)$$ (i) field coupling

$$\boldsymbol{P}(t)=e\sum_{nmk}\rho_{nmk}(t)\boldsymbol{x}_{nmk}$$ (ii) observable

Velocity gauge A*j: $$U^{ext}(t)=-e\sum_{nmk}\rho_{nmk}(t)\boldsymbol{v}_{nmk}\circ\boldsymbol{A}(t)$$ (i) field coupling

$$\boldsymbol{J}(t)=e\sum_{nmk}\rho_{nmk}(t)\boldsymbol{v}_{nmk}$$ (ii) observable

$$\boldsymbol{x}_{nmk}(t)=\frac{\boldsymbol{v}_{nmk}}{\Delta\epsilon_{nmk}}$$

Gauges

Length gauge E*P: $U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk} \circ \boldsymbol{E}(t)$ (i) field coupling

$\boldsymbol{P}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk}$ (ii) observable

Velocity gauge A*j: $U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk} \circ \boldsymbol{A}(t)$ (i) field coupling

$\boldsymbol{J}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk}$ (ii) observable

$\boldsymbol{v}_{nmk}$ Intraband dipoles are included → correct at any order

Issue: sum rules need to be imposed (numerically unstable)

Gauges

Coded in yambo_rt

Length gauge E*P: $$U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk} \circ \boldsymbol{E}(t)$$ (i) field coupling

$$\boldsymbol{P}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk}$$ (ii) observable

Velocity gauge A*j: $$U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk} \circ \boldsymbol{A}(t)$$ (i) field coupling

$$\boldsymbol{J}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk}$$ (ii) observable

$$\boldsymbol{x}_{nmk}(t) = \frac{\boldsymbol{v}_{nmk}}{\Delta \epsilon_{nmk}}$$ Intraband dipoles are ill defined → correct up to 1st order

Beyond 1st order:

→ Berry phase needed beyond 1st order (opt. 1)

→ Compute the gradient of the density (opt. 2)

Gauges

Coded in yambo_rt

Length gauge E*P: $U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk} \circ \boldsymbol{E}(t)$ (i) field coupling

$$\boldsymbol{P}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{x}_{nmk}$$ (ii) observable

Velocity gauge A*j: $U^{ext}(t) = -e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk} \circ \boldsymbol{A}(t)$ (i) field coupling

$$\boldsymbol{J}(t) = e\sum_{nmk} \rho_{nmk}(t)\, \boldsymbol{v}_{nmk}$$ (ii) observable

$$\boldsymbol{x}_{nmk}(t) = \frac{\boldsymbol{v}_{nmk}}{\Delta\epsilon_{nmk}}$$ Intraband dipoles are ill defined → correct up to 1st order

Beyond 1st order:

→ Berry phase needed beyond 1st order (opt. 1)

→ Compute the gradient of the density (opt. 2)

See lecture by M. Gruning

Gain with real-time propagation

(1) go beyond the non linear regime up to High Harmonic Generation (HHG)

$$\Delta P(r,t) = \int \alpha(t-t', r, r') E(t' r') dt' dr' + \int dt^1 dt^2 \alpha^2(\ldots) E(t^1) E(t^2) + O(E^3)$$

See lecture by M. Gruning

Gain with real-time propagation

(1) go beyond the non linear regime up to High Harmonic Generation (HHG)

$$\Delta P(r,t) = \int \alpha(t-t',r,r') E(t'r') dt' dr' + \int dt^1 dt^2 \alpha^2(\dots) E(t^1) E(t^2) + O(E^3)$$

(2) Model pump and probe expriments

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = -\eta\rho_{nm\mathbf{k}}(t)$$

$\boldsymbol{E}^{pump}(t)$ $\boldsymbol{E}^{probe}(t)$

Gain with real-time propagation

(1) go beyond the non linear regime up to High Harmonic Generation (HHG)

$$\Delta P(r,t)=\int \alpha(t-t',r,r')E(t'r')dt'dr'+\int dt^1 dt^2 \alpha^2(\ldots)E(t^1)E(t^2)+O(E^3)$$

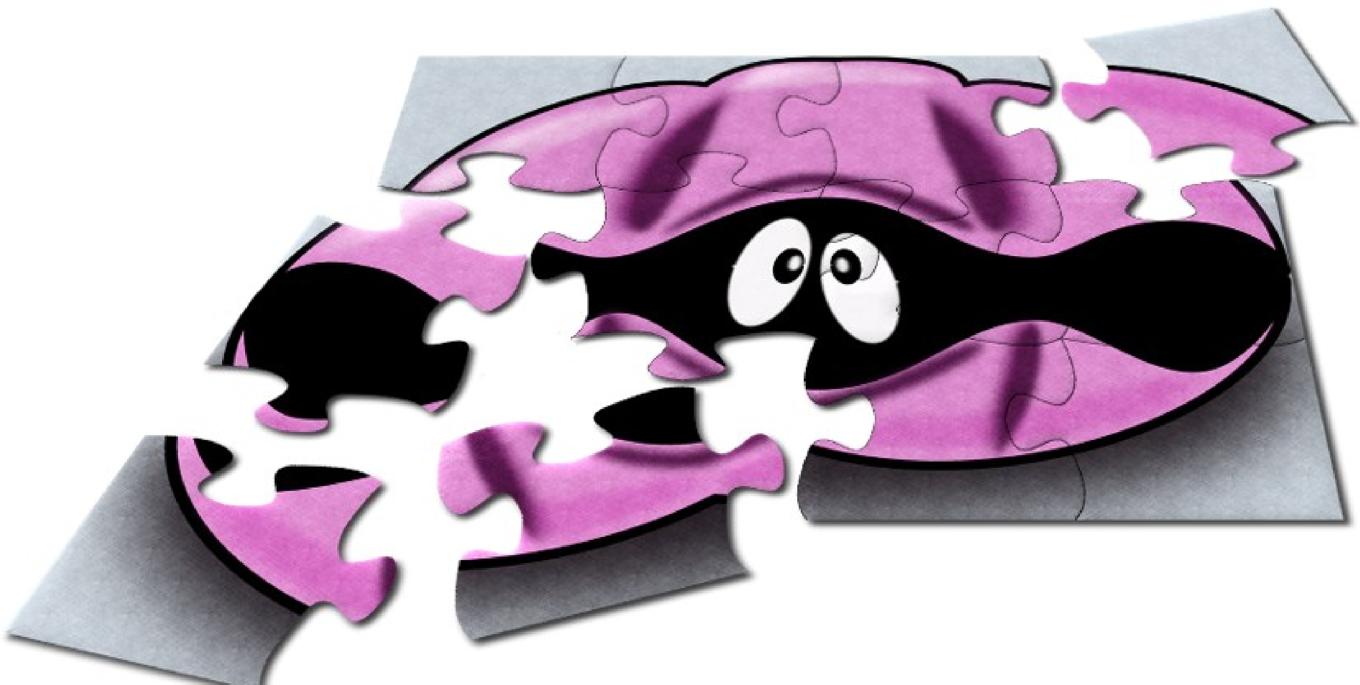
(2) Model pump and probe expriments

$$\frac{d}{dt}\rho_{nm\mathbf{k}}(t) - i\left[h^{eq} + \Delta\Sigma^{static}_{Hxc} + U^{ext}(t), \rho(t)\right]_{nm\mathbf{k}} = -\left(I^{<}(t,t) + \mathrm{h.c}\right)$$

$\boldsymbol{E}^{pump}(t)$ $\boldsymbol{E}^{probe}(t)$

…. also including relaxation and dissipation mechanisms (?)

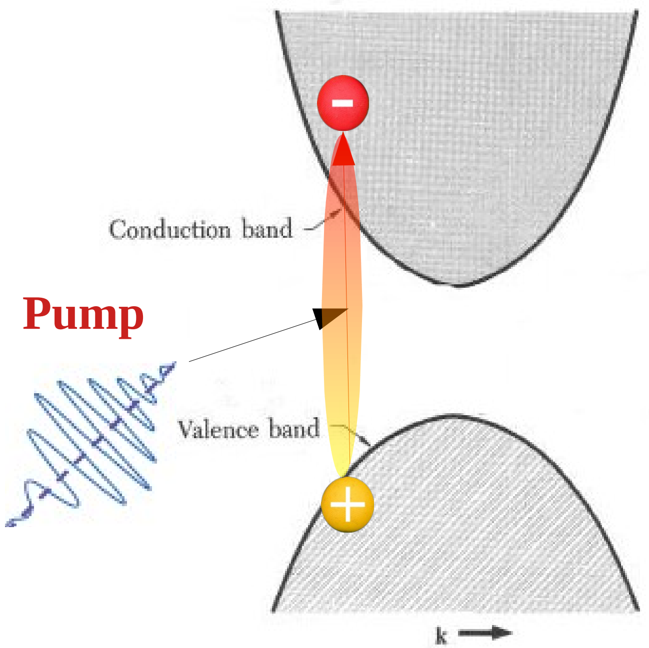
Questions ?



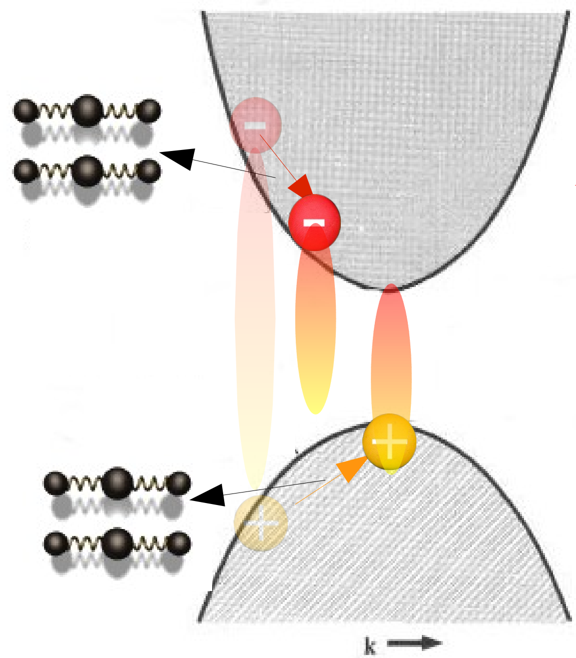
1. Many-body perturbation theory calculations using the yambo code
   Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
   Comp. Phys. Comm. 144, 180 (2009)

the Yambo team

Pump and probe experiments

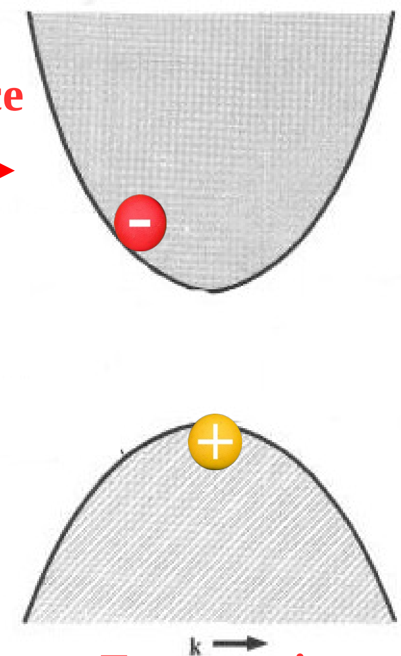


1 – Photo-excitation process



2 – relaxation towards (quasi)equilibrium

Decoherence →



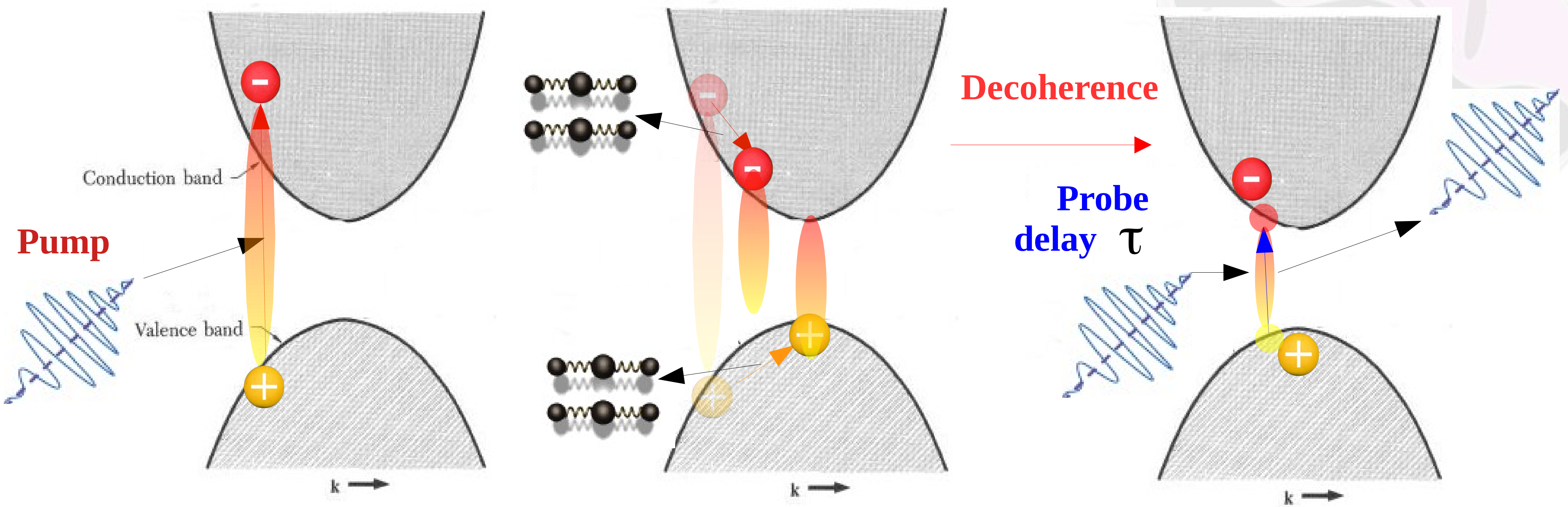
Free carriers approximation

$$\rho_{nmk}(t)$$

$$\rho_{cvk+q_1}(t) \qquad \approx \rho_{cc\,k+q_1}(t) = f_{ck+q_1}(t)$$

$$\rho_{cvk+q_2}(t) \qquad \approx \rho_{vv\,k+q_2}(t) = f_{vk+q_2}(t)$$

Pump and probe experiments



1 – Photo-excitation process

$$\rho_{nmk}(t)$$

2 – relaxation towards (quasi)equilibrium

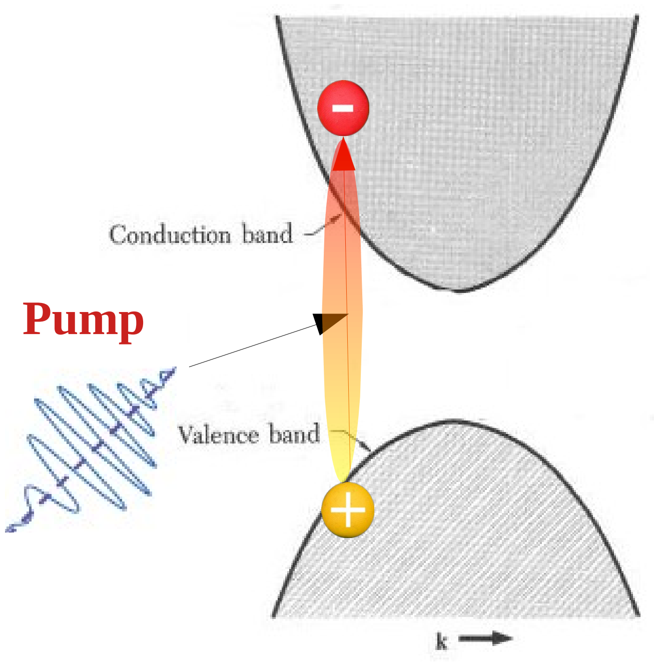
$$\rho_{cvk+q_1}(t)$$

$$\rho_{cvk+q_2}(t)$$

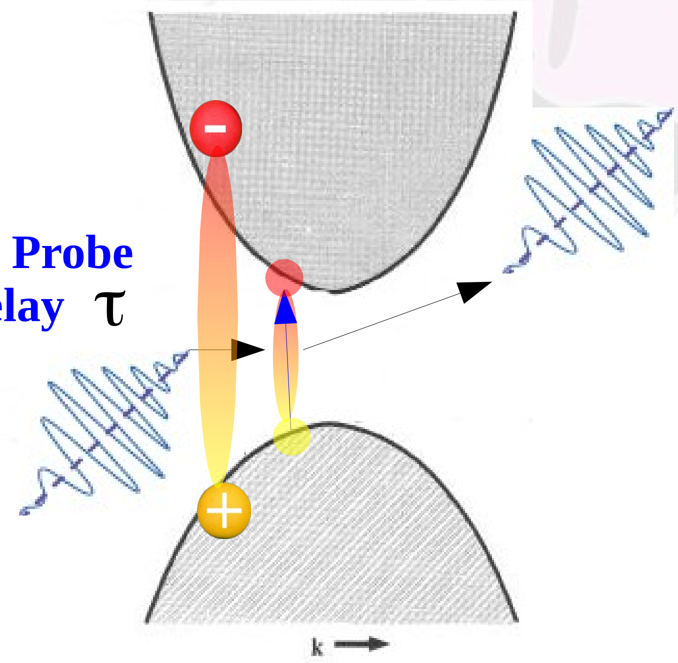
3 – Measurement process

$$\approx \chi(\omega)[\,f_{nk}(\tau)]$$

Transient absorption



Early times regime:
No dissipation /decoherence



$$\rho_{nmk}(t)$$

$$\chi(\omega,\tau)[\rho_{nmk}] \approx \chi(\omega)[f_{nk}(\tau)]$$

E. Perfetto, D. Sangalli, A. Marini, G. Stefanucci, Phys. Rev. B 92, 205304 (2015)
D. Sangalli, Phys. Rev. Mat. 5, 083803 (2021)

MBPT

1 - Screened interaction

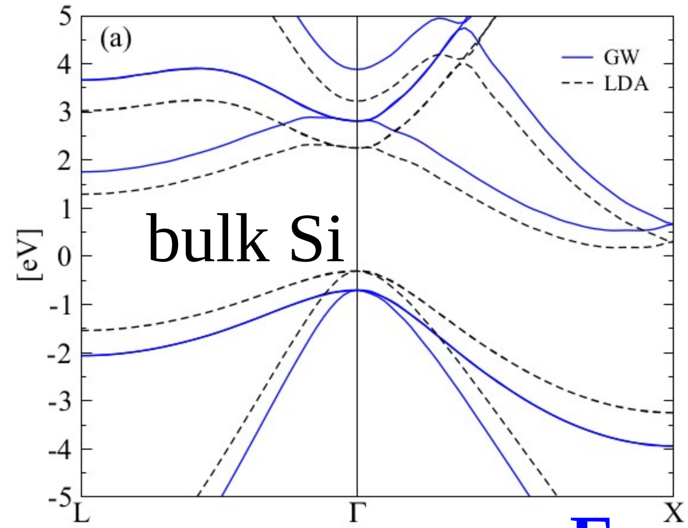
$$W^{RPA}[f_{nk}^{eq}](\omega)$$

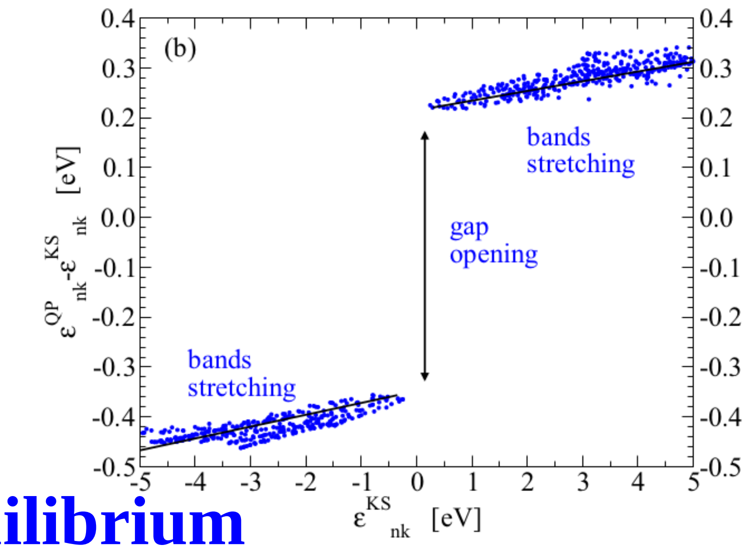
2 - QP corrections

$$\Sigma^{GW}[f_{nk}^{eq}](\omega)$$

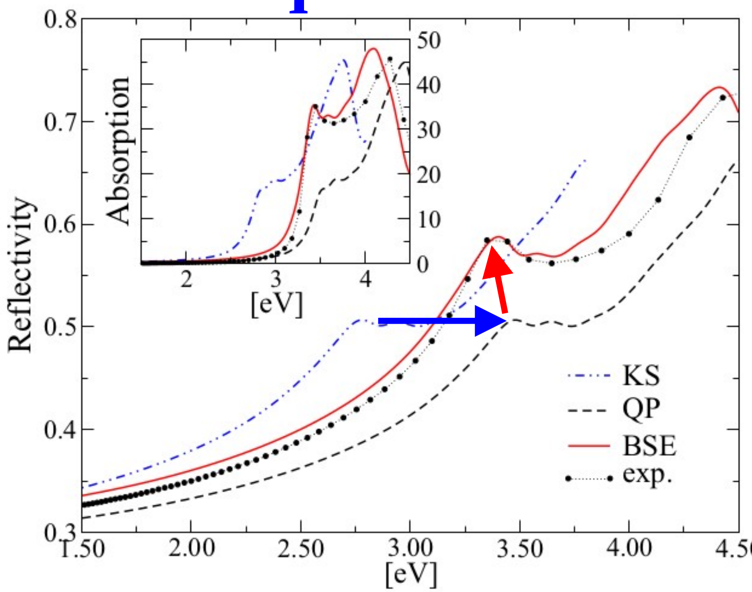
3 - Absorption spectra (exciton)

$$\chi^{GW+BSE}[f_{nk}^{eq}](\omega)$$





Equilibrium



NEQ-MBPT

1 - Screened interaction

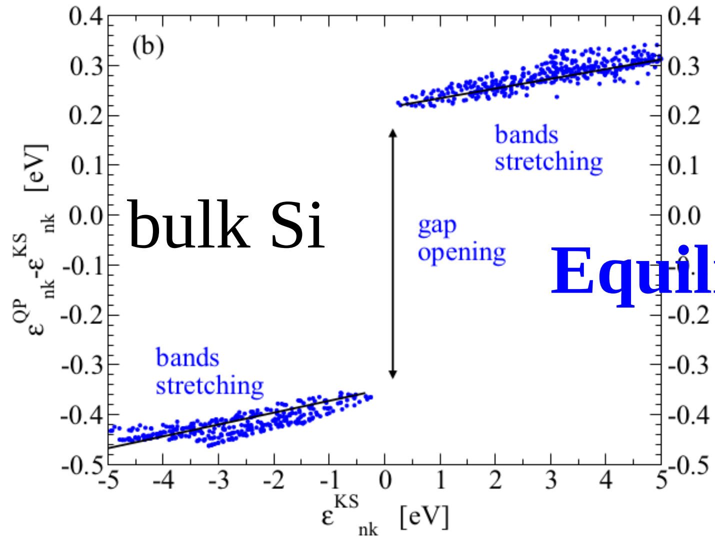
$$W^{RPA}[f^{neq}_{nk}(\tau)](\omega)$$

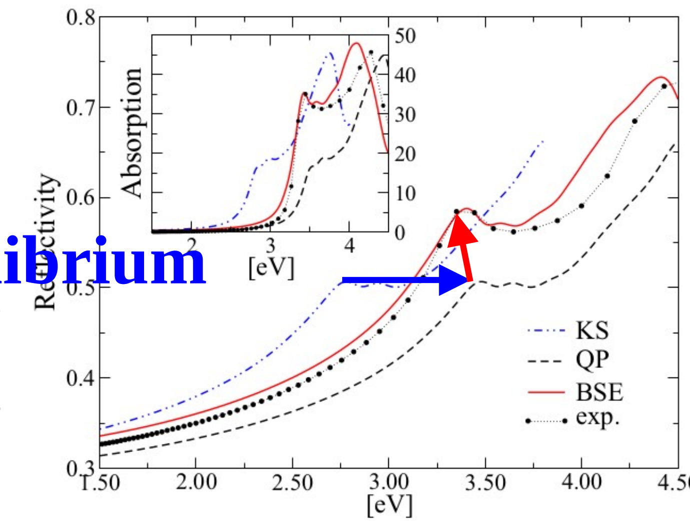
2 - QP corrections

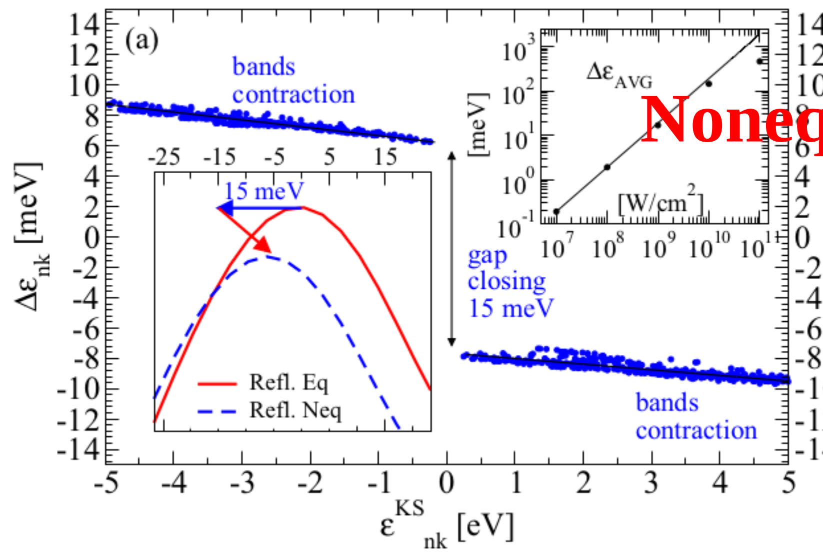
$$\Sigma^{GW}[f^{eq}_{nk}](\omega)$$

3 - Absorption spectra (exciton)

$$\chi^{GW+BSE}[f^{eq}_{nk}](\omega)$$







the Yambo team

NEQ-MBPT

1 - Screened interaction

$$W^{RPA}\left[f^{neq}_{nk}(\tau) \right](\omega)$$

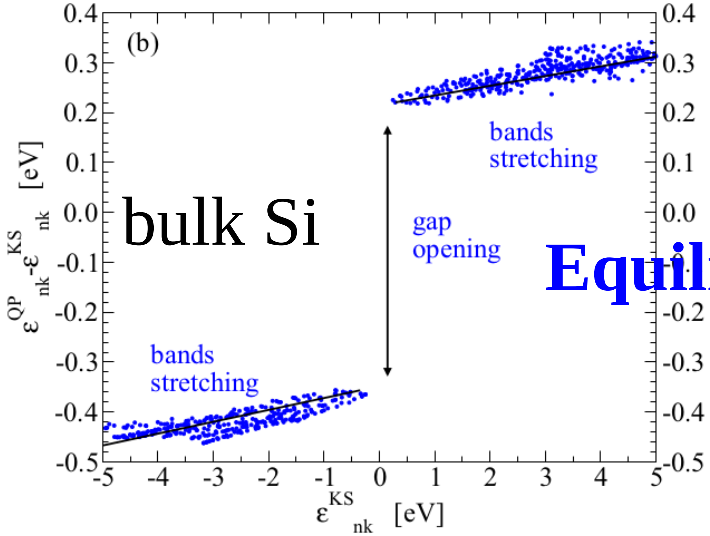
2 - QP corrections

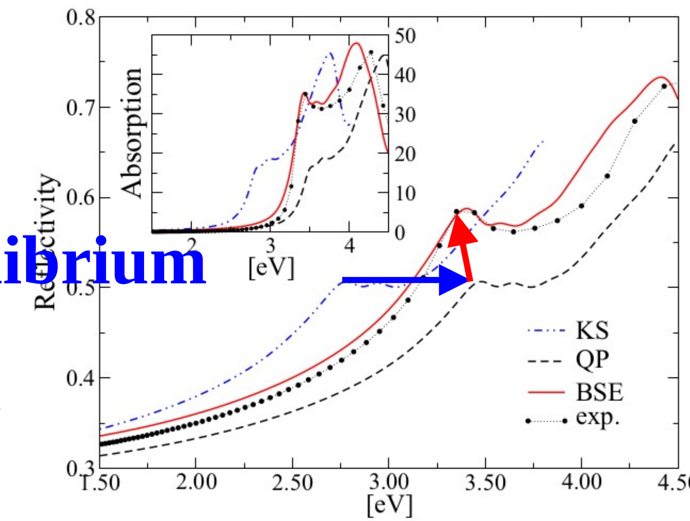
$$\Sigma^{GW}\left[f^{eq}_{nk} \right](\omega) +$$

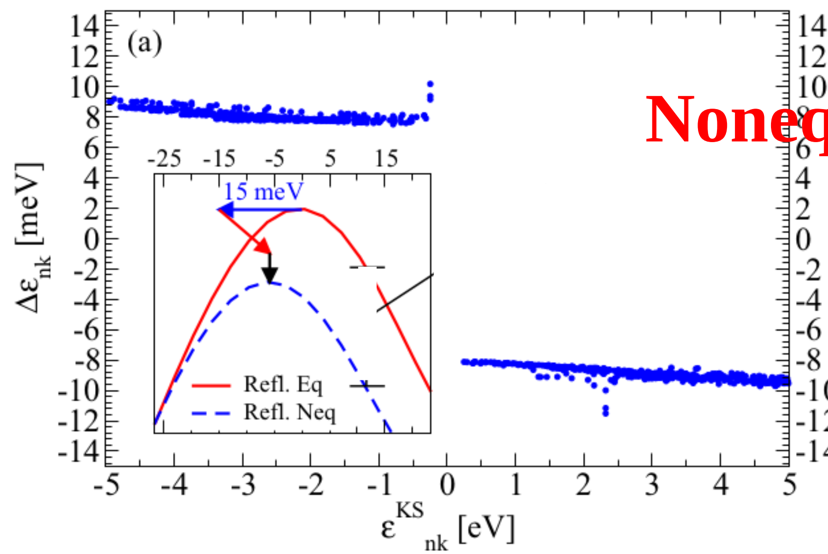
$$+\left(\Sigma^{HSEX}\left[f^{neq}_{nk}(\tau) \right] - \Sigma^{HSEX}_{eq} \right)$$

3 - Absorption spectra (exciton)

$$\chi^{GW+BSE}\left[f^{neq}_{nk}(\tau) \right](\omega)$$



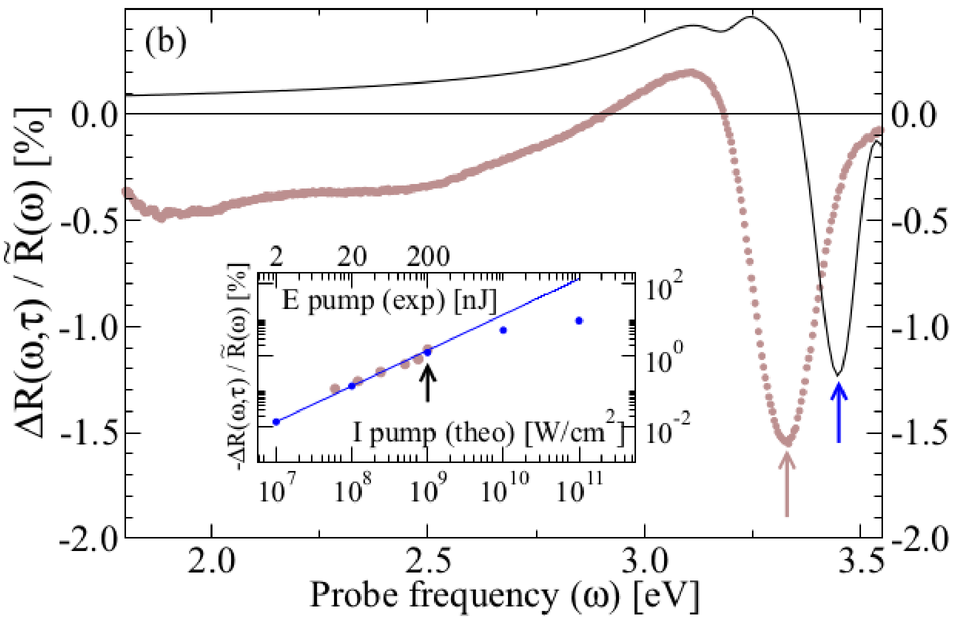




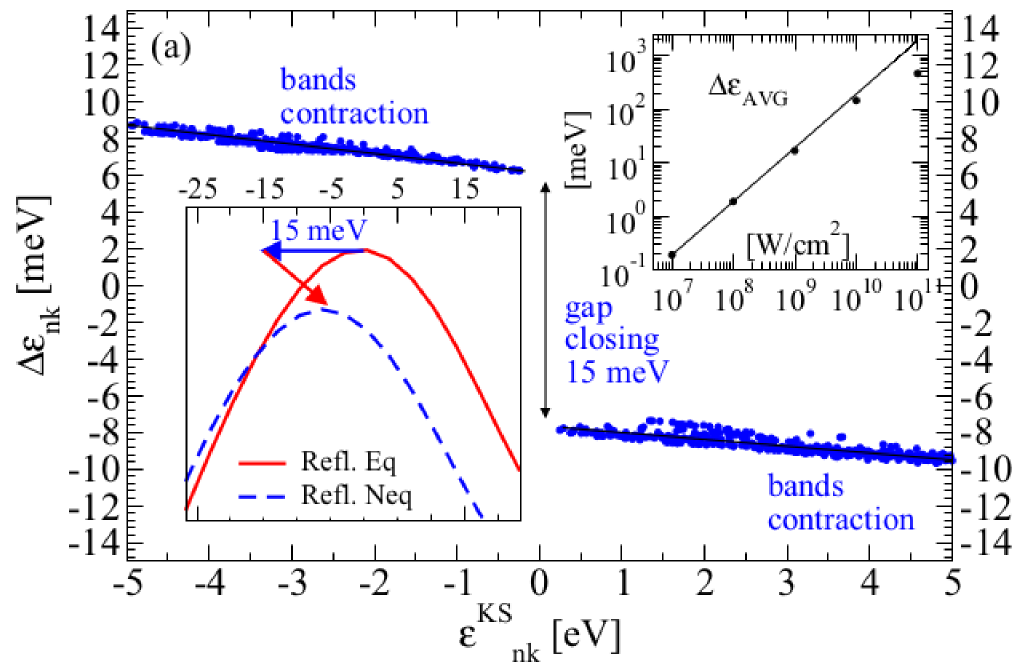
PHYSICAL REVIEW B **93**, 195205 (2016)

Nonequilibrium optical properties in semiconductors from first principles: A combined theoretical and experimental study of bulk silicon

Davide Sangalli,[1,2] Stefano Dal Conte,[3] Cristian Manzoni,[3] Giulio Cerullo,[3] and Andrea Marini[1,2]



Screening induced Optical Gap Renormalization



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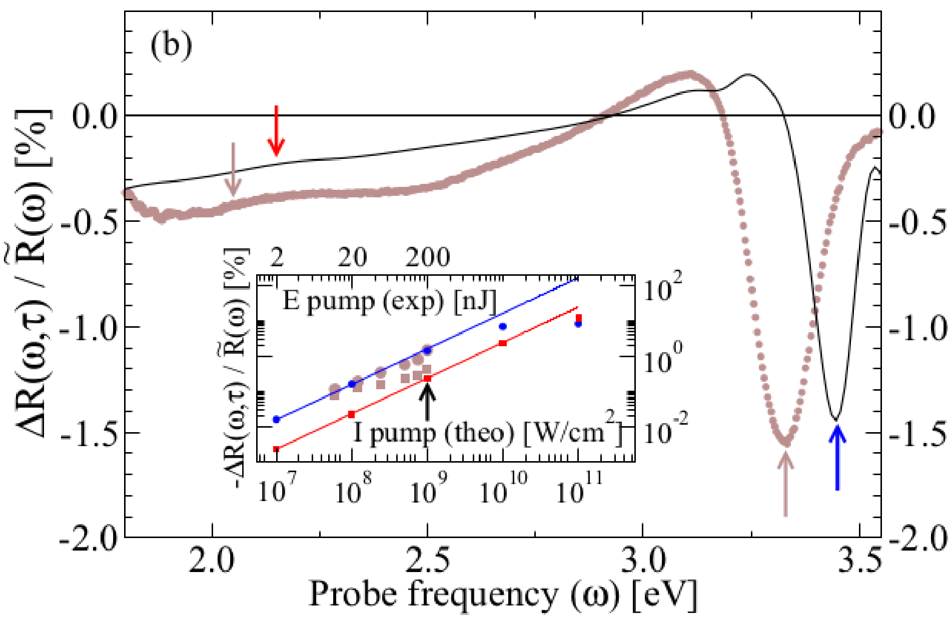
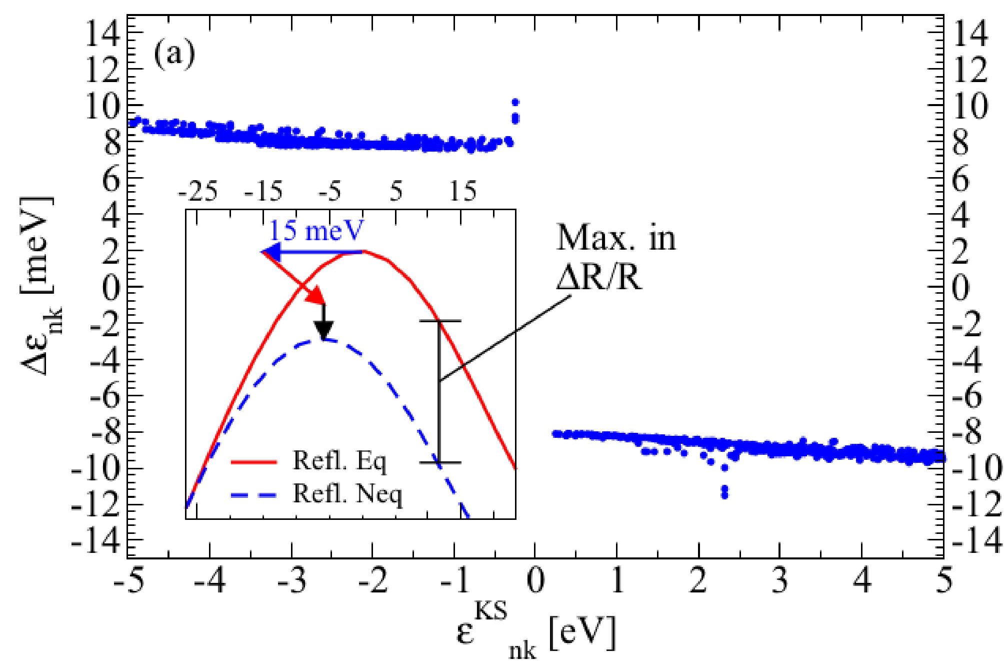
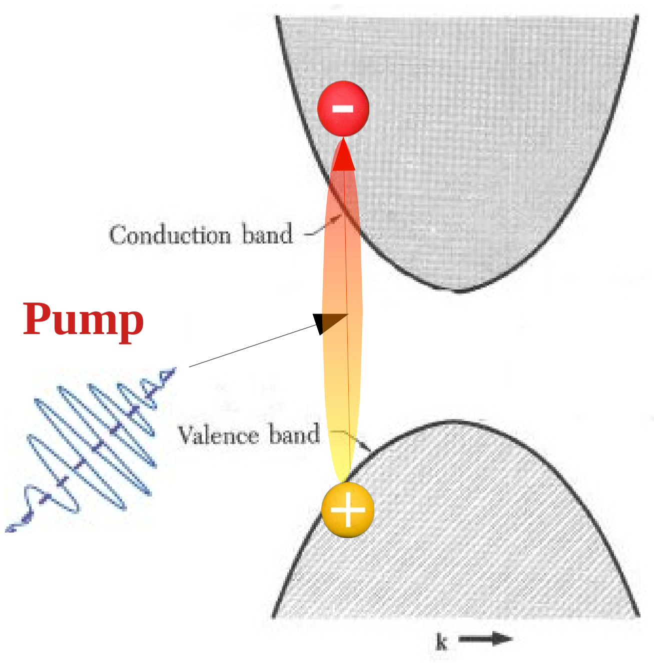
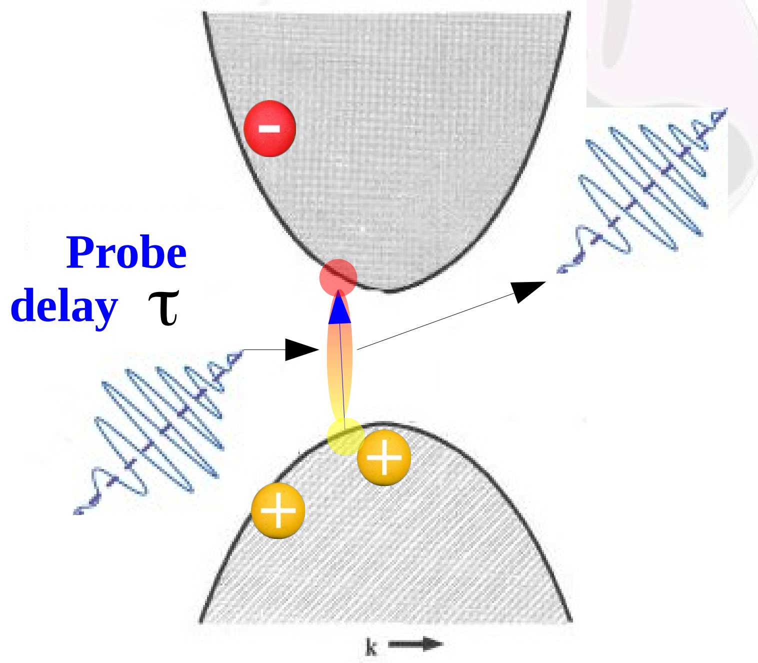


Optical Gap & Residuals Renormalization



Pump and probe experiments





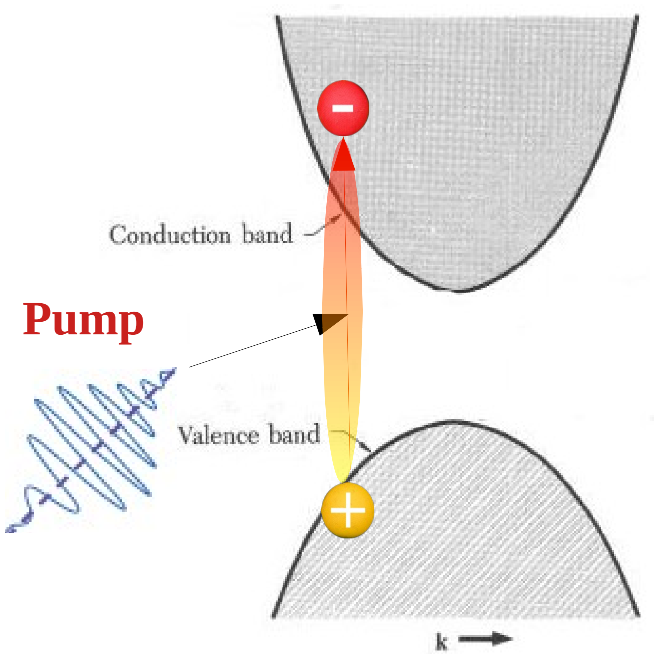
$$\rho_{nmk}(t)$$

$$\approx \chi(\omega)[f_{nk}(\tau)]$$

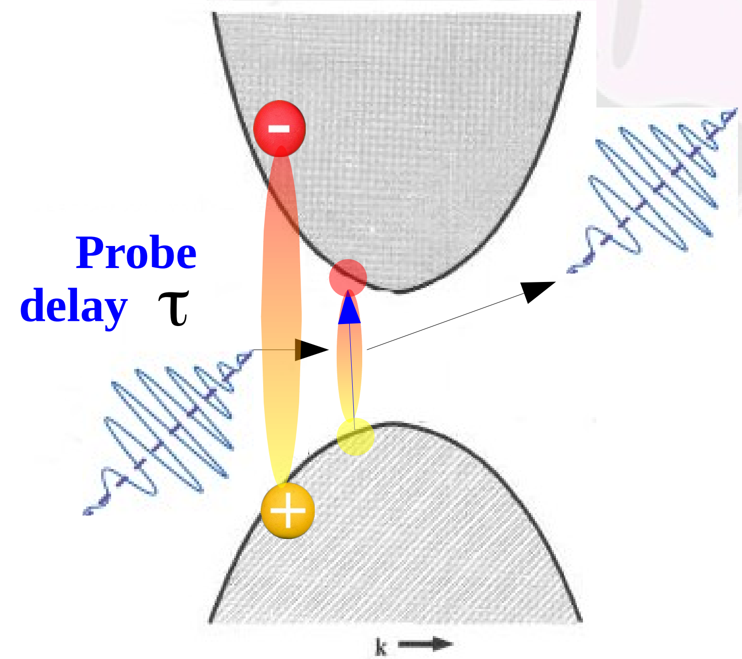
1) RT propagation for the pump

2) "GW+BSE" for the probe

Transient absorption



Early times regime:
No dissipation /decoherence



$$\rho_{nmk}(t)$$

$$\chi(\omega,\tau)[\rho_{nmk}] \approx \cancel{\chi(\omega)[f_{nk}(\tau)]}$$

1) RT propagation for the pump

2) RT propagation for the probe as well

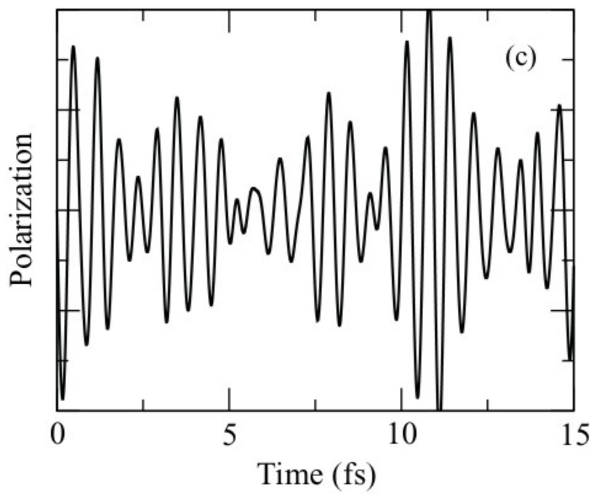
E. Perfetto, D. Sangalli, A. Marini, G. Stefanucci, Phys. Rev. B 92, 205304 (2015)
D. Sangalli, Phys. Rev. Mat. 5, 083803 (2021)

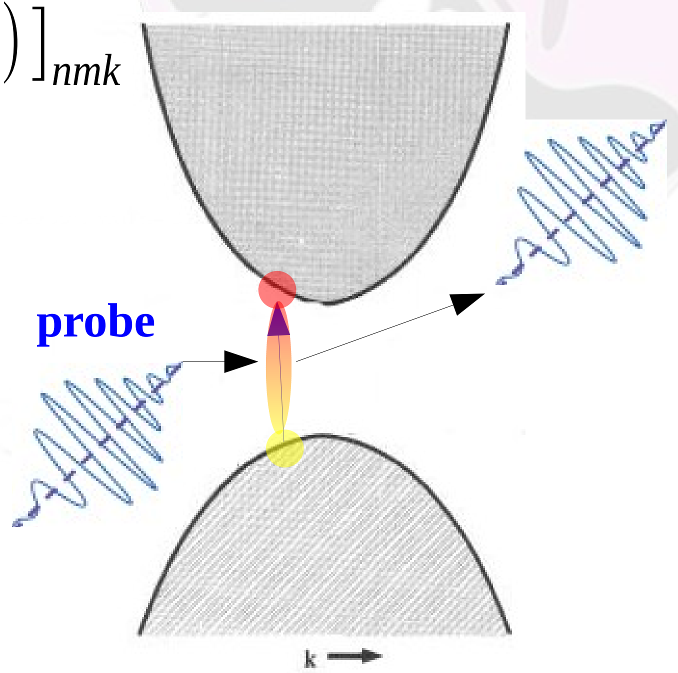
TD-HSEX equation: probe only

$$U^{ext}(t)=U^{probe}$$

$$i\,\partial_t \rho_{nmk}(t)=[h^{GW-eq}+\Delta\Sigma^{HSEX}[\rho(t)]+U^{ext}(t),\rho(t)]_{nmk}$$

$$\rightarrow P(t)$$



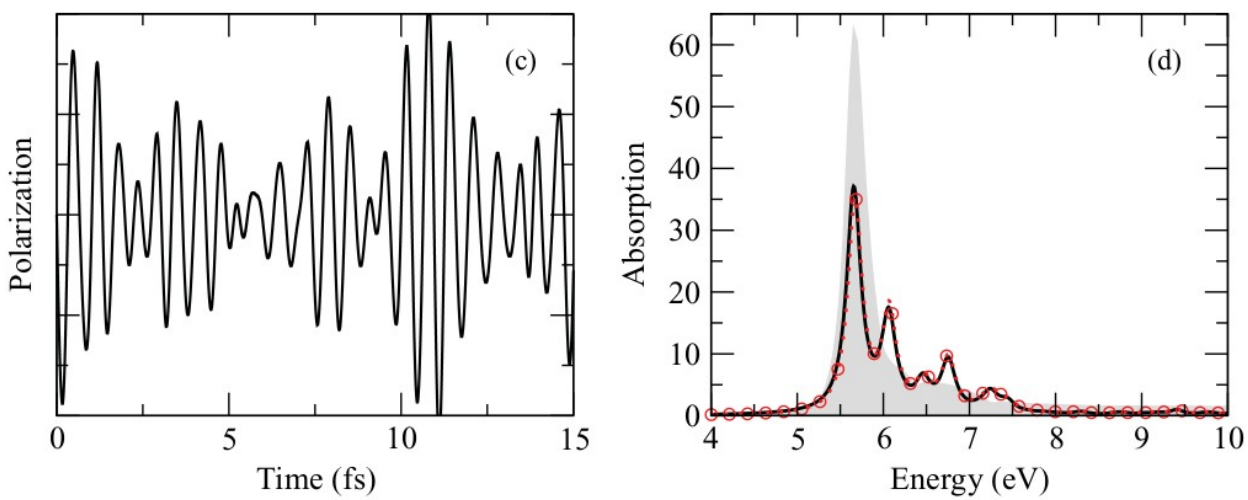


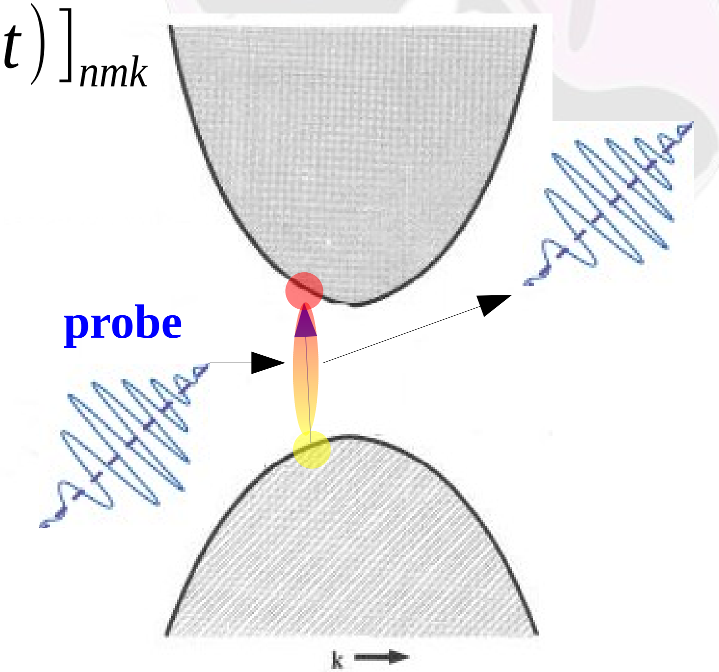
TD-HSEX equation: probe only

$$U^{ext}(t)=U^{probe}$$

$$i\,\partial_t \rho_{nmk}(t)=[\,h^{GW-eq}+\Delta\Sigma^{HSEX}[\rho(t)]+U^{ext}(t),\rho(t)\,]_{nmk}$$

$$P(t) \xrightarrow{\text{Fourier Transform}} \chi^{TD-HSEX}(\omega)$$





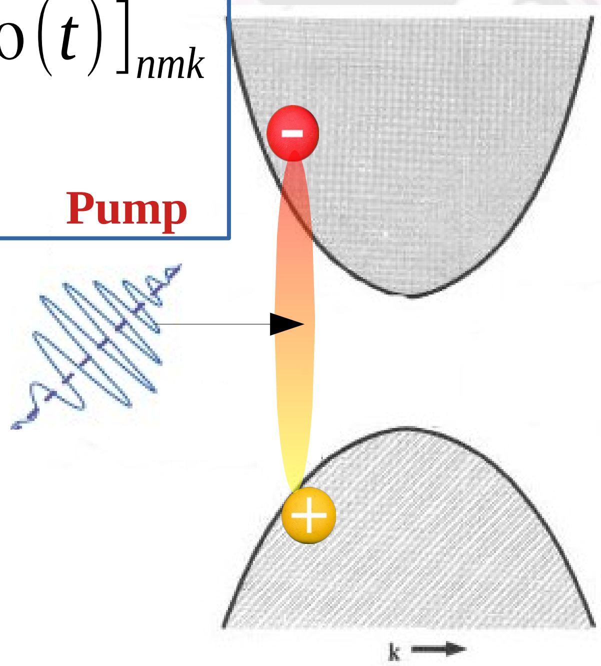
$$\chi^{TD-HSEX}(\omega)=\chi^{GW+BSE}[\,f^{eq}\,]$$

TD-HSEX equation: pump and probe

$$i\,\partial_t \rho_{nmk}(t) = [\,h^{GW-eq} + \Delta\Sigma^{HSEX}[\rho(t)] + U^{ext}(t), \rho(t)\,]_{nmk}$$

$$U_1^{ext}(t) = U^{pump} \qquad P_1(t),\, f_{nk}(t)$$

Pump



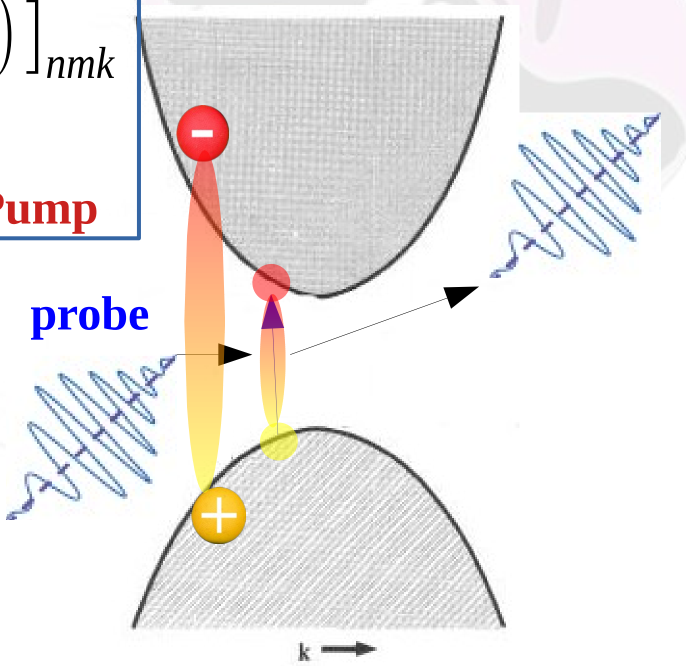
TD-HSEX equation: pump and probe

$$i\,\partial_t \rho_{nmk}(t) = \left[h^{GW-eq} + \Delta\Sigma^{HSEX}[\rho(t)] + U^{ext}(t), \rho(t) \right]_{nmk}$$

$$U_1^{ext}(t) = U^{pump}$$

$$P_1(t), f_{nk}(t)$$

Pump



Option 1 (approximated)

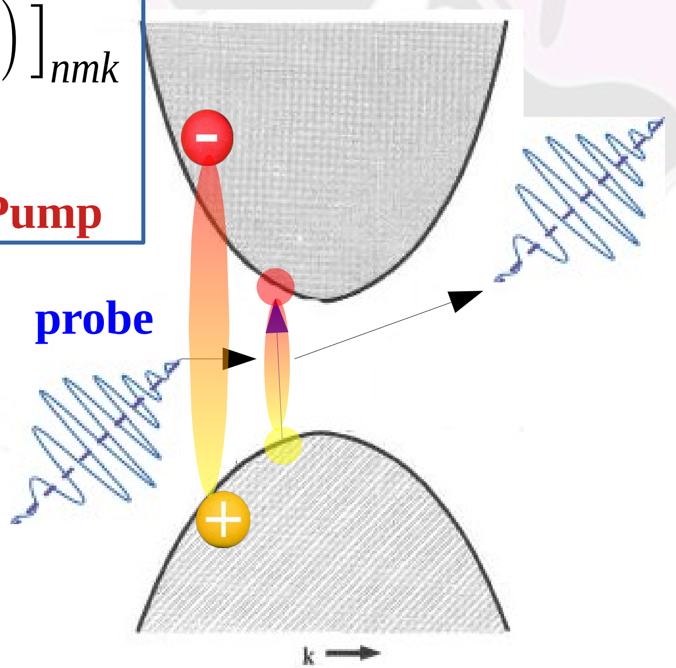
$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f_{nk}(\tau)]$$

TD-HSEX equation: pump and probe

$$i\,\partial_t \rho_{nmk}(t) = [\, h^{GW-eq} + \Delta\Sigma^{HSEX}[\rho(t)] + U^{ext}(t), \rho(t)\,]_{nmk}$$

$$U_1^{ext}(t) = U^{pump} \qquad P_1(t), f_{nk}(t)$$

Pump



Option 1 (approximated)

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[\, f_{nk}(\tau)\,]$$

Option 2 (exact)

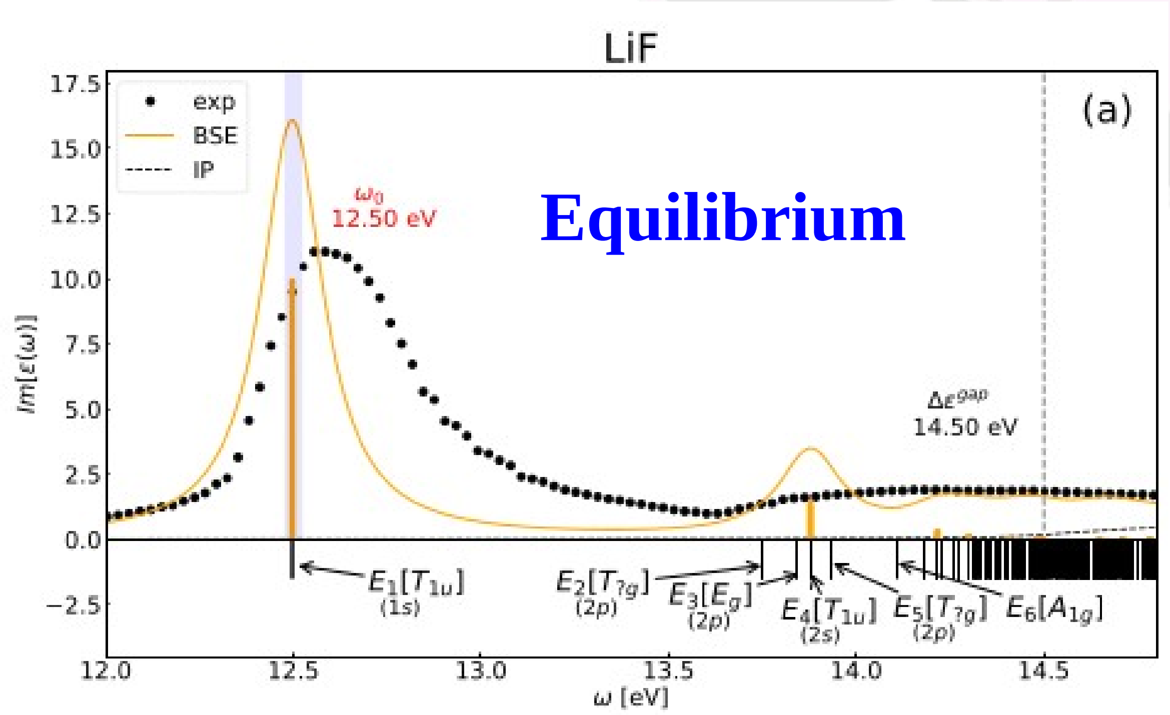
$$U_2^{ext}(t) = U^{pump} + U^{probe}(\tau) \qquad P_2(t,\tau)$$

$$\chi^{TD-HSEX}(\omega,\tau) = \frac{P_2(\omega,\tau) - P_1(\omega)}{U^{probe}(\omega)}$$

Comparison of the two approaches

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f^{eq}_{nk}]$$

Contains poles ω_λ



$$\chi^{TD-HSEX}[\rho](\omega)$$

Contains poles ω_λ

$$E^N_I - E^N_0$$

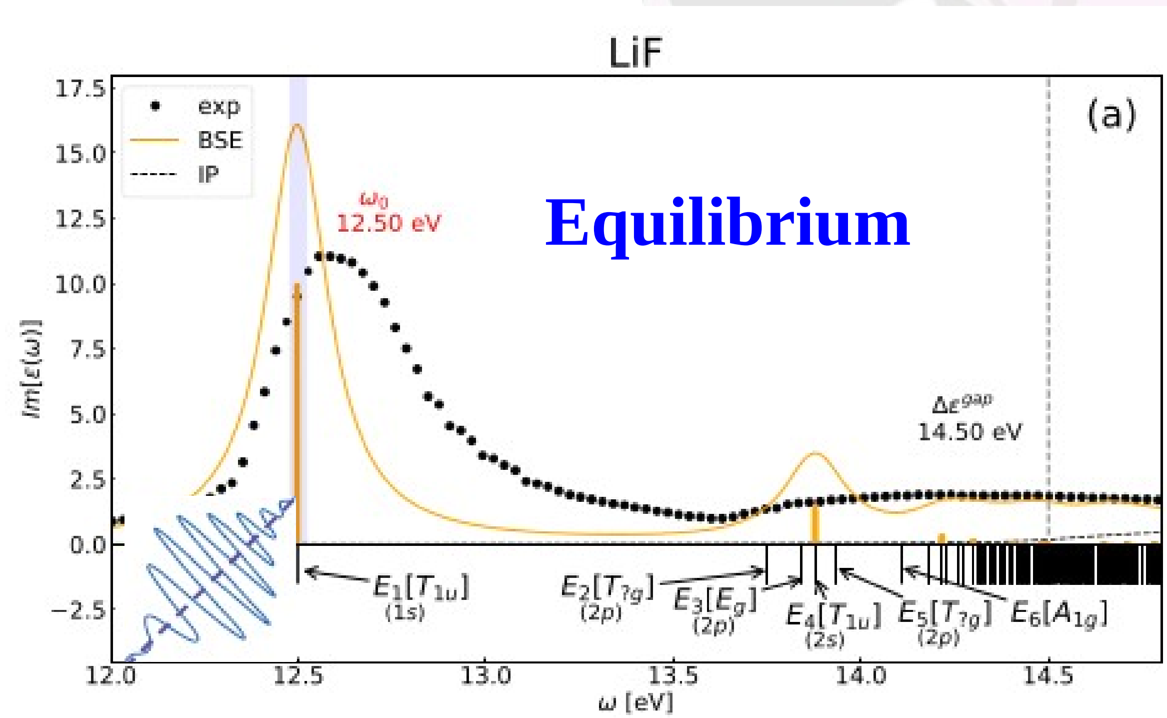
Comparison of the two approaches

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f_{nk}^{eq}]$$

Contains poles ω_λ

$$\chi^{TD-HSEX}[\rho](\omega)$$

Contains poles ω_λ



Pump

$$\omega_P = 12.5$$

$$E_I^N - E_0^N$$

Comparison of the two approaches

Option 1 (approximated)

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f_{nk}(\tau)]$$

Contains poles ω_λ and

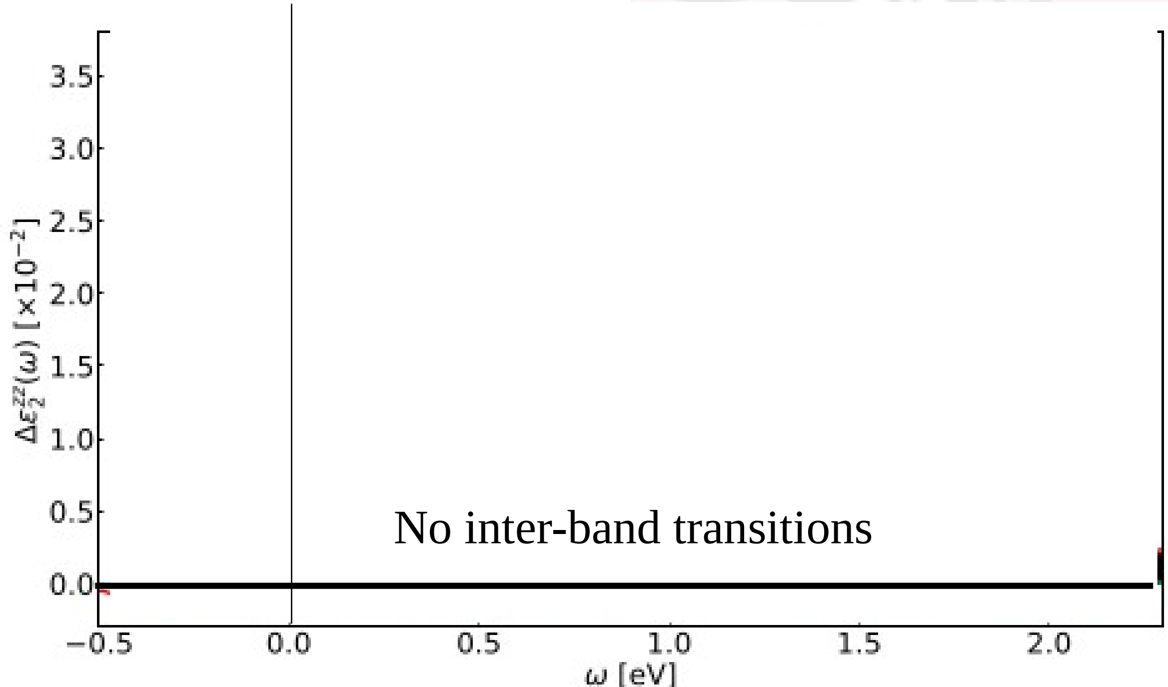
$$(\epsilon_{ck}-\epsilon_{c'k})$$

Option 2 (exact)

$$\chi^{TD-HSEX}[\rho](\omega,\tau)$$

Contains poles ω_λ and

$$(\omega_\lambda-\omega_{\lambda'})$$



Pump

$$\omega_P = 12.5$$

Nonequilibrium

$E_I^N - E_0^N$ and ???

the Yambo team

D. Sangalli, M. D'alessandro, C. Attaccalite, Phys. Rev. B 107, 205203 (2023)

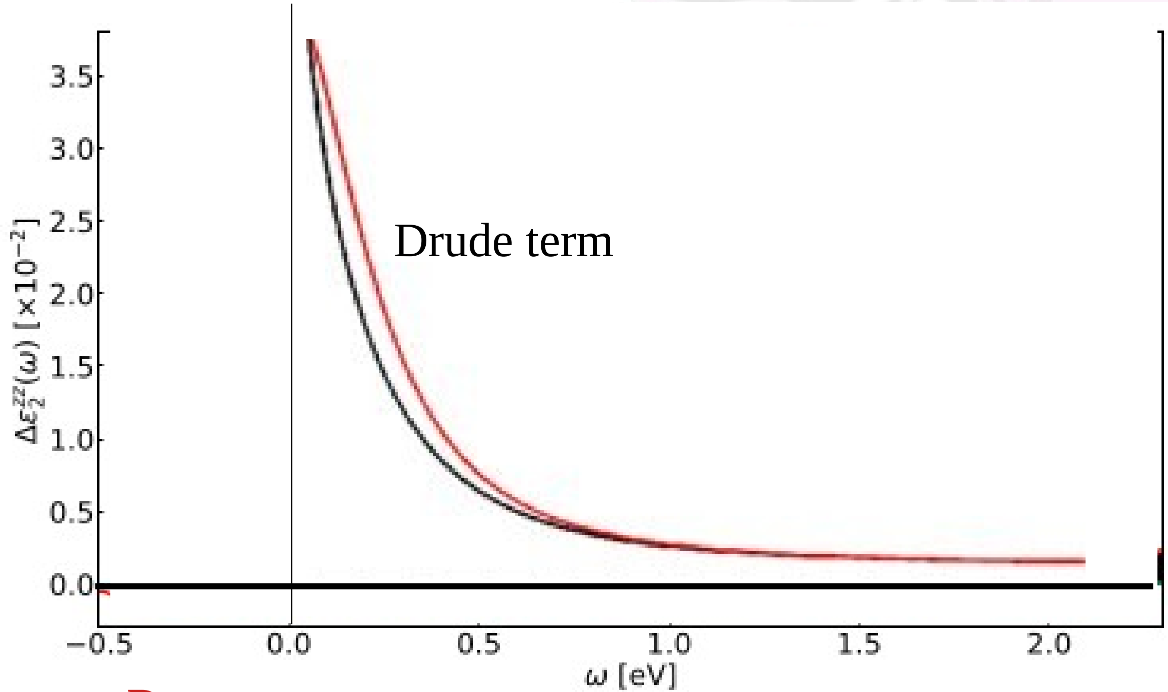
Comparison of the two approaches

Option 1 (approximated)

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f_{nk}(\tau)]$$

Contains poles ω_λ and

$$(\epsilon_{ck}-\epsilon_{c'k})$$



Pump

$$\omega_P = 12.5$$

Nonequilibrium

Option 2 (exact)

$$\chi^{TD-HSEX}[\rho](\omega,\tau)$$

Contains poles ω_λ and

$$(\omega_\lambda-\omega_{\lambda'})$$

$E_I^N - E_0^N$ and ???

the Yambo team

D. Sangalli, M. D’alessandro, C. Attaccalite, Phys. Rev. B 107, 205203 (2023)

Comparison of the two approaches

Option 1 (approximated)

$$\chi^{\text{NEQ-GW+BSE}}(\omega)[f_{nk}(\tau)]$$

Contains poles ω_λ and

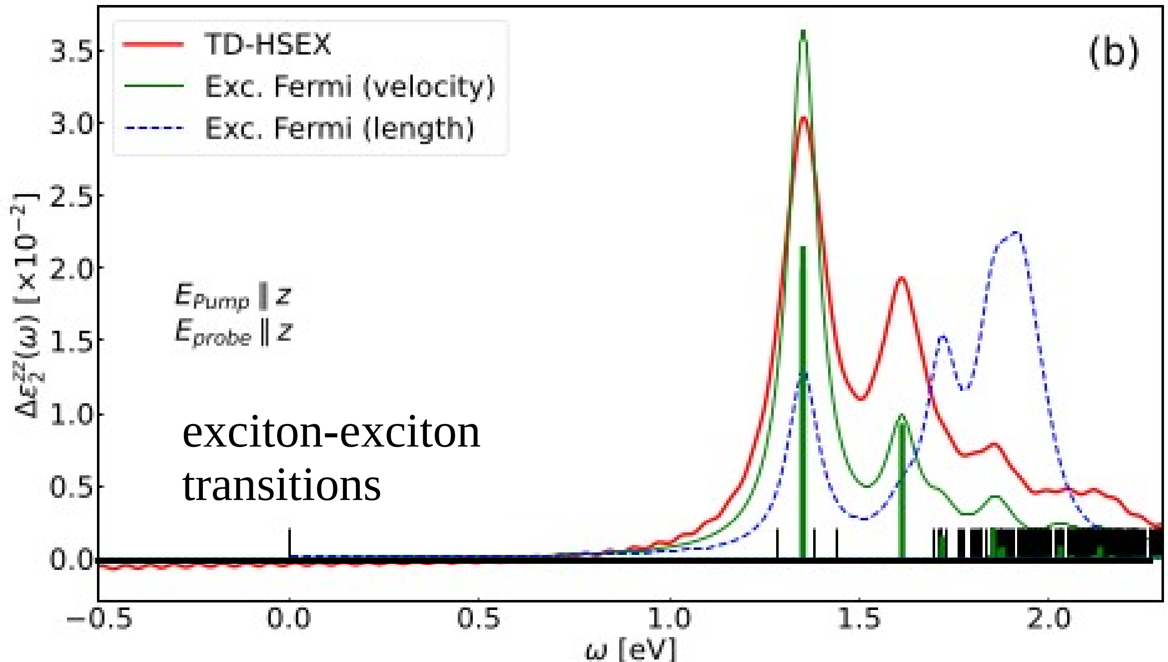
$$(\epsilon_{ck}-\epsilon_{c'k})$$

Option 2 (exact)

$$\chi^{TD-HSEX}[\rho](\omega,\tau)$$

Contains poles ω_λ and

$$(\omega_\lambda-\omega_{\lambda'})$$



Pump

$$\omega_P = 12.5$$

Nonequilibrium

$E_I^N - E_0^N$ and $E_I^N - E_J^N$

D. Sangalli, M. D'alessandro, C. Attaccalite, Phys. Rev. B 107, 205203 (2023)

TR-ARPES

Option 1 (approximated)

$$I(\omega,k)[f_{nk}(\tau)]=\sum_c f_{ck}(\tau)\delta(\omega-\epsilon_{ck})$$

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Option 2 (exact with static self-energy)

$$I[\rho](\omega,k,\tau)=G^{<}_{\tau}[\rho](k,w)$$

Generalized Kadanoff Baym Equation

$$G^{(r)}(t,t') = -i\theta(t-t')T\left[e^{-i\int_{t'}^{t} h^{HSEX}[\rho(t)]dt}\right]$$

$$G^{<}_{cc'\mathbf{k}}(t,t') = \sum_n \rho_{cn\mathbf{k}}(t)G^{(r)}_{nc'\mathbf{k}}(t,t') - G^{(a)}_{cn\mathbf{k}}(t,t')\rho_{nc'\mathbf{k}}(t')$$

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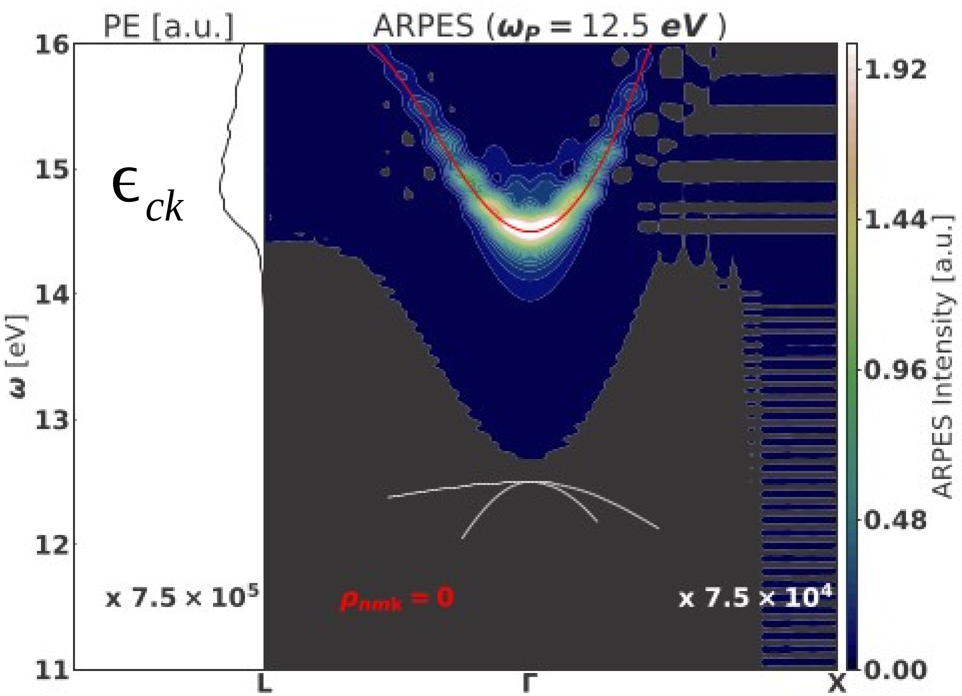
At equilibrium the two approaches are identical

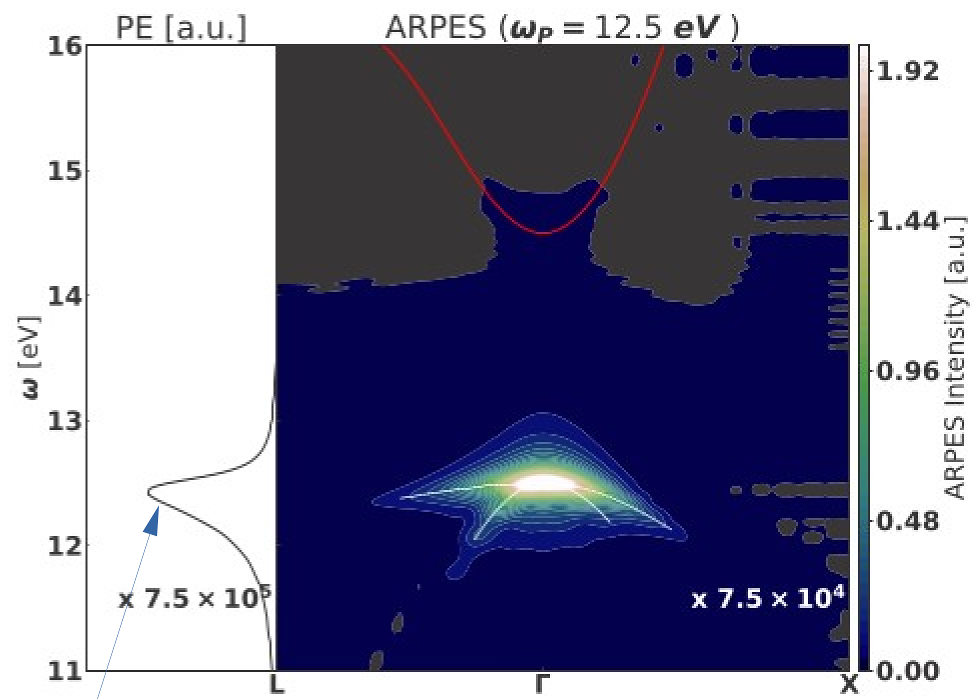
Comparison of the two approaches

Pump

$\omega_P = 12.5$



D. Sangalli, Phys. Rev. Mat. 5, 083803 (2021)



$$I(\omega, k)[f_{nk}(\tau)]$$

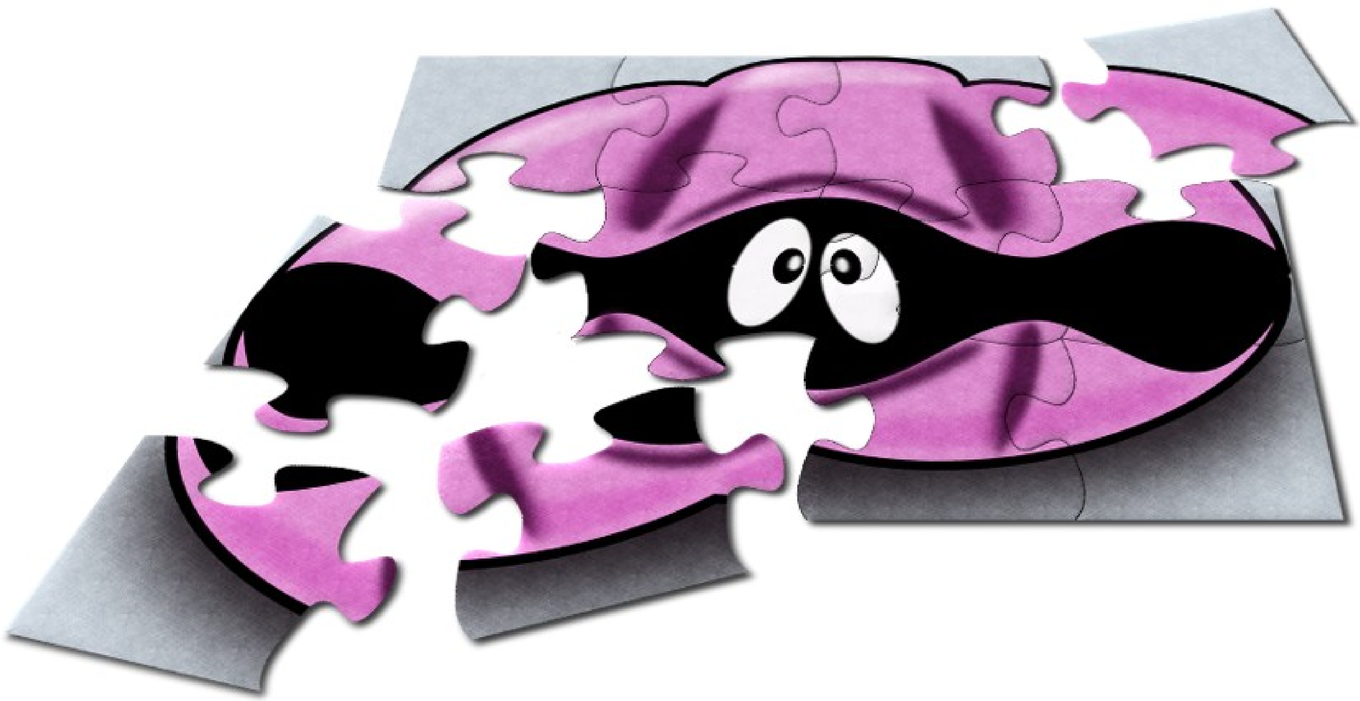
Option 1 (approximated)

$$I[\rho](\omega, k, \tau)$$

Option 2 (exact with static self-energy)

the Yambo team

Thank you for your attention



the Yambo team

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