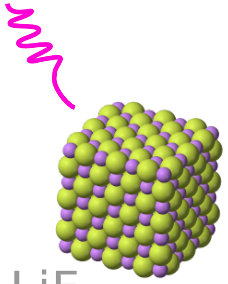
MAX DRIVING THE EXASCALE TRANSITION

In real time: nonlinear optical spectroscopy

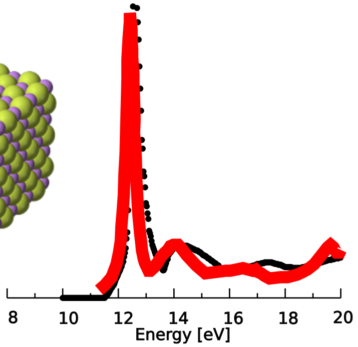
Myrta Grüning - Queen's University Belfast

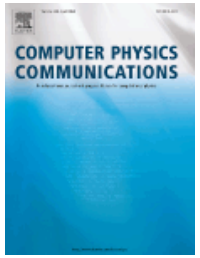
MaX “*Materials Design at the Exascale*”, has received funding from the European Union’s Horizon 2020 project call H2020-INFRAEDI-2018-1, grant agreement 824143

ab initio...



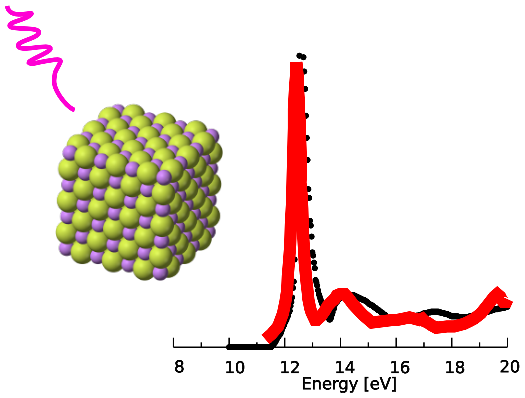
LiF

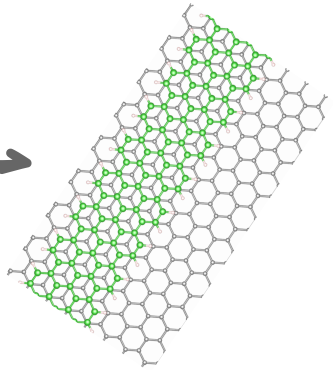


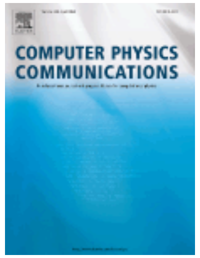


Marini et al.

...towards larger systems



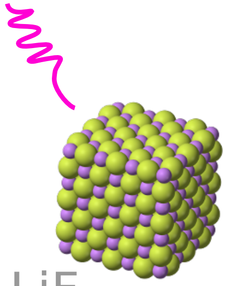




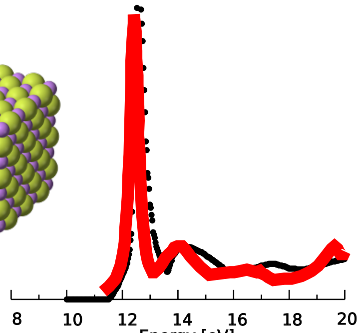
Marini et al.

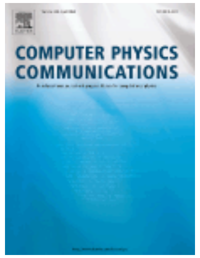
DRIVING THE EXASCALE TRANSITION

ab initio...



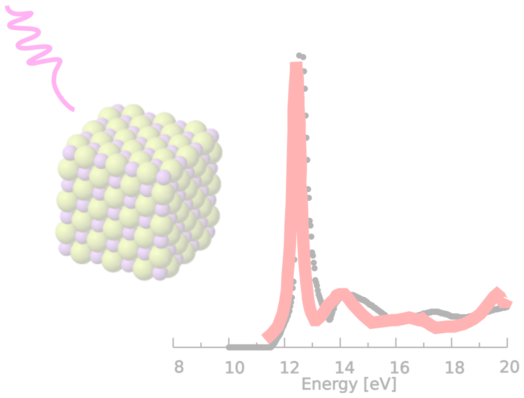
LiF

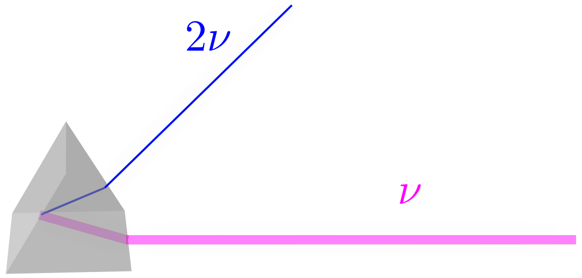




Marini et al.

...towards other spectroscopies



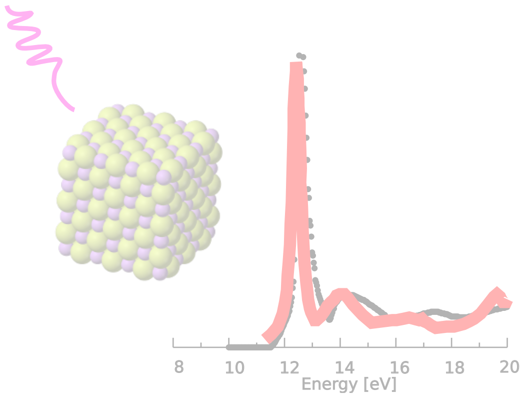


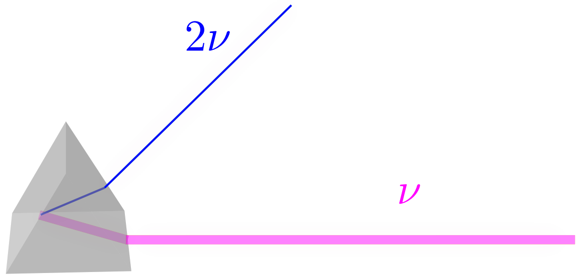
Nonlinear
optics

Linear
response

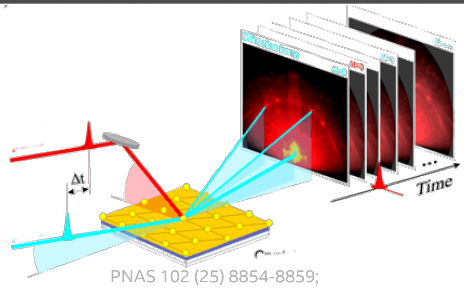
Nonlinear
regime

...towards other spectroscopies



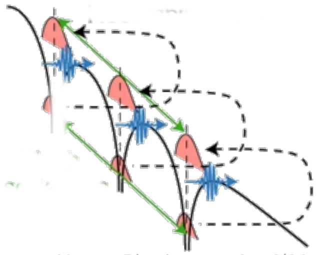


Nonlinear optics



PNAS 102 (25) 8854-8859;

pump-probe

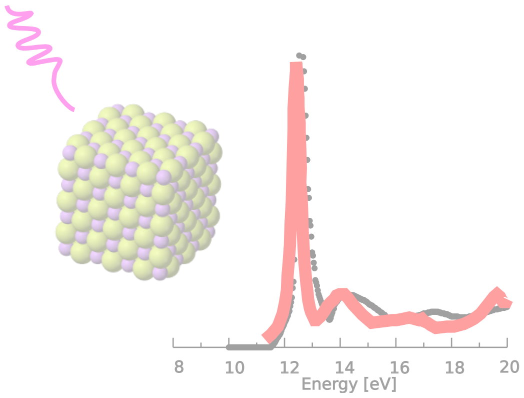


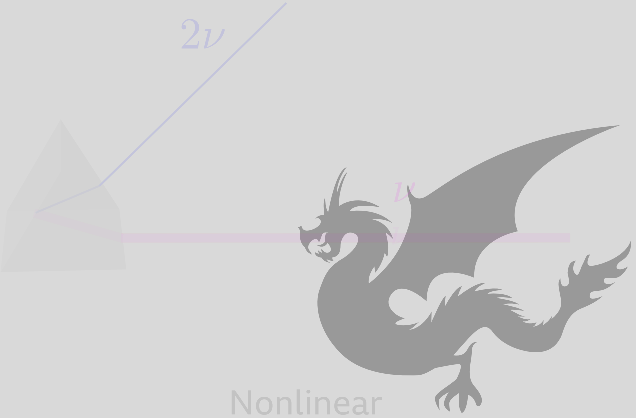
Nature Physics 15, 10–16(2019)

extreme nonlinear

Linear response → Nonlinear regime → Out-of-equilibrium regime

an uncharted territory





Nonlinear optics

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Nature Physics 15, 10–16(2019)

extreme nonlinear

Hic sunt Dracones

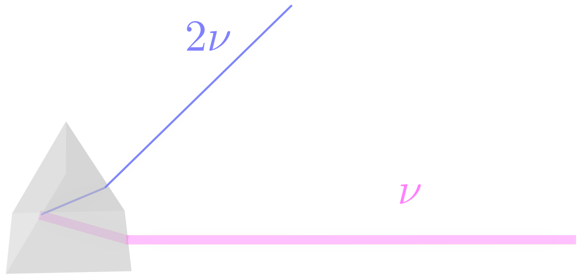
Linear response

Nonlinear regime

Out-of-equilibrium regime

DRIVING THE EXASCALE TRANSITION

the dragons



HIGH ORDER
E-H DIAGRAMS

PNAS 102 (25) 8854-8859;

pump-probe

Nature Physics 15, 10–16(2019)

extreme nonlinear

Linear response

Nonlinear regime

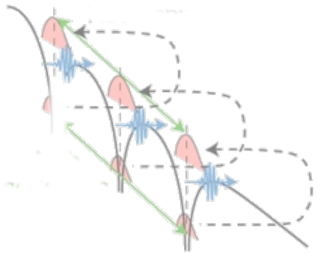
Out-of-equilibrium regime

the dragons

PNAS 102 (25) 8854-8859;

pump-probe

Non Perturbative



Nature Physics 15, 10–16(2019)

extreme nonlinear

Linear response

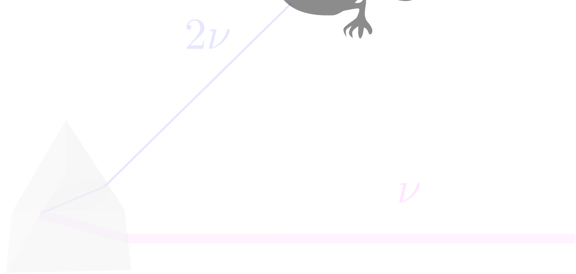
Nonlinear regime

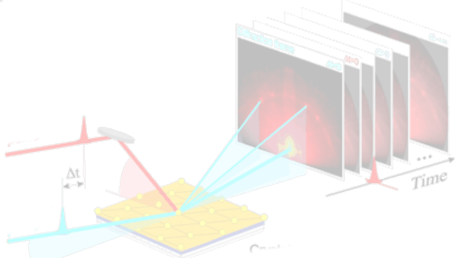
Out-of-equilibrium regime

MAX DRIVING THE EXASCALE TRANSITION

the dragons

SCATTERING





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pump-probe

Nature Physics 15, 10–16(2019)

extreme
nonlinear

Linear
response

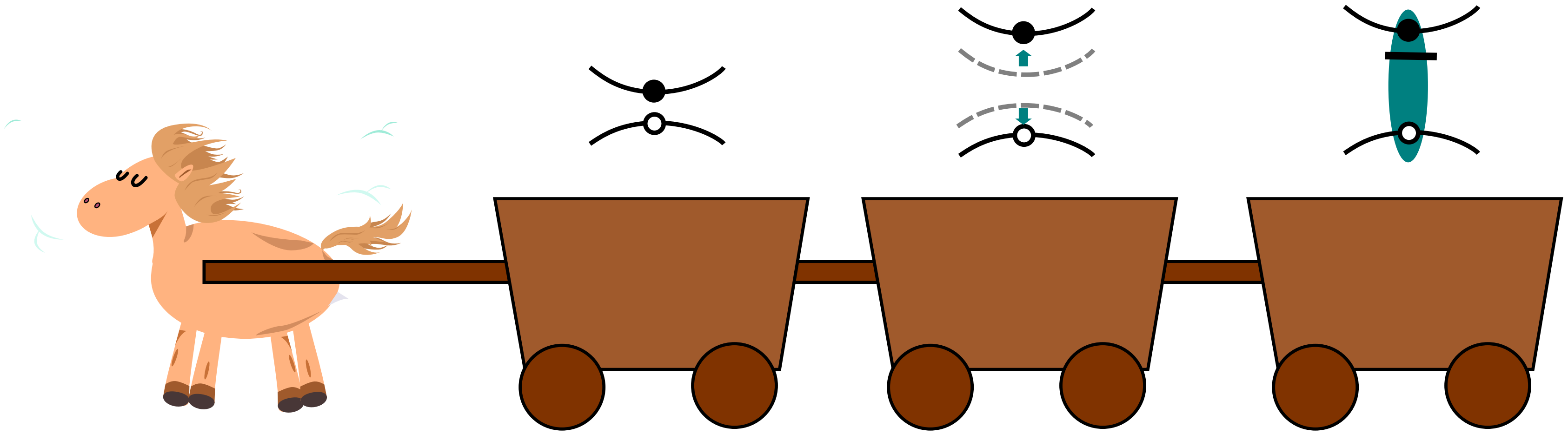
Nonlinear
regime

Out-of-equilibrium
regime

MAX DRIVING THE EXASCALE TRANSITION

real-time

the GW+BSE recipe for success



many-body perturbation theory

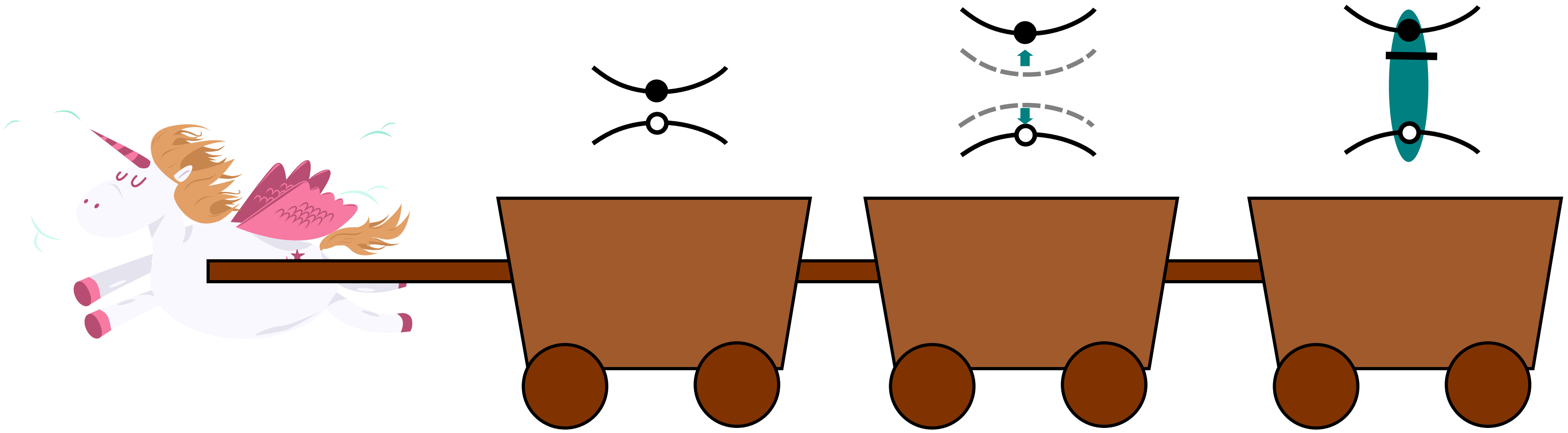
KS energies and Bloch functions

Quasiparticle corrections within GWA

COHSEX approximation

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

the GW+BSE recipe for success in real-time



non-equilibrium
Green's function

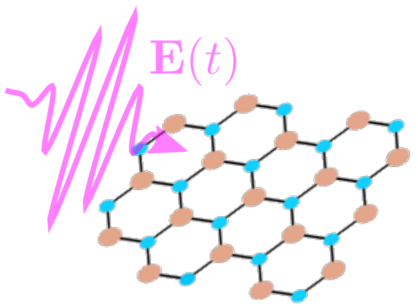
KS energies and
Bloch functions

Quasiparticle
corrections
within GWA

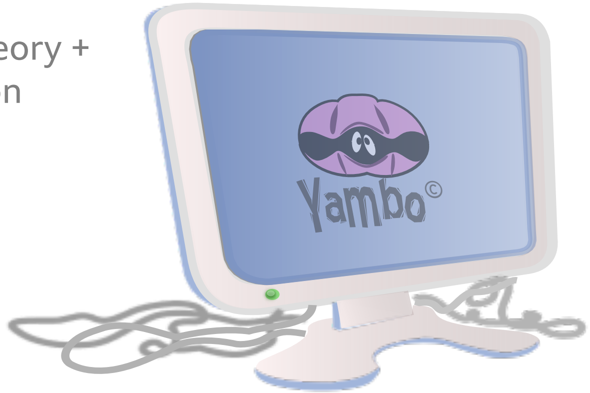
COHSEX
approximation

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

yambo real-time implementation



Density functional theory + GW approximation



off-diagonal term: polarization

$$\mathbf{P}(t)$$

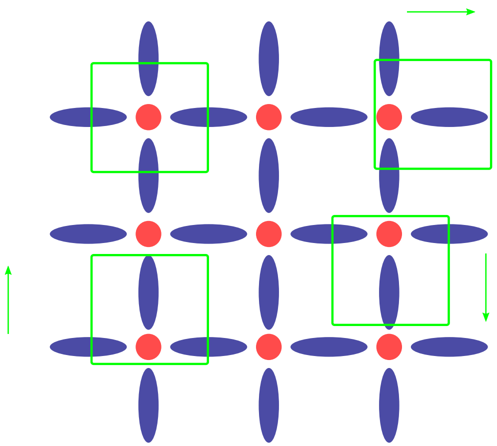
on diagonal terms: occupations

$$f_{n\mathbf{k}} = -iG^{<}_{nn\mathbf{k}}$$

$$i\hbar \frac{\partial}{\partial t} G^{<}_{nm\mathbf{k}}(t) = \left[\mathbf{h}_{\mathbf{k}} + \Delta\mathbf{h}_{\mathbf{k}} + \mathbf{U}_{\mathbf{k}} + \Delta\mathbf{V}^{H}_{\mathbf{k}}[\rho] + \Delta\mathbf{\Sigma}^{\mathrm{cohsex}}_{\mathbf{k}}[G^{<}], \mathbf{G}^{<}_{\mathbf{k}}(t)\right]_{nm}$$

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

bulk polarization

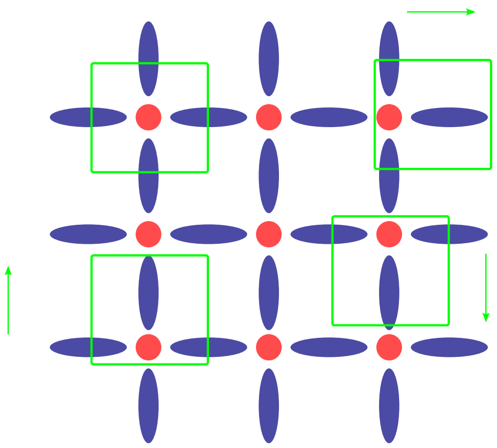


✗ $\Delta P = \int_{\text{space}} d\mathbf{r}\, \mathbf{r} \Delta\rho(\mathbf{r})$ diverge!

✗ $\Delta P \propto \int_{\text{BZ}} d\mathbf{r}\, \mathbf{r} \Delta\rho(\mathbf{r})$ depends on cell choice

see e.g. Resta, Troisieme Cycle de la Physique en Suisse Romande (1999), "Berry's Phase and Geometric Quantum Distance"

bulk polarization



✗ $\Delta P = \int_{\text{space}} d\mathbf{r}\, \mathbf{r} \Delta\rho(\mathbf{r})$ diverge!

✗ $\Delta P \propto \int_{\text{BZ}} d\mathbf{r}\, \mathbf{r} \Delta\rho(\mathbf{r})$ depends on cell choice

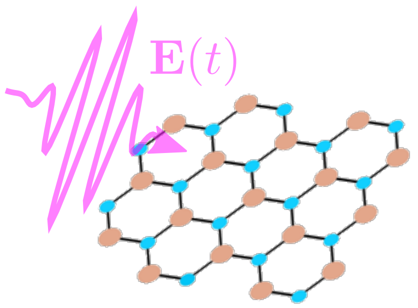
✓  Polarization as a Berry-Phase

$$\Delta P \propto \langle X \rangle = \frac{L}{2\pi} \text{Im} \log \langle \Psi_0 | e^{i \frac{2\pi}{L} \hat{X}} | \Psi_0 \rangle \longrightarrow \propto i \int d\mathbf{k} \sum_m^{\text{occ}} \langle u_{\mathbf{k},m} | \partial_{\mathbf{k}} u_{\mathbf{k},m} \rangle$$

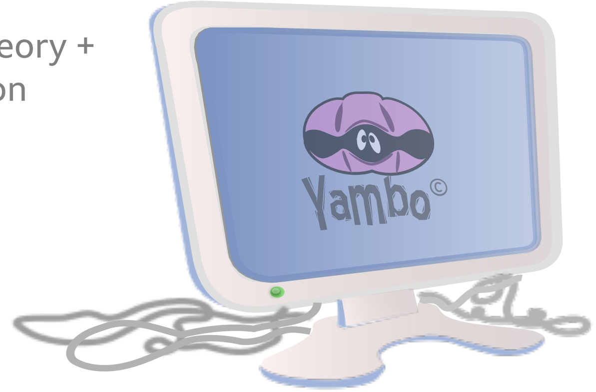
$\Psi_0 \approx$ Slater determinant

see e.g. Resta, Troisieme Cycle de la Physique en Suisse Romande (1999), "Berry's Phase and Geometric Quantum Distance"

dynamics of Bloch electrons for coherent response



Density functional theory +
GW approximation



$$P(t) = i\frac{e}{V}\int d\mathbf{k}\sum_{m}^{\text{fill}}\langle v_{\mathbf{k},m}|\partial_{\mathbf{k}} v_{\mathbf{k},m}\rangle$$

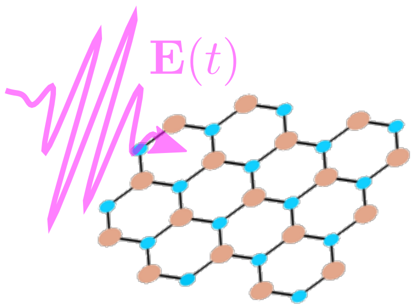
$$i\hbar\frac{d}{dt}|v_{\mathbf{k},m}\rangle = \left(\mathbf{h}_{\mathbf{k}} + \Delta\mathbf{h}_{\mathbf{k}} + \Delta\mathbf{V}^{H}_{\mathbf{k}}[\rho] + \Delta\mathbf{\Sigma}^{\text{cohsex}}_{\mathbf{k}}[G^{<}] + \mathrm{w}_{\mathbf{k}}(\boldsymbol{\mathcal{E}})\right)|v_{\mathbf{k},m}\rangle$$

w: covariant dipole operator, consistent with def of P(t)

$$G^{<}(\mathbf{r},\mathbf{r}';t) = i\int d\mathbf{k}\sum_{m}^{\text{fill}} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}v_{\mathbf{k},m}(\mathbf{r};t)v^{*}_{\mathbf{k},m}(\mathbf{r}';t)$$

Souza el al PRB 69, 085106 (2004), C. Attaccalite, MG PRB 88, 235113 (2013)

real-time and nonlinear runlevels



yambo_rt

$$i\hbar\frac{\partial}{\partial t}G^{<}_{nm\mathbf{k}}(t) = \left[\mathbf{h_k} + \Delta\mathbf{h_k} + \mathbf{U_k} + \Delta\mathbf{V}^{H}_{\mathbf{k}}[\rho] + \Delta\mathbf{\Sigma}^{\mathrm{cohsex}}_{\mathbf{k}}[G^{<}], \mathbf{G}^{<}_{\mathbf{k}}(t)\right]_{nm}$$

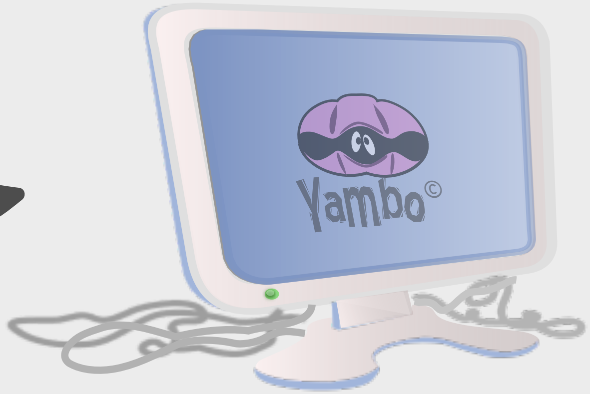
yambo_nl

$$i\hbar\frac{d}{dt}|v_{\mathbf{k},m}\rangle = \left(\mathbf{h_k} + \Delta\mathbf{h_k} + \mathrm{w}_{\mathbf{k}}(\mathcal{E}) + \Delta\mathbf{V}^{H}_{\mathbf{k}}[\rho] + \Delta\mathbf{\Sigma}^{\mathrm{cohsex}}_{\mathbf{k}}[G^{<}]\right)|v_{\mathbf{k},m}\rangle$$

Sangalli et al. Journal of Physics: Condensed Matter, 31, 325902 (2019)

how it works? Choice of experiment

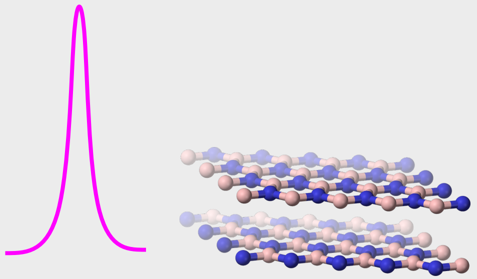
time-dependent electric field



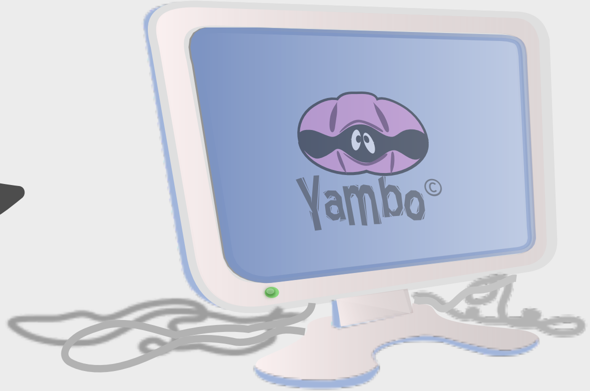
$$i\hbar\frac{d}{dt}|v_{\mathbf{k},m}\rangle = (\mathbf{h}_{\mathbf{k}} + \mathrm{w}_{\mathbf{k}}(\mathcal{E}))\,|v_{\mathbf{k},m}\rangle$$

signal post-processing

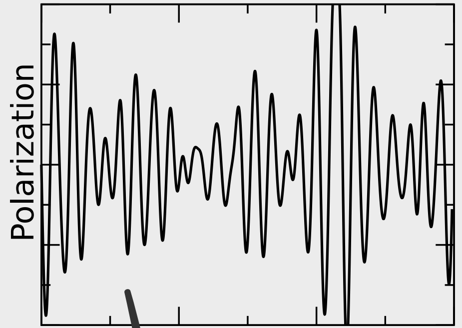
example: linear response



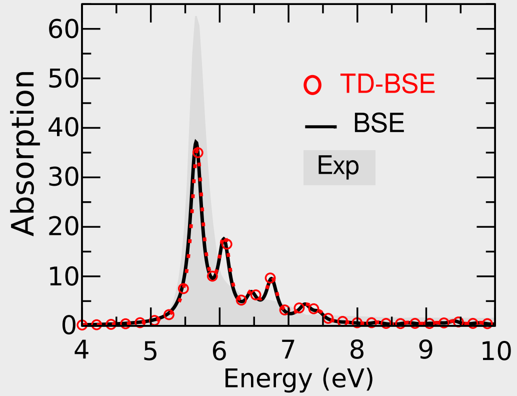
delta-kick



$$i\hbar\frac{d}{dt}|v_{\mathbf{k},m}\rangle = (\mathbf{h}_{\mathbf{k}} + \mathrm{w}_{\mathbf{k}}(\mathcal{E}))\,|v_{\mathbf{k},m}\rangle$$

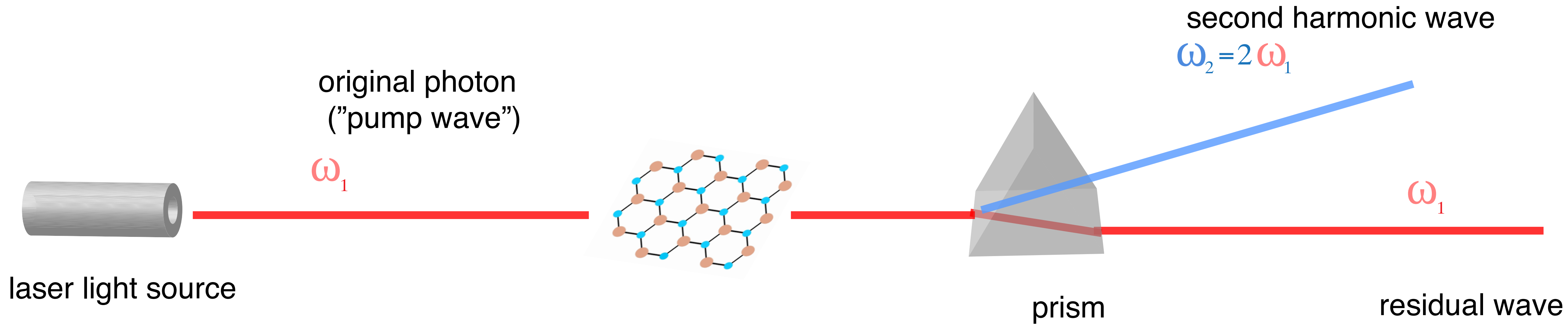


Fourier transform

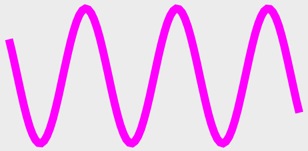


C. Attaccalite, M.G, A Marini PRB 84, 245110 (2011)

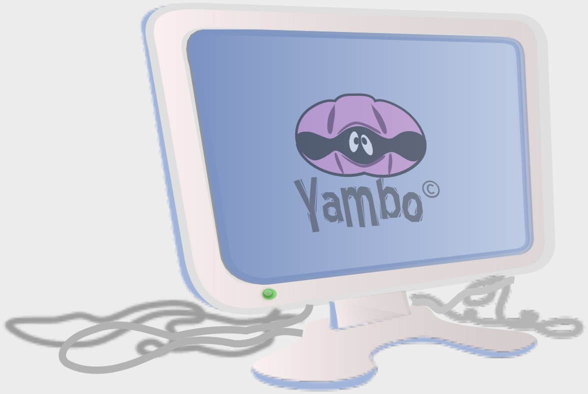
example: nth harmonic generation



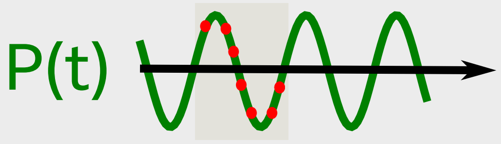
example: nth harmonic generation



$$\mathcal{E}(t) = \mathcal{E}_0 sin(\omega_L t)$$



$$i\hbar \frac{d}{dt}|v_{\mathbf{k},m}\rangle = (\mathbf{h}_\mathbf{k} + \mathrm{w}_\mathbf{k}(\mathcal{E}))\,|v_{\mathbf{k},m}\rangle$$



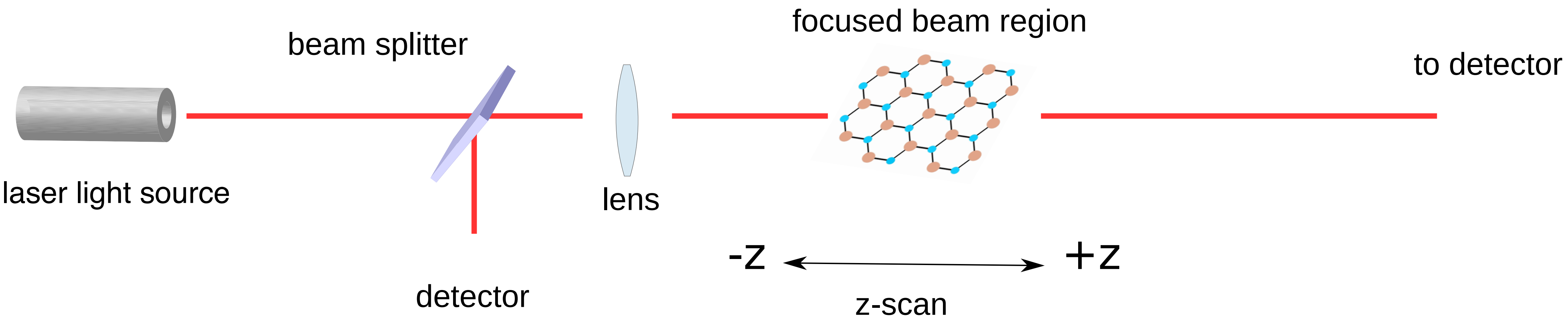
$$P(t_j) = \sum_{n=-N}^{N} F_{jn}\hat{P}_n$$

$F_{jn} = \exp(i\,n\omega_L t_j)$

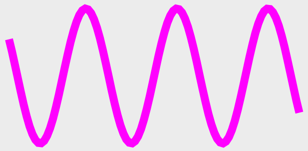
$$\hat{P}_n = \sum_{j=0}^{2N} F^{-1}_{nj} P(t_j)$$

$$\chi^{(n)}(n\omega_L) = \frac{\hat{P}_n}{\mathcal{E}^n}$$

example: two-photon absorption

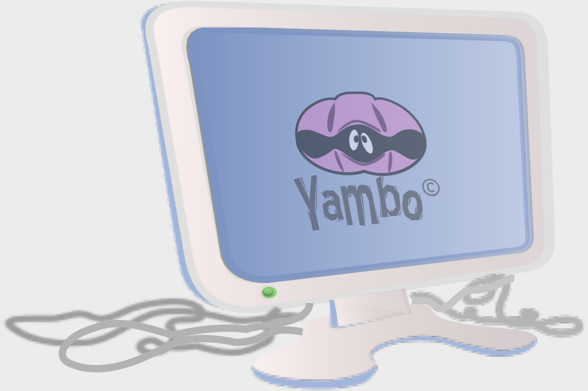


example: two-photon absorption

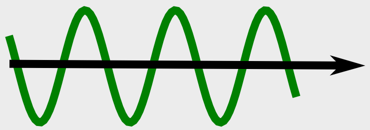


$$\mathcal{E}(t) = \mathcal{E}_0 sin(\omega_L t)$$

@varying
field intensity



$$i\hbar \frac{d}{dt}|v_{\mathbf{k},m}\rangle = (\mathbf{h}_{\mathbf{k}} + \mathrm{w}_{\mathbf{k}}(\mathcal{E}))\,|v_{\mathbf{k},m}\rangle$$

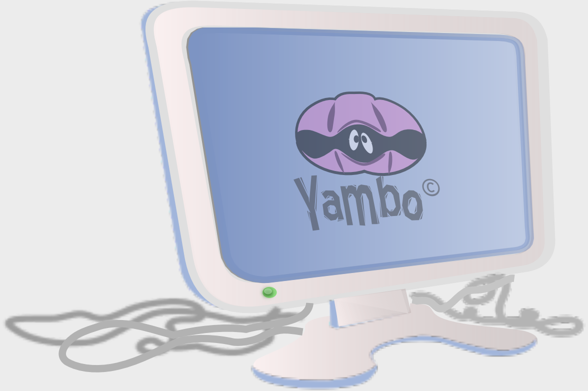
P(t) 

$$\begin{aligned} \mathbf{P}(\mathcal{E}) &= \chi^{(1)}\mathcal{E} + \chi^{(3)}\mathcal{E}^3 + O(\mathcal{E}^5), \\ \mathbf{P}\left(\frac{\mathcal{E}}{2}\right) &= \chi^{(1)}\frac{\mathcal{E}}{2} + \chi^{(3)}\frac{\mathcal{E}^3}{8} + O(\mathcal{E}^5), \\ \mathbf{P}\left(\frac{\mathcal{E}}{4}\right) &= \chi^{(1)}\frac{\mathcal{E}}{4} + \chi^{(3)}\frac{\mathcal{E}^3}{64} + O(\mathcal{E}^5) \end{aligned}$$

$$\chi^{(3)} = \frac{8}{3}\frac{\mathbf{P}(\boldsymbol{\mathcal{E}}) - 6\mathbf{P}(\frac{\boldsymbol{\mathcal{E}}}{2}) + 8\mathbf{P}(\frac{\boldsymbol{\mathcal{E}}}{4})}{\boldsymbol{\mathcal{E}}^3}$$

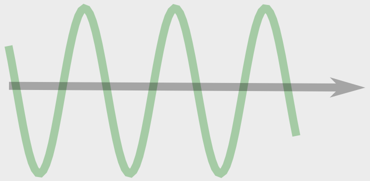
how it works? Choice of level of theory

$$\mathcal{E}(t) = \mathcal{E}_0 sin(\omega_L t)$$



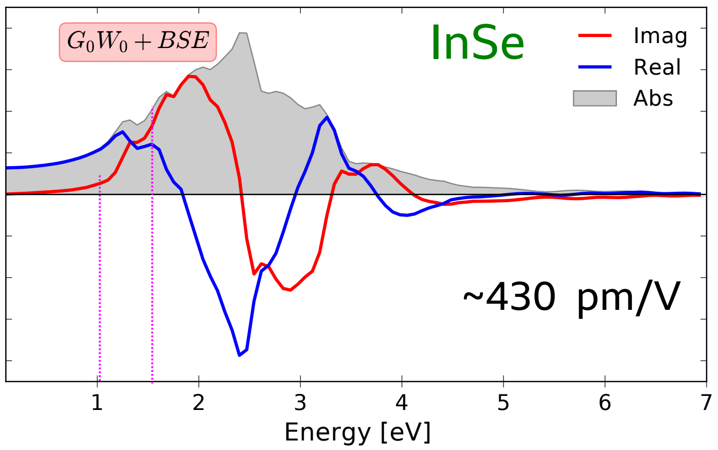
$$i\hbar\frac{d}{dt}|v_{\mathbf{k},m}\rangle = (\mathbf{h_k} + \mathrm{w}_{\mathbf{k}}(\boldsymbol{\mathcal{E}}))\,|v_{\mathbf{k},m}\rangle$$

P(t)



non-linear optics at GW+BSE

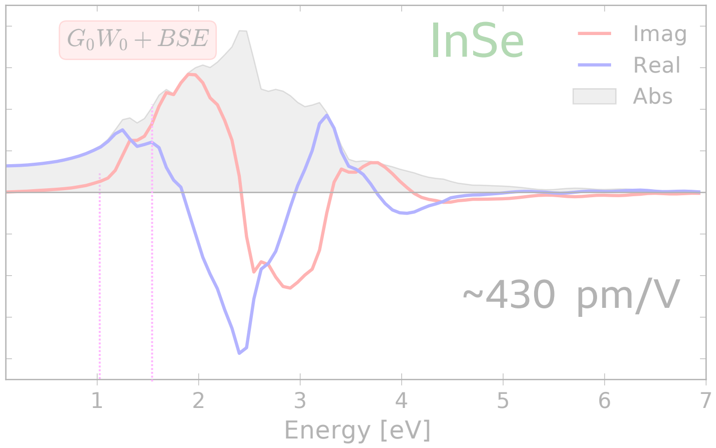
SHG in 2D materials



Phys. Rev. Mat. 3, 074003 (2019)

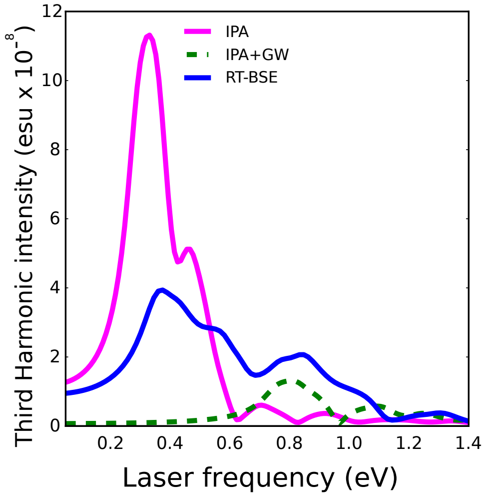
non-linear optics at GW+BSE

SHG in 2D materials



Phys. Rev. Mat. 3, 074003 (2019)

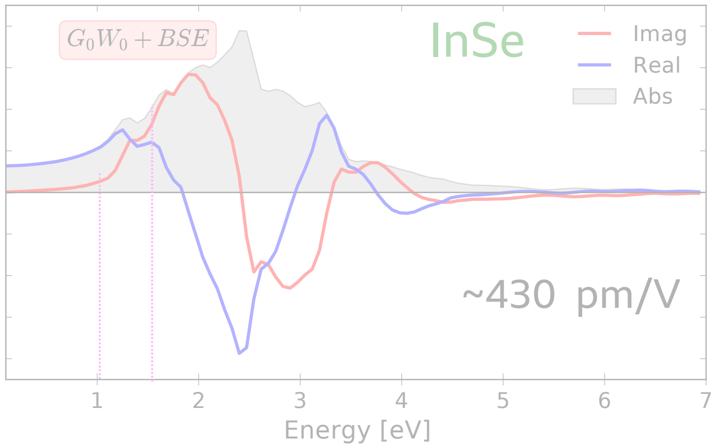
THG in 1D nanostructures



Phys. Rev. B 95, 125403 (2017)

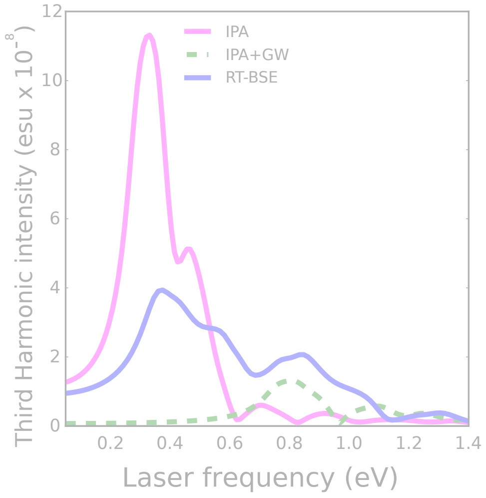
non-linear optics at GW+BSE

SHG in 2D materials



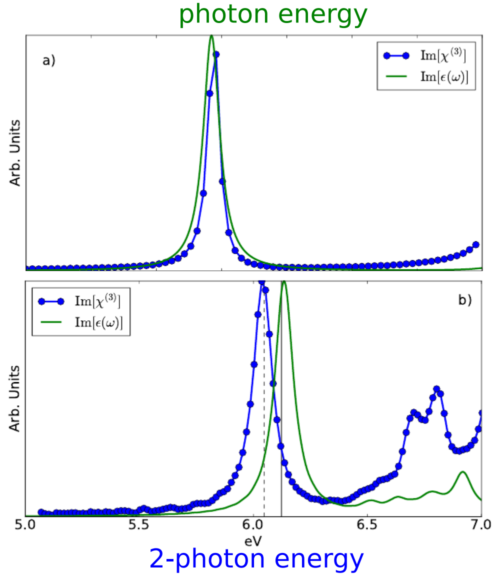
Phys. Rev. Mat. 3, 074003 (2019)

THG in 1D nanostructures



Phys. Rev. B 95, 125403 (2017)

2-photon absorption in hBN bulk and ML

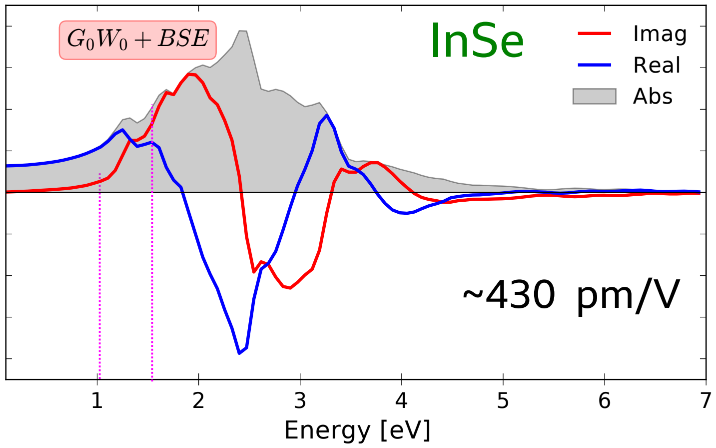


Phys. Rev. B 98, 1651126 (2018)

MAX DRIVING THE EXASCALE TRANSITION

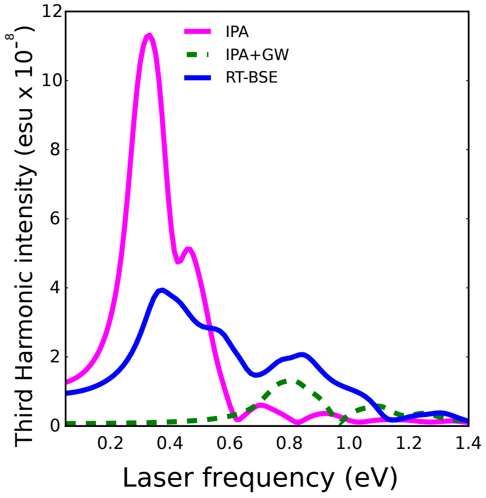
non-linear optics at GW+BSE

SHG in 2D materials



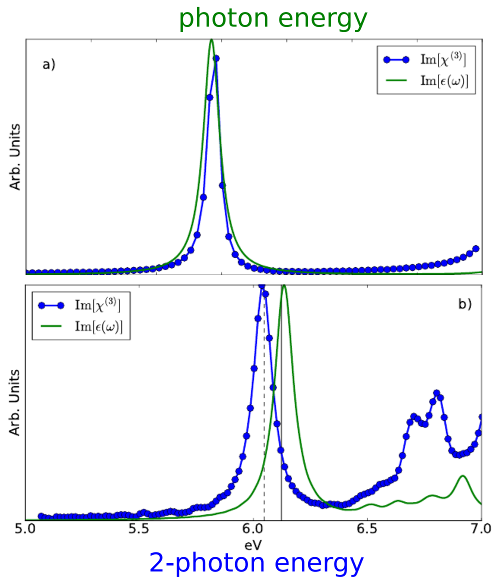
Phys. Rev. Mat. 3,   074003 (2019)

THG in 1D nanostructures



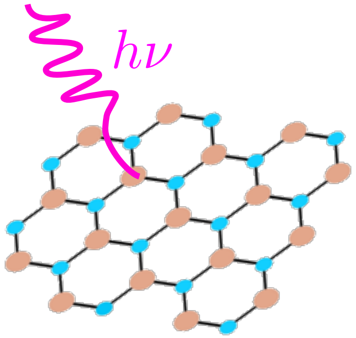
Phys. Rev. B 95, 125403 (2017)

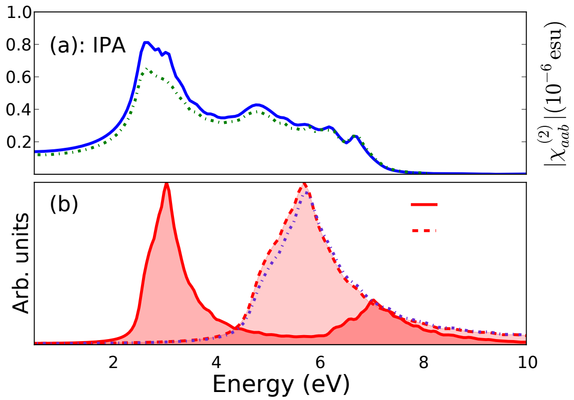
2-photon absorption in hBN bulk and ML



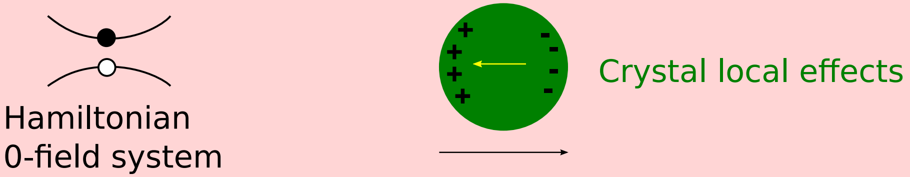
Phys. Rev. B 98, 1651126 (2018)

example: SHG in h-BN monolayer

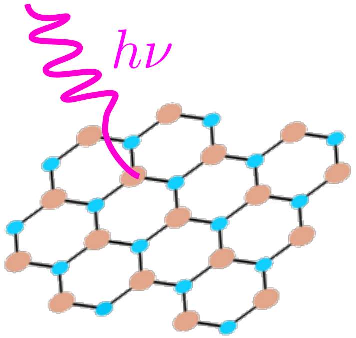


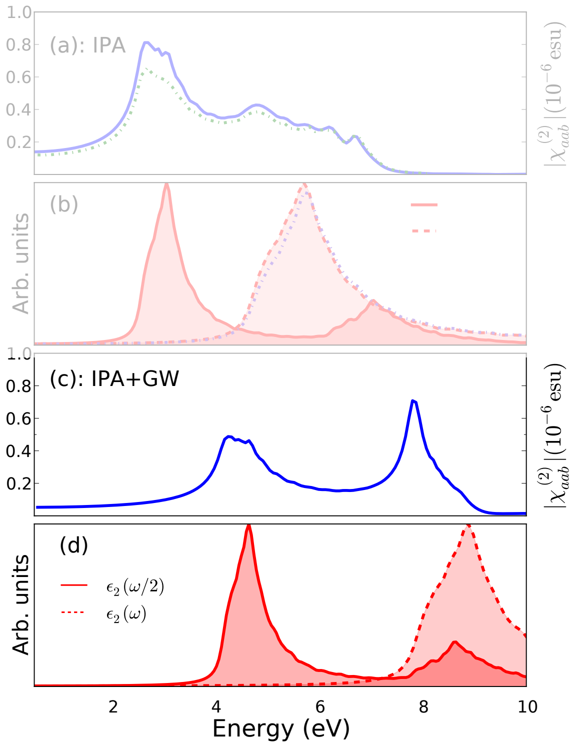


$$\hat{H}^0 + \hat{\Delta}^{\text{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\text{CoSeX}}[\Delta\gamma]$$

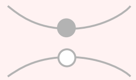


example: SHG in h-BN monolayer

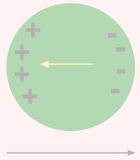




$$\hat{H}^0 + \hat{\Delta}^{\mathrm{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\mathrm{CoSeX}}[\Delta\gamma]$$

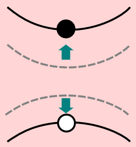


Hamiltonian
0-field system



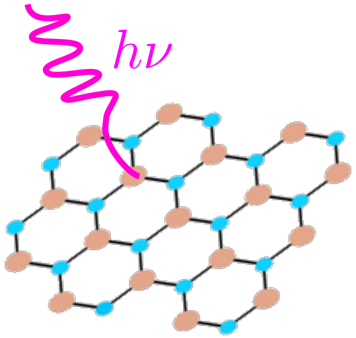
Crystal local effects

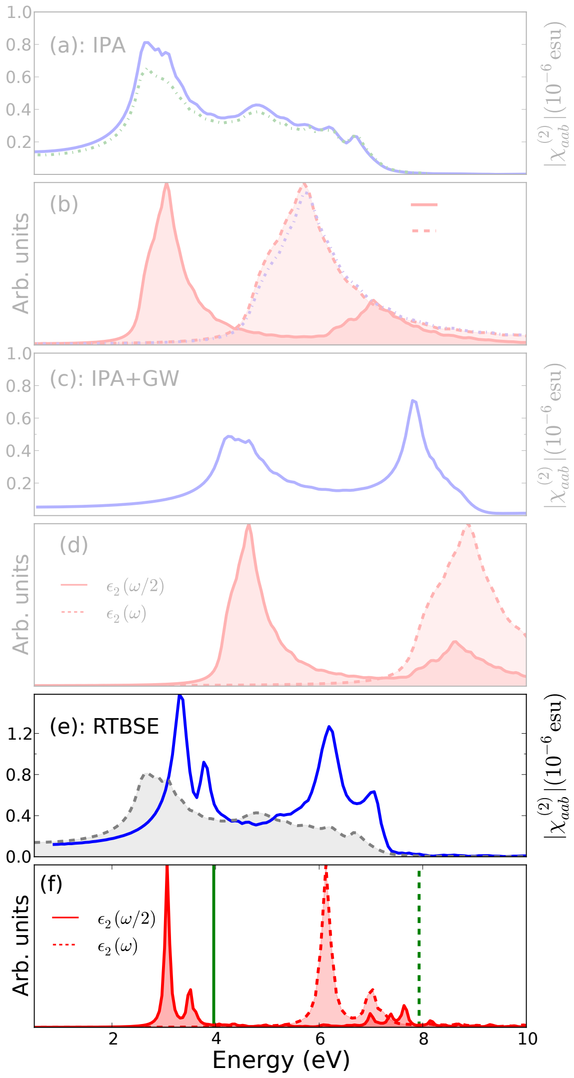
$$\hat{H}^0 + \hat{\Delta}^{\mathrm{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\mathrm{CoSeX}}[\Delta\gamma]$$



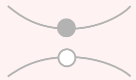
QP renormalization effects (@GW)
on the unperturbed system

example: SHG in h-BN monolayer

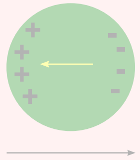




$$\hat{H}^0 + \hat{\Delta}^{\mathrm{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\mathrm{CoSeX}}[\Delta\gamma]$$

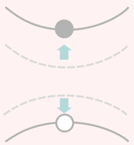


Hamiltonian
0-field system



Crystal local effects

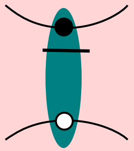
$$\hat{H}^0 + \hat{\Delta}^{\mathrm{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\mathrm{CoSeX}}[\Delta\gamma]$$



QP renormalization effects (@GW)
on the unperturbed system

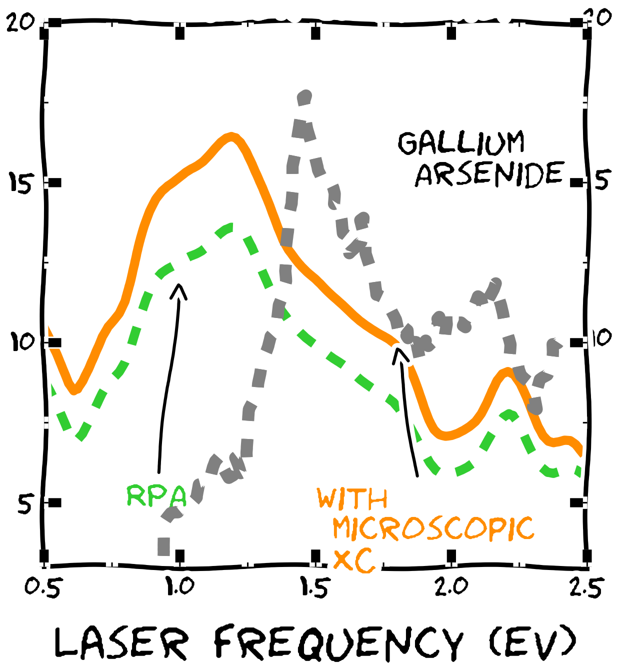
$$\hat{H}^0 + \hat{\Delta}^{\mathrm{QP}} + \hat{V}_H(\Delta\rho) + \hat{\Sigma}^{\mathrm{CoSeX}}[\Delta\gamma]$$

TD renormalization effects
on QP energies/optical excitations



C. Attaccalite, M. G. Phys. Rev. B 88, 235113 (2013) M. G and C. Attaccalite, Phys. Rev. B 89(R), 081102 (2014)

example: SHG in bulk semiconductors

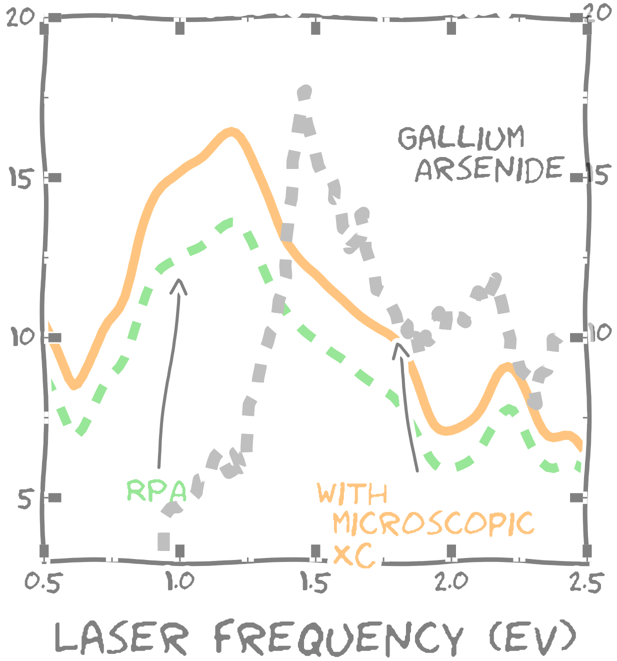


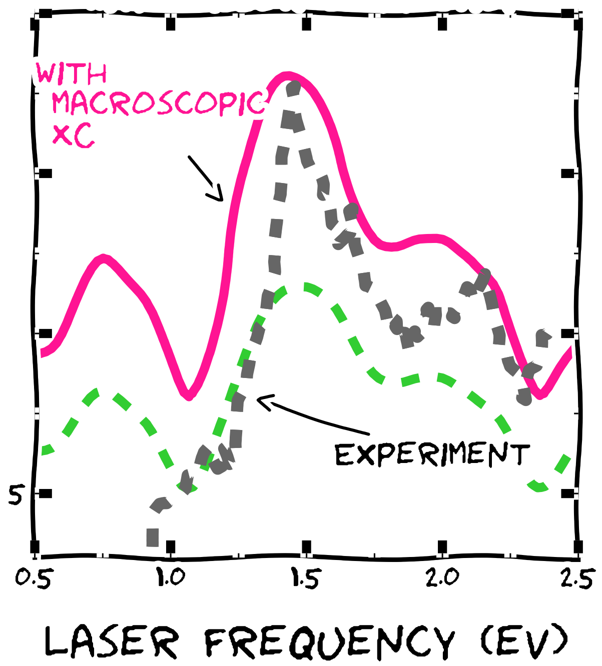
$$H^0 + \Delta V^H[\rho] + \Delta V^{xc}[\rho]$$

MG, D. Sangalli, C. Attaccalite PRB 94, 035149 (2016))

DRIVING THE EXASCALE TRANSITION

example: SHG in bulk semiconductors





$$H^0 + \Delta V^H[\rho] + \Delta V^{xc}[\rho]$$

$$H^0 + \Delta^{\text{scissor}} + \Delta V^H[\rho] + \alpha^{xc} P$$

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THANKS

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