Nonlinear response of solids within the GW plus Bethe-Salpeter approximation

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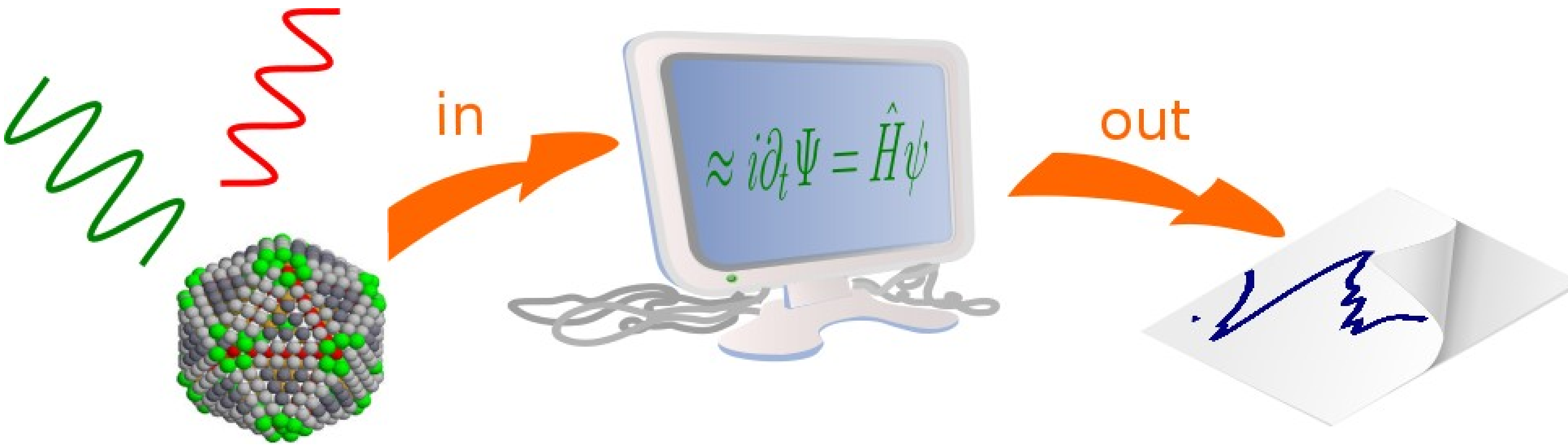

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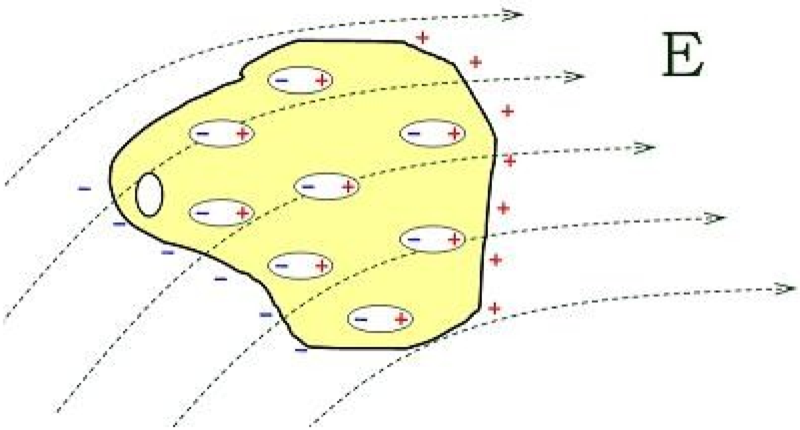
What is non-linear optics?



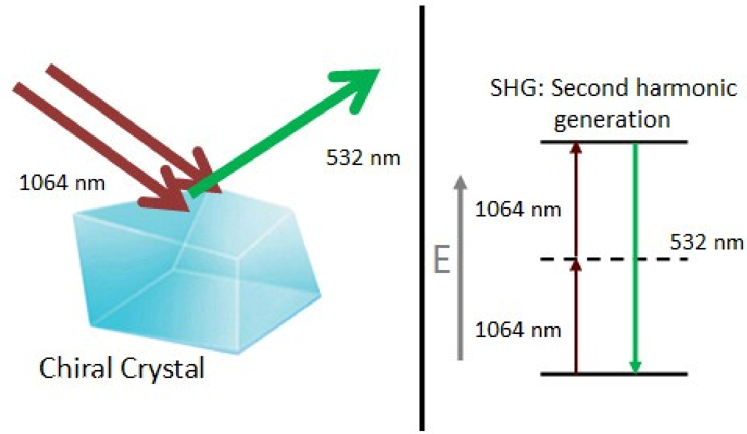


Figure 1. Two photons of IR (1064 nm) interact with a chiral crystal to generate SHG (532 nm).

$$P(r,t)=P_0+\chi^{(1)}E+\chi^{(2)}E^2+O(E^3)$$

First experiments on linear-optics by P. Franken 1961

Nicolaas Bloembergen — Arthur Leonard Schawlow — Kai M. Siegbahn

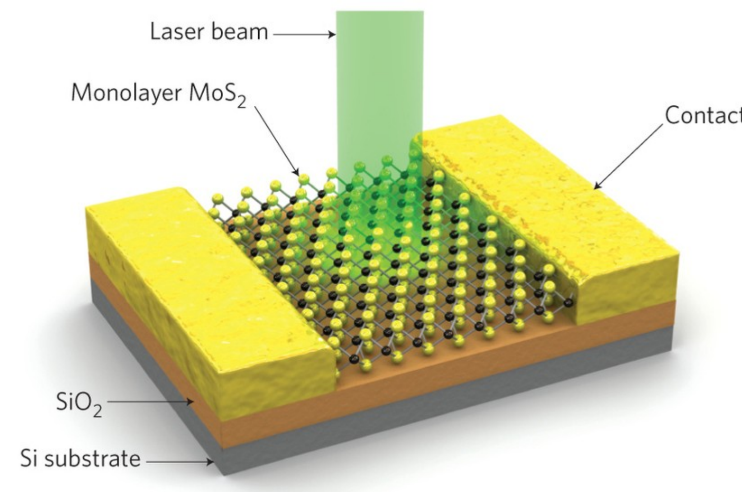
Ref: Nonlinear Optics and Spectroscopy
The Nobel Prize in Physics 1981
Nicolaas Bloembergen

Why non-linear optics?

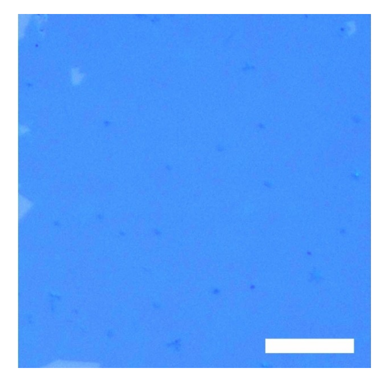
..applications..

Ref: supermaket

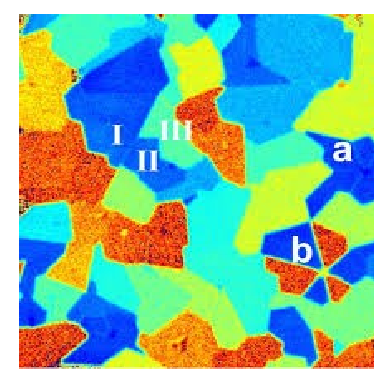
..research..



linear



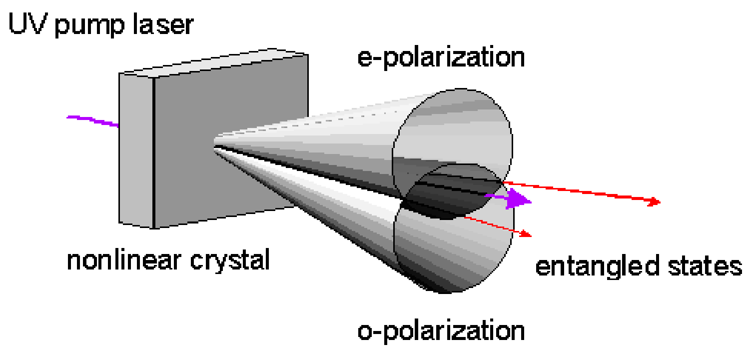
non-linear

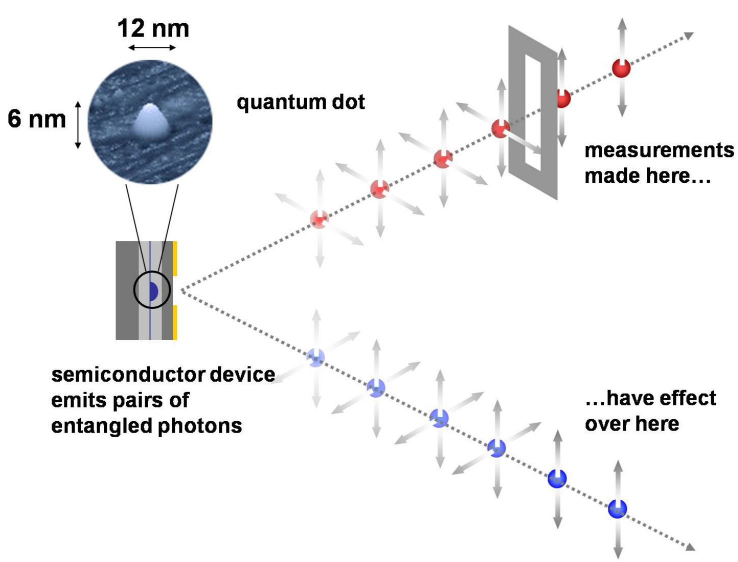


Ref: X. Yin et al. Science, 344, 488(2014)

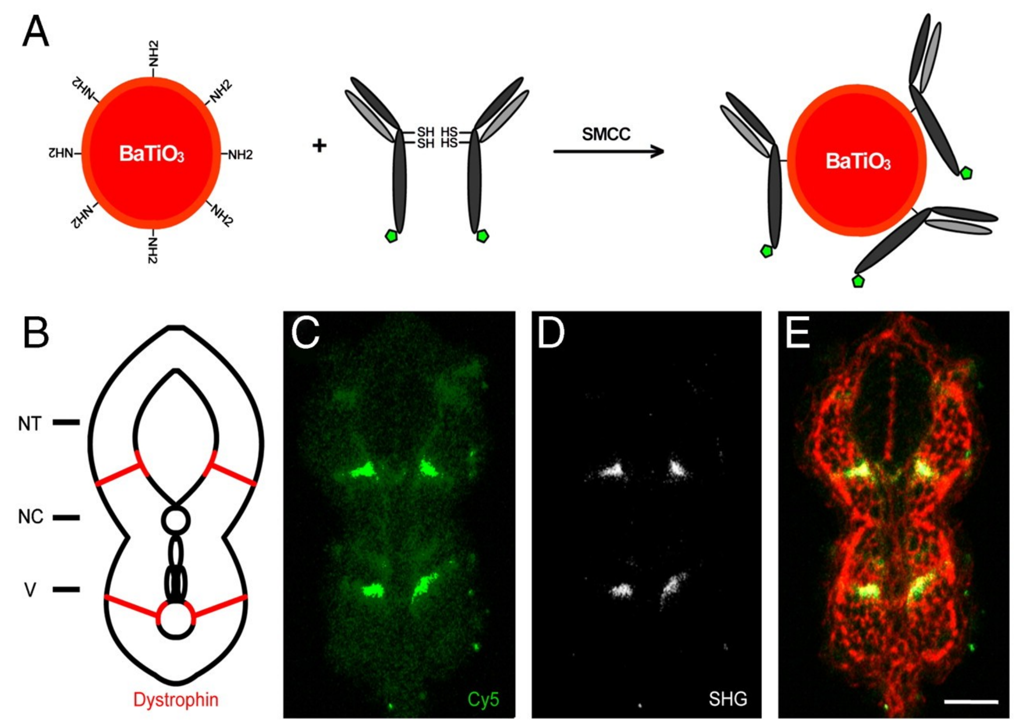
...and more...

photon entanglement





in vivo imaging



Ref: P Pantazis et al.
PNAS 107, 14535 (2007)

How to calculate non-linear response?

1) Direct evaluation of $\chi^{(1)}, \chi^{(2)}....$

$$\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$$

2) Sternheimer equation

R. M. Sternheimer, Phys. Rev. 96, 951(1954)

$$\left(H_{KS}^0 - \epsilon_n^0\right) \psi_n^1 = \left(H_{KS}^1 - \epsilon_n^1\right) \psi_n^0$$

3) Real-time propagation

$$-i \partial_t \psi = H_{ks} \psi$$

$$P(t) = P_0 + \chi^{(1)} E + \chi^{(2)} E^2 + O(E^3)$$

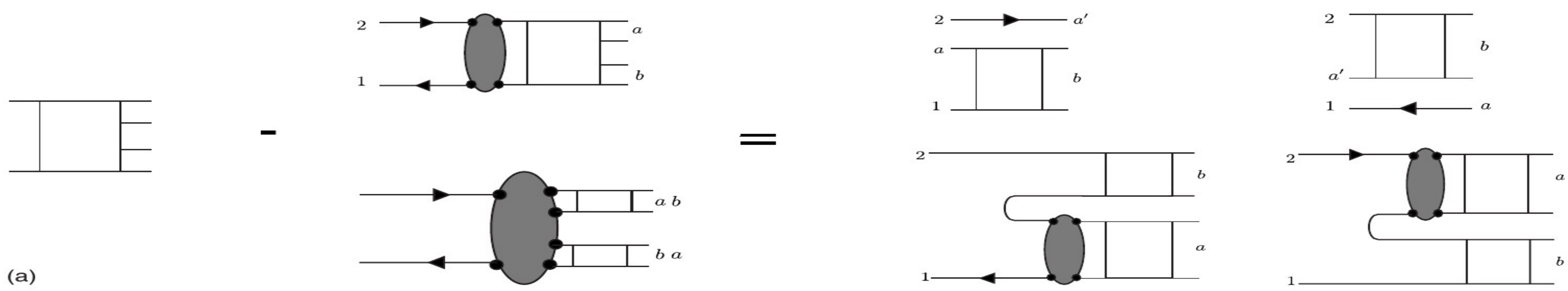
Direct evaluation of $X^{(1)}, X^{(2)} \ldots$.

Sternheimer equation

<u>Disadvantages:</u>

No flexibility: one eq. for each response function, difficult to include more fields

Complexity: equations become more and more complex with the response order



Ref: KS. Virk et al. PRB 80, 165318(2009),
H. Hubener, PRA 83, 062122(2011),
X. Andreade et al.JCP 126, 184106(2007)

Real-time propagation

Advantages

No complexity: The same equation for all response functions

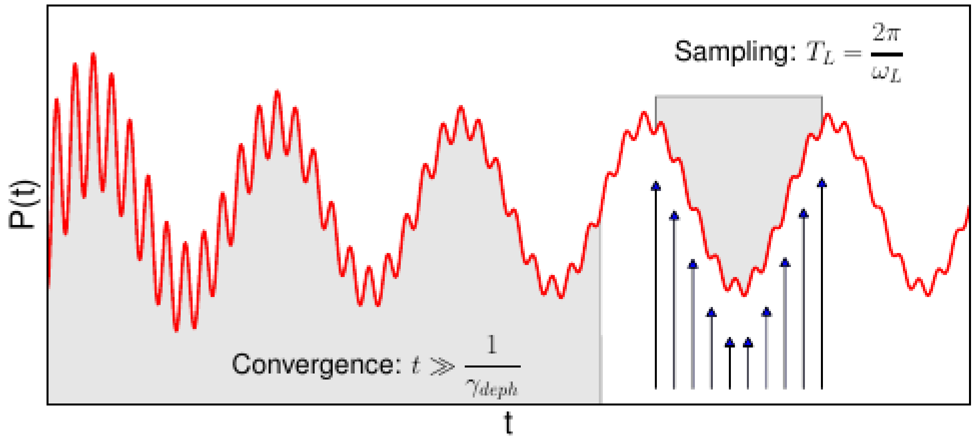
Flexibility: Can deal with complex spectroscopic tecniques (SFG, FWM, etc...)

Disadvantages

Results are more difficult to analize

Ref:
Y. Takimoto et al.
JCP, 127,154114(2007)

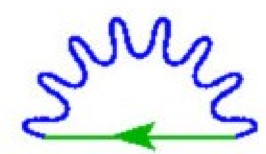
C. Attaccalite et al.
PRB, 89,081102(2014)

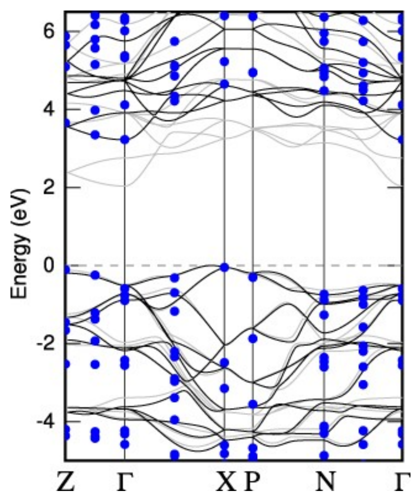


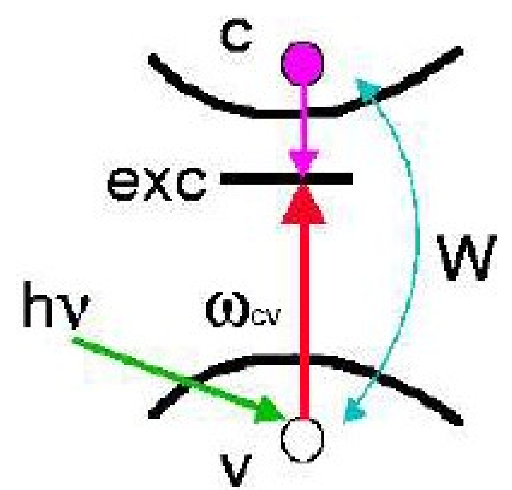
Correlation

Correlation effects are derived from non-equilibrium Green's theory within the GW approximation (see X. Blase talk)

$$\Sigma = i\,G\,W$$







Ref: C. Attaccalite et al. PRB 84, 245110(2011),
L. P. Kadanoff & G. A. Baym,
Quantum statistical mechanics, Benjamin(1962).
G. Strinati, La Rivista del Nuovo Cimento, 11,1-86 (1998)

Coupling with the external field

$$\langle u_{n\boldsymbol{k}}|\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle =$$

Dipole is ill-defined in periodic systems

We can use Modern Theory of Polarization. But the Polarization becomes a many-body operator

$$P=\frac{e}{2\pi}\Im\log\langle\psi|e^{\frac{2\pi}{L}\sum\hat{x}_i}|\psi\rangle$$

R. Resta PRL 80, 1800 (1998)

But correlation from GW+BSE can be mapped in an effective one-body Hamiltonian and so we can use

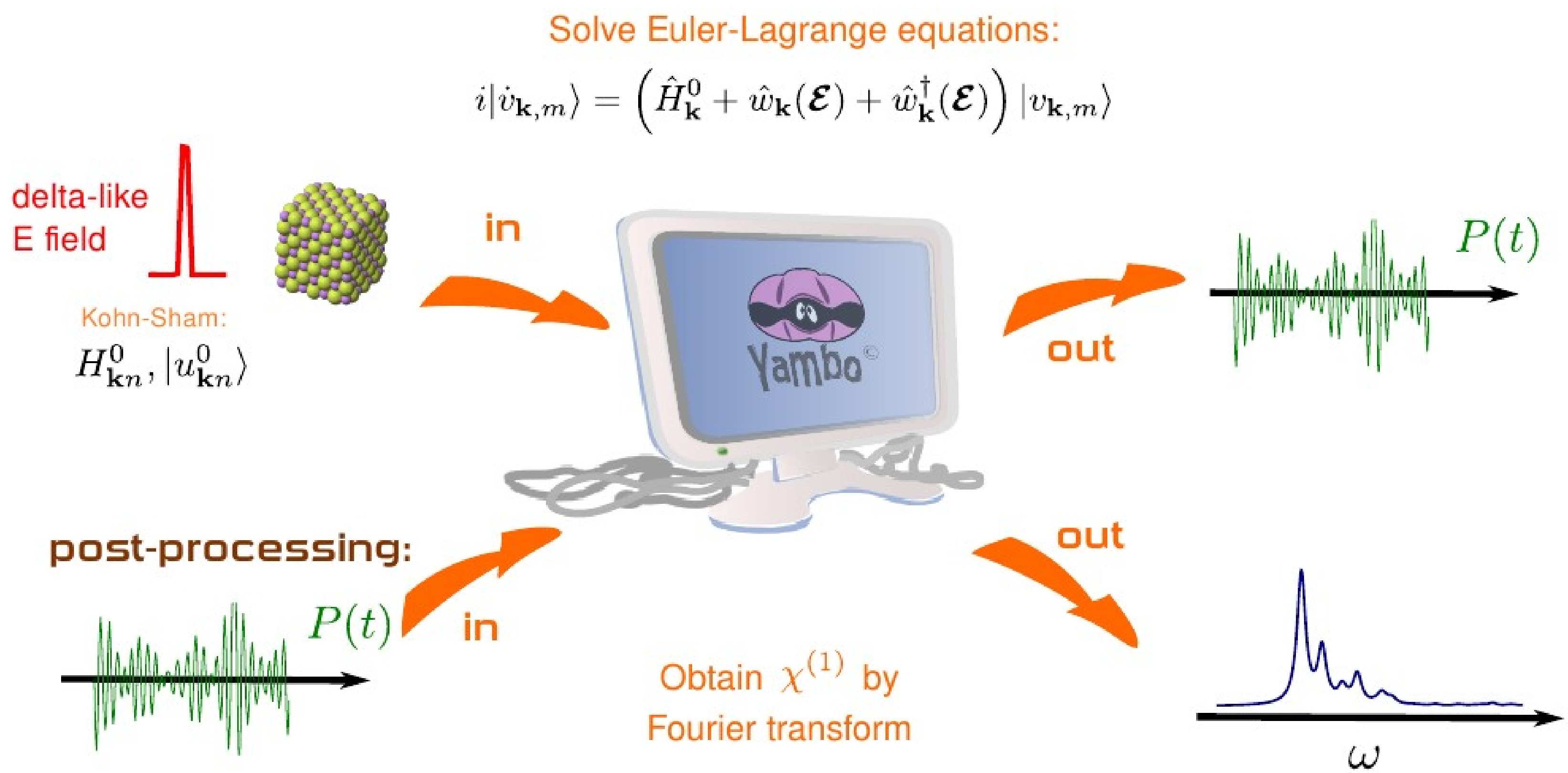
$$P_\alpha=\frac{2ie}{(2\pi)^3}\int_{BZ}d\boldsymbol{k}\sum_{n=1}^{n_b}\langle u_{n\boldsymbol{k}}|\frac{\partial}{\partial\boldsymbol{k}_\alpha}|u_{n\boldsymbol{k}}\rangle$$

King-Smith and Vanderbilt formula
PRB 47, 1651 (1993)

Our computational setup

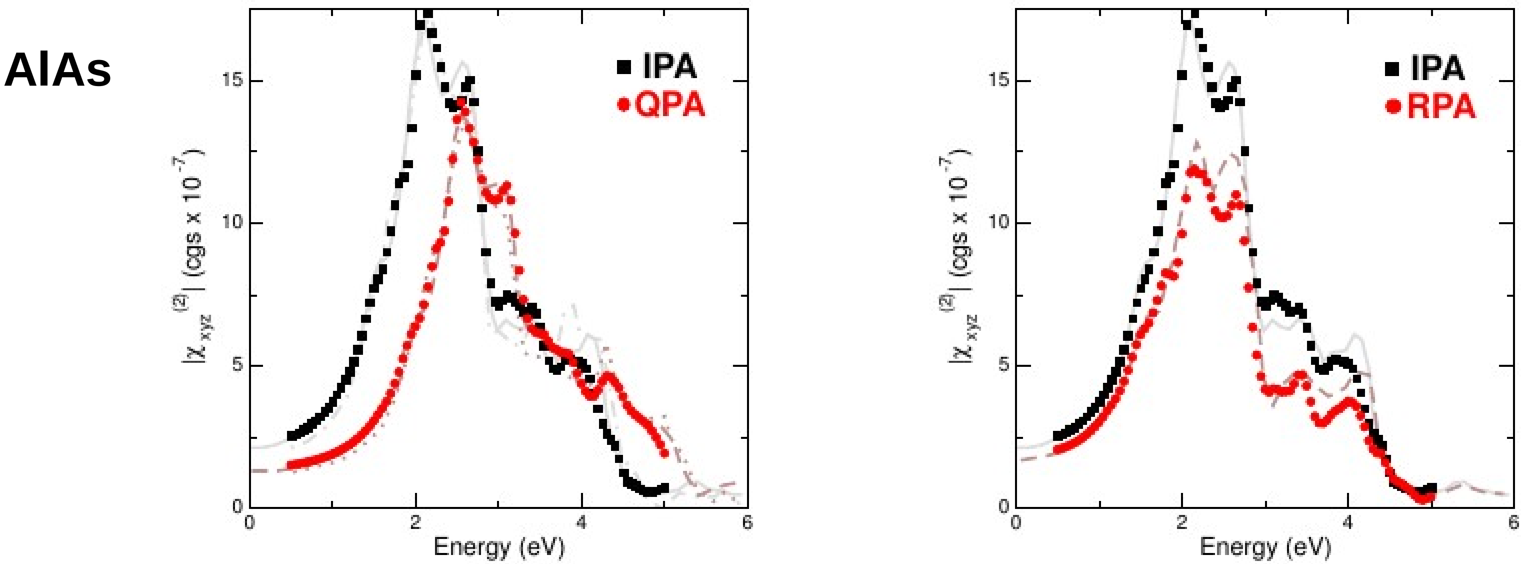
Correlation:
Green's function theory (GW+BSE)

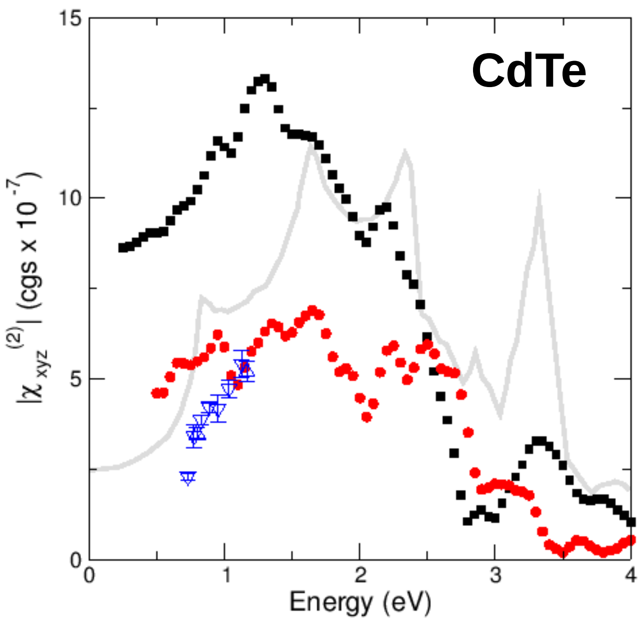
Coupling:
Modern-Theory of Polarization



Ref: C. Attaccalite et al.PRB 88, 235113(2013)

$\chi^{(2)}$ results: semiconductors

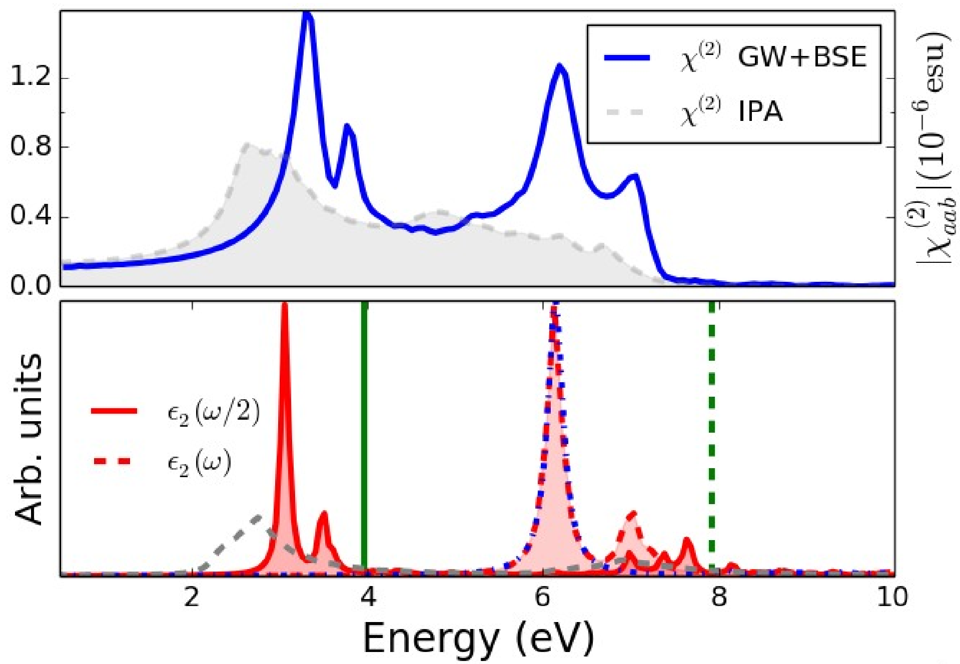


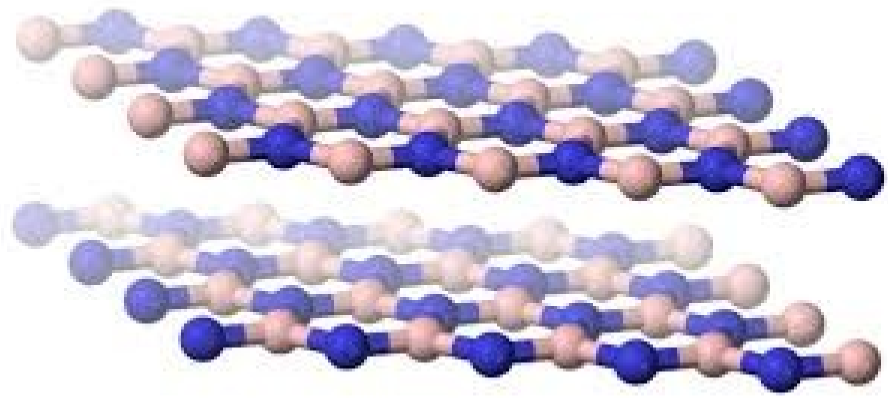


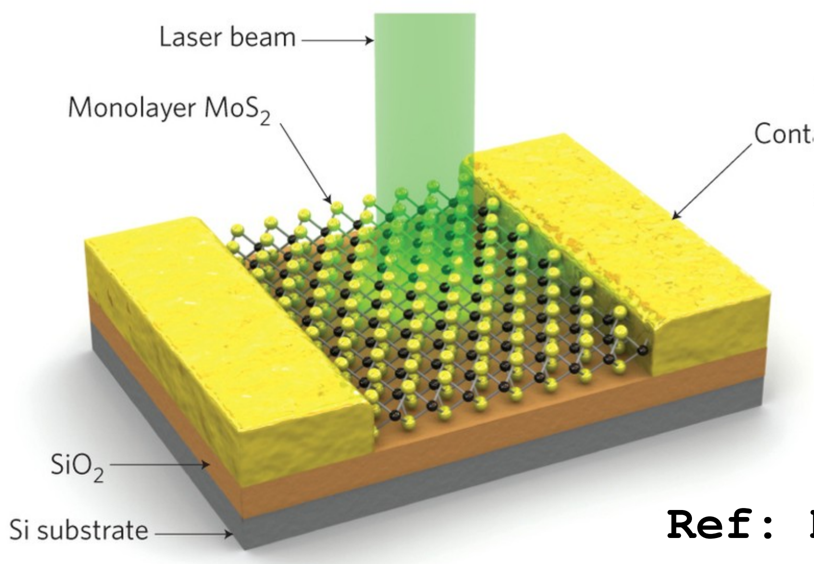
Local field effects are more important than in the linear reposonse

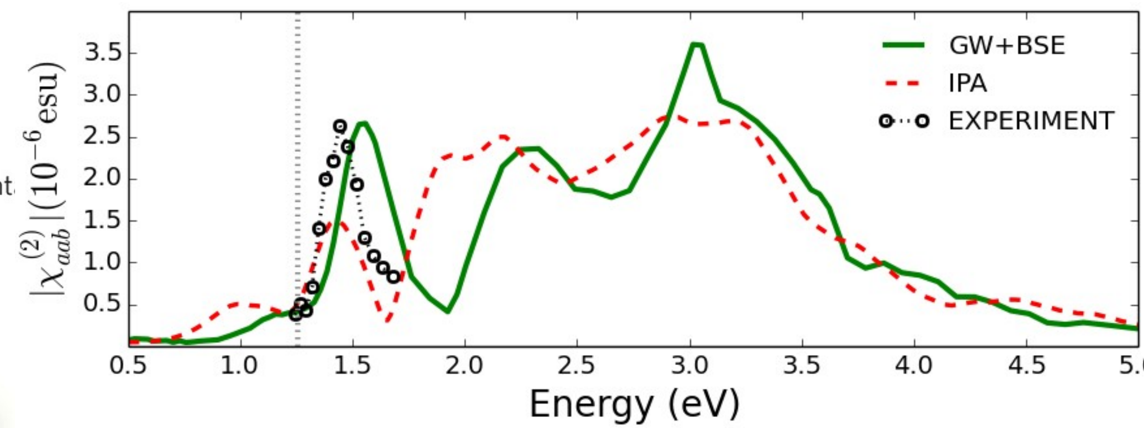
Ref:
E. Luppi el al.,PRB 82, 235201 (2010)
E. Ghahramani et al., PRB 43, 9700 (1991)
I. Shoji,et al. J.Opt.Soc.Am. B 14, 2268 (1997)
J.I.Jang,et al. J.Opt.Soc. Am.B 30, 2292 (2013)
M. Grüning at al. PRB 88, 235113(2013)

$\chi^{(2)}$ results: monolayers





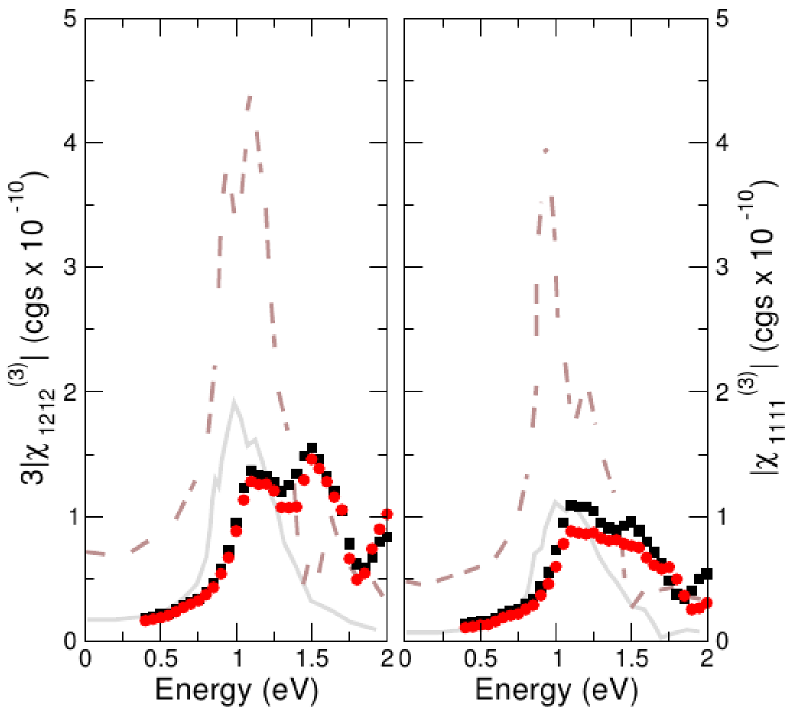


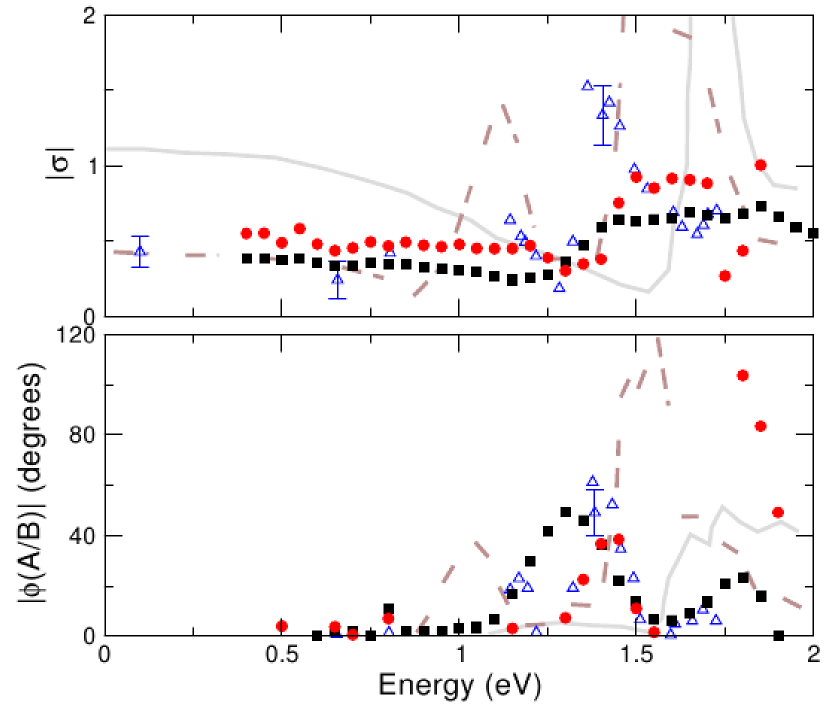


Ref: M. Grüning et al PRB 89,081102(2014)
L.M. Malard et al. PRB 87, 201401(2014)

$\chi^{(3)}$ in silicon

$$P_i(3\omega) = 3\chi^{(3)}_{1212}\boldsymbol{\mathcal{E}}_i(\omega)|\boldsymbol{\mathcal{E}}(\omega)|^2 + (\chi^{(3)}_{1111} - 3\chi^{(3)}_{1212})\boldsymbol{\mathcal{E}}_i^3(\omega)$$





$A = \chi^{(3)}_{1111}$ $\quad |\sigma| = |(B-A)/A|$

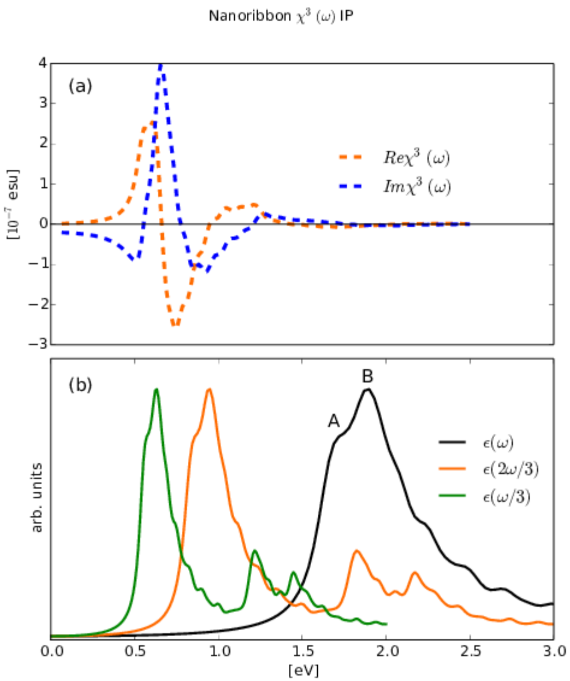
$B = 3\chi^{(3)}_{1212}$ $\quad B/A$

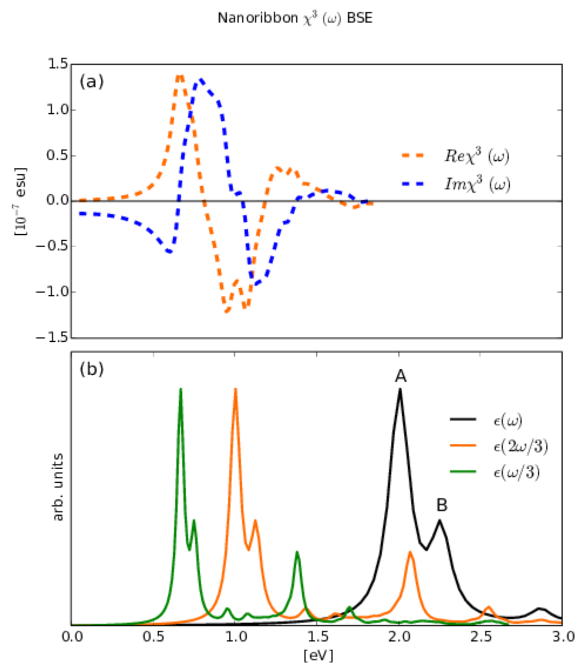
Ref:
D. J. Moss et al.
PRB 41, 1542 (1990)

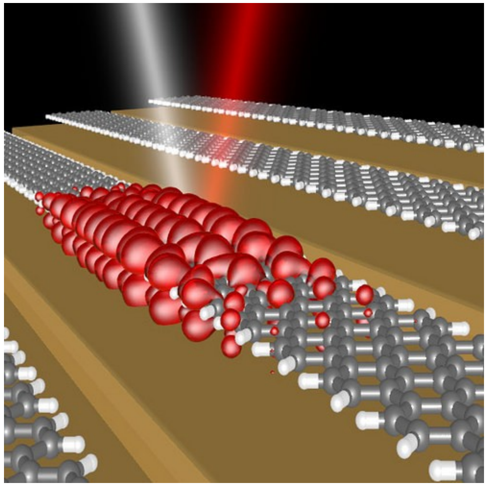
D.J. Moss et al.
Optical letters, 14,57 (1989)

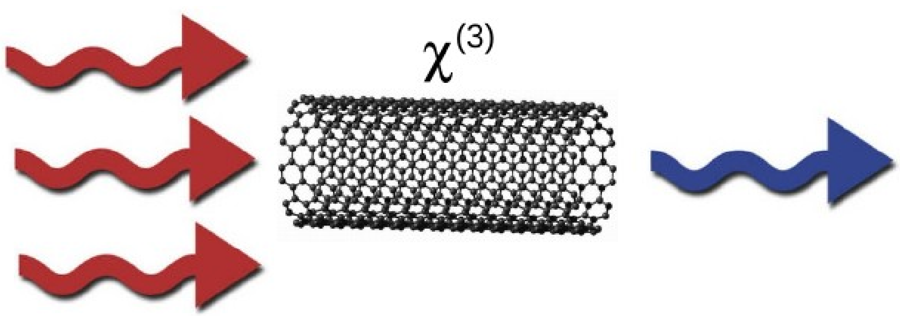
$\chi^{(3)}$ in nanostructures

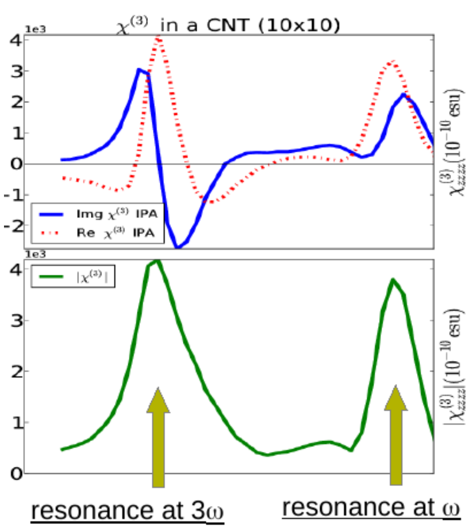
Interference between excitons
is not trivial the case of ANGR7





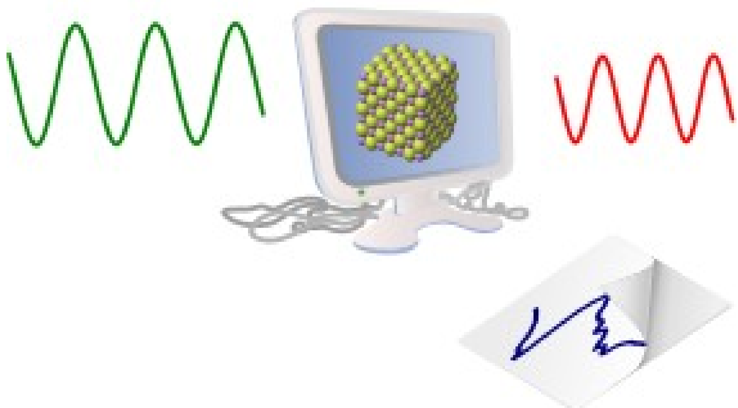






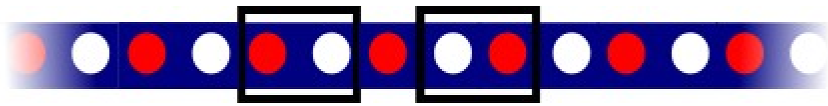
Ref: R. Denk, Nature Comm. 5, 4253 (2014)
A. Maeda, PRL 94, 047404 (2005)

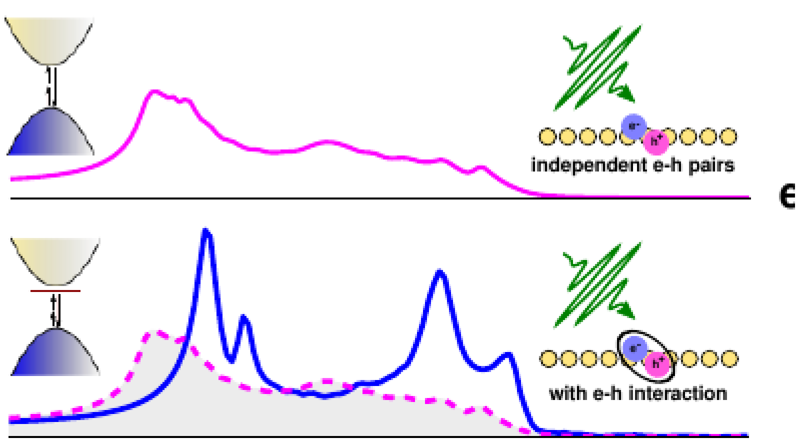
Conclusions



Develop an approach that 'ímports' successful GW+BSE recipe into versatile real-time approach:
correlation in nonlinear-optics

e-laser interaction treated within **modern polarization theory**





e-h interaction key to understand
SHG spectra of 2D materials (such as hBN, MoS2)

Acknowledgement:

Myrta Grüning,
Queen's University Belfast

Related work:

Implementation of dynamical Berry phase:
C. Attaccalite, M. Grüning, PRB 88, 235113 (2013)

Application to SHG of 2D materials:
M. Grüning. C. Attaccalite, PRB 89, 081102 (2014)
C. Attaccalite et al., PCPC 17, 9533 (2015)

Time-dependent BSE theory:
C. Attaccalite ,M. Grüning. A. Marini PRB 84, 245110 (2011)

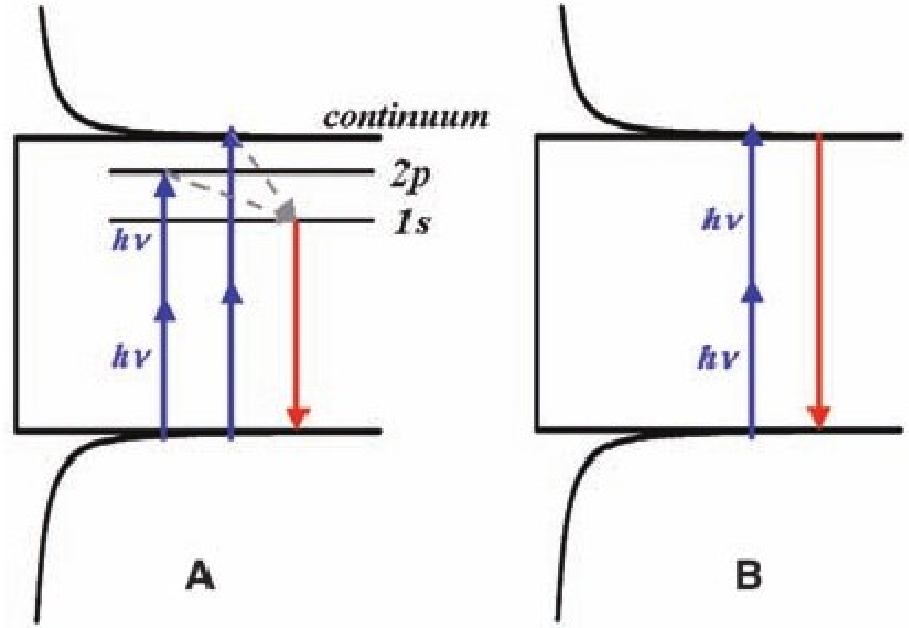
The codes:
A. Marini et al. Comp. Phys. Comm. 180, 1392 (2009)
P. Giannozzi et al. J. of Phys.: Cond. Matter, 21, 395502 (2009)

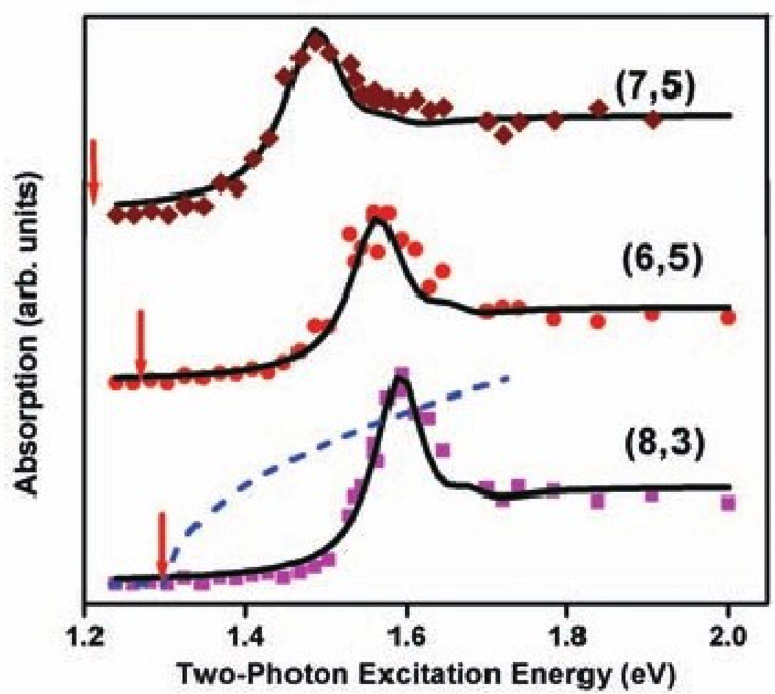
To see "invisible" excitations

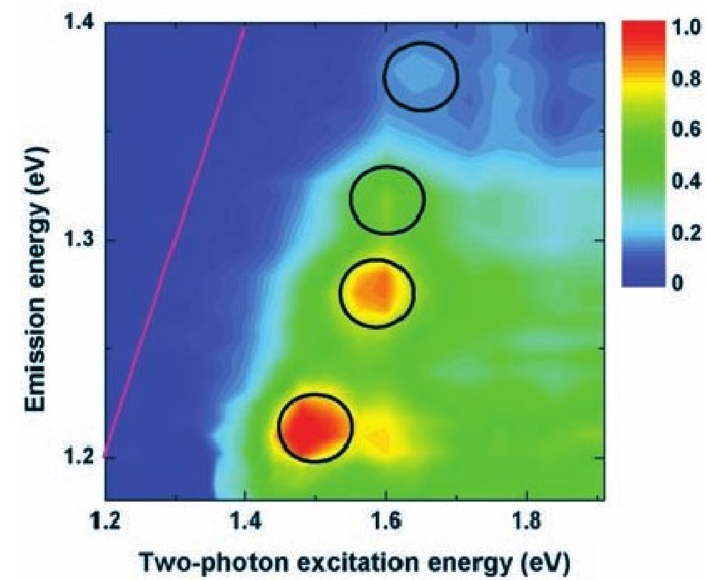
The Optical Resonances in Carbon Nanotubes Arise from Excitons

Feng Wang, et al.

Science **308**, 838 (2005);







Wrong ideas on velocity gauge

In recent years different wrong papers using velocity gauge have been published (that I will not cite here) on:

1) real-time TD-DFT
2) Kadanoff-Baym equations + GW self-energy
3) Kadanoff-Baym equations + DMFT self-energy

Length gauge:

$$\boldsymbol{H} = \frac{\boldsymbol{p}^2}{2m} + \boldsymbol{r}E + V(\boldsymbol{r}) \quad \longleftrightarrow \quad \Psi(\boldsymbol{r}, t)$$

Velocity gauge:

$$\boldsymbol{H} = \frac{1}{2m}(\boldsymbol{p} - eA)^2 + V(\boldsymbol{r}) \quad \longleftrightarrow \quad e^{-\boldsymbol{r}\cdot A(t)}\Psi(\boldsymbol{r}, t)$$

Analitic demostration:
K. Rzazewski and R. W. Boyd,
J. of Mod. optics **51**, 1137 (2004)
W. E. Lamb, et al.
Phys. Rev. A **36**, 2763 (1987)

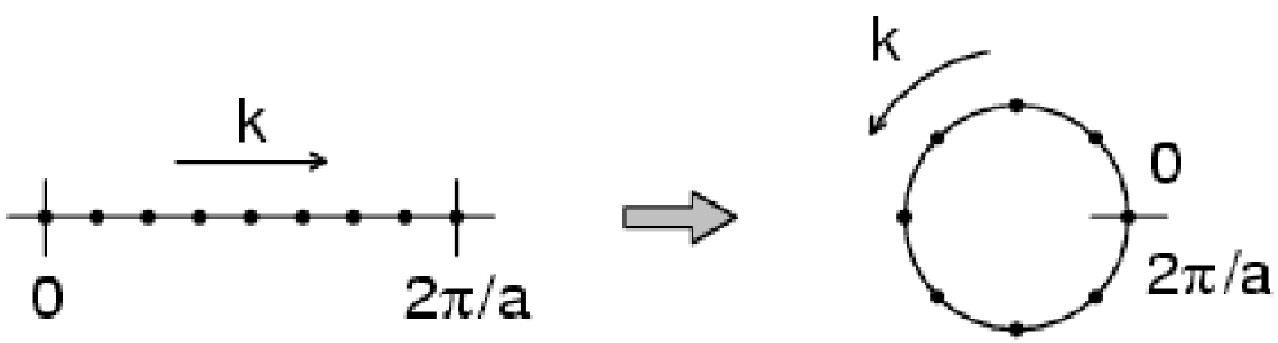
Well done velocity gauge:
M. Springborg, and B. Kirtman
Phys. Rev. B **77**, 045102 (2008)
V. N. Genkin and P. M. Mednis
Sov. Phys. JETP **27**, 609 (1968)

The King-Smith Vanderbilt polarization

$$P_\alpha = \frac{2ie}{(2\pi)^3} \int_{BZ} d\boldsymbol{k} \sum_{n=1}^{n_b} \langle u_{n\boldsymbol{k}} | \frac{\partial}{\partial \boldsymbol{k}_\alpha} | u_{n\boldsymbol{k}} \rangle$$

King-Smith and Vanderbilt formula
Phys. Rev. B **47**, 1651 (1993)

Berry's connection !!



1) it is a bulk quantity
2) time derivative gives the current
3) reproduces the polarizabilities at all orders
4) is not an Hermitian operator

From Polarization to the Equations of Motion

$$L = \frac{i\hbar}{N} \sum_{n=1}^{M} \sum_{\boldsymbol{k}} \langle v_{\boldsymbol{k}n} | \dot{v}_{\boldsymbol{k}n} \rangle - \langle H^0 \rangle - v\, E \cdot P$$

$$\boxed{i\hbar \frac{\partial}{\partial t} | v_{\boldsymbol{k}n} \rangle = \boldsymbol{H}_{\boldsymbol{k}}^{0} | v_{\boldsymbol{k}n} \rangle + i\, e\, E \cdot | \partial_{\boldsymbol{k}} v_{\boldsymbol{k}n} \rangle}$$

$\partial_{\boldsymbol{k}}$ It is an object difficult to calculate numerically due to the gauge freedom of the Bloch functions

$$| v_{\boldsymbol{k}m} \rangle \rightarrow \sum_{n}^{occ} U_{\boldsymbol{k},nm} | v_{\boldsymbol{k}n} \rangle$$

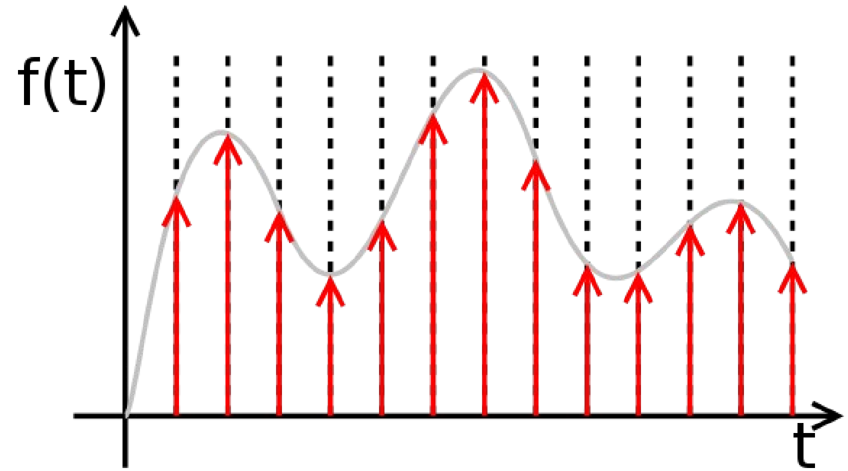
I. Souza, J. Iniguez and D. Vanderbilt, Phys. Rev. B **69**, 085106 (2004)

Post-processing real-time data

P(t) is a periodic function of period $T_L=2p/w_L$

$$\mathbf{P}(t) = \sum_{n=-\infty}^{+\infty} \mathbf{p}_n e^{-i\omega_n t}.$$

$$\omega_n = n\omega_L$$



$$\mathbf{p}_n = \mathscr{F}\{\mathbf{P}(\omega_n)\} = \int_0^{T_L} dt\mathbf{P}(t)e^{i\omega_n t}$$

$\mathbf{p}_n$ is proportional to χ^n by the n-th order of the external field

$$\mathcal{F}_{in} \equiv \exp(-i\omega_n t_i)$$

$$\mathcal{F}_{in}p_n^\alpha = P_i^\alpha$$

Performing a discrete-time signal sampling we reduce the problem to the solution of a systems of linear equations

Ref: C. Attaccalite et al. PRB 88, 235113(2013)
F. Ding et al. JCP 138, 064104(2013)

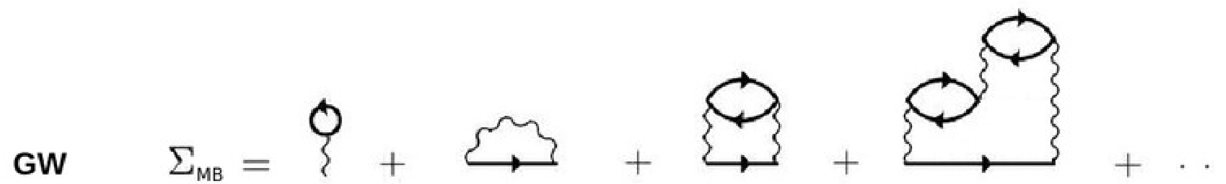
Let's add some correlation in 4 steps

1) We start from the Kohn-Sham Hamiltonian:

$$h_k$$ universal, parameter free approach

2) Single-particle levels are renormalized within the G_0W_0 approx.

$$h_k + \Delta h_k$$



3) Local-field effects are included in the response function

$$h_k + \Delta h_k + V_H[\Delta\rho]$$ Time-Dependent Hartree

4) Excitonic effects included by means of the Screened-Exchange

$$h_k + \Delta h_k + V_H[\Delta\rho] + \Sigma_{sex}[\Delta\gamma]$$