Linear-Response TDDFT in Frequency-Reciprocal space on a Plane-Waves basis: the DP (Dielectric Properties) code

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September 1, 2004

Why and Where the Frequency-Reciprocal space could be convenient

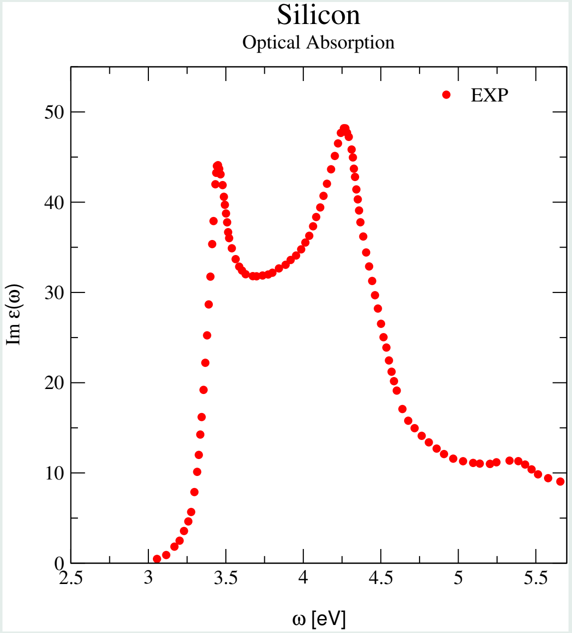
- Reciprocal Space $\Rightarrow$ Infinite Periodic Systems (Bulk, but also Surfaces, Wires, Tubes with the use of Supercells)

- Frequency Space $\Rightarrow$ Spectra

Outlook

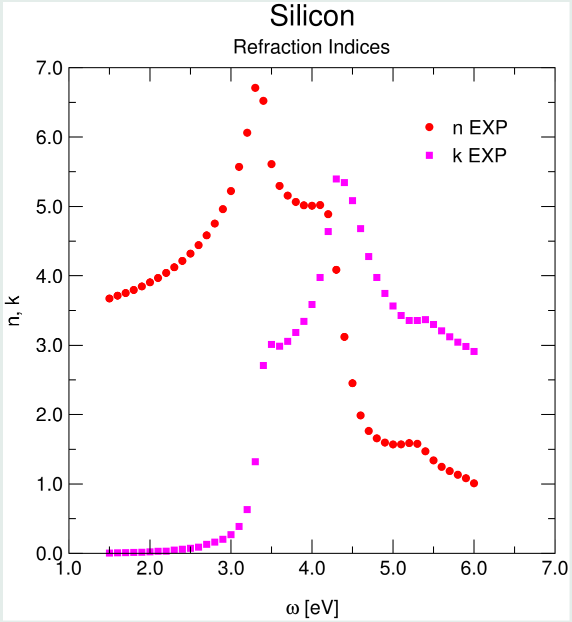
- Motivation
- TDDFT
- Linear Response TDDFT
- Frequency-Reciprocal space TDDFT
- TDDFT on a PW basis: the DP code
- Approximations and Results

Optical Absorption



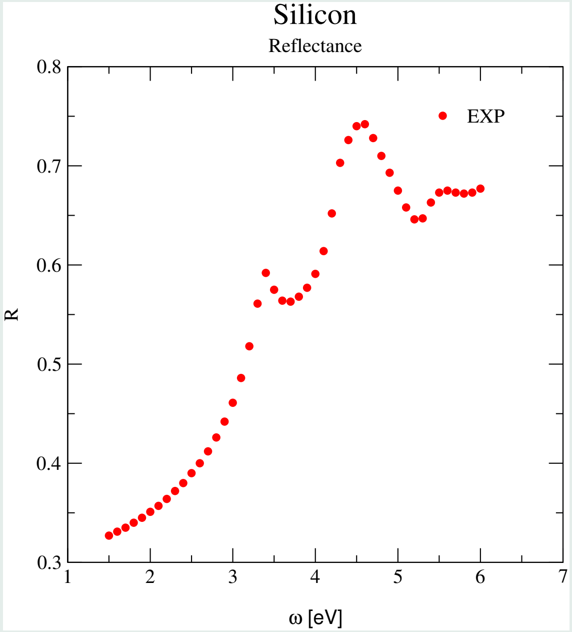
Lautenschlager et al., PRB **36**, 4821 (1987).

Refraction Indices



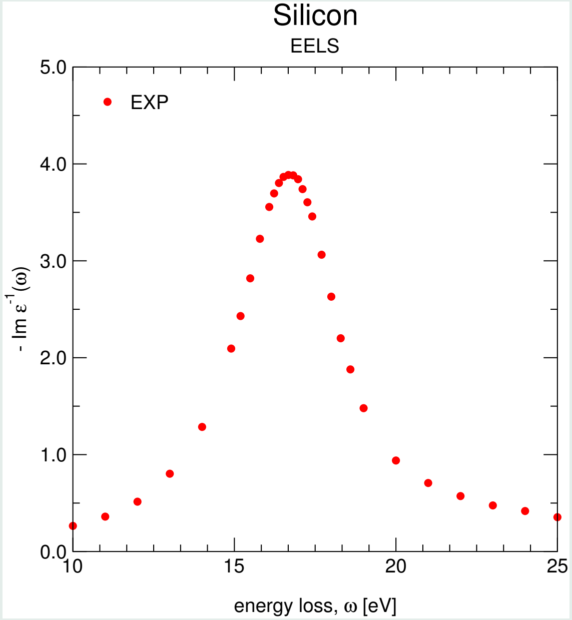
Aspnes and Studna, PRB **27**, 985 (1983).

Reflectance



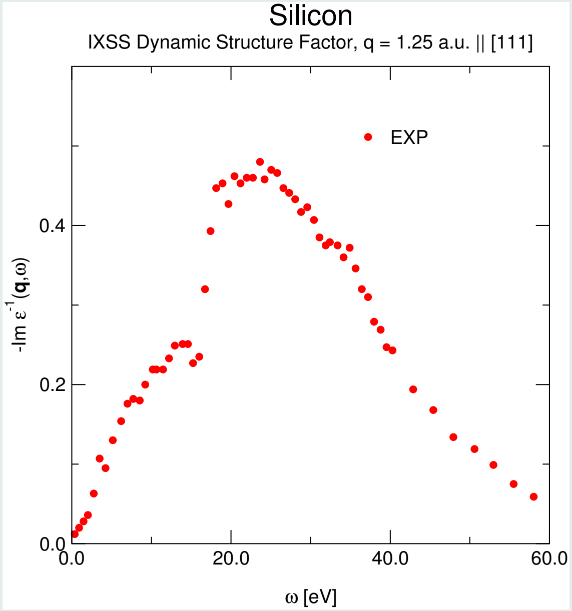
Aspnes and Studna, PRB **27**, 985 (1983).

Energy-Loss (EELS)



Stiebling, Z. Phys. B **31**, 355 (1978).

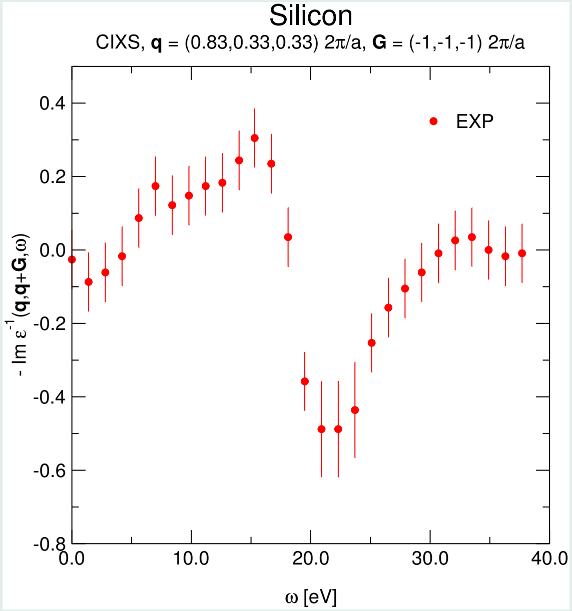
Inelastic X-ray Scattering Spectroscopy (IXXS)



Sturm et al., PRL **48**, 1425 (1982).

Coherent Inelastic Scattering Spectroscopy (CIXS)

Schülke and Kaprolat, PRL **67**, 879 (1991).



Problems for the Theory

- Reproduce Experimental Spectra
- Offer Reference Spectra to the Experiment
- Predict Optical and Dielectric Properties $\Rightarrow$ Theoretical Spectroscopy Facility

Accessed Observable: the Macroscopic Dielectric Function $\varepsilon_{\mathrm{M}}(\mathbf{q}, \omega)$

$\varepsilon_\infty = \varepsilon_{\mathrm{M}}(\mathbf{q} = 0, \omega = 0)$ dielectric constant

$\mathrm{ABS} = \mathrm{Im}\, \varepsilon_{\mathrm{M}}(\mathbf{q} = 0, \omega)$ optical absorption

$\mathrm{EEL} = -\mathrm{Im}\, \dfrac{1}{\varepsilon_{\mathrm{M}}(\mathbf{q}, \omega)}$ energy loss

What is the TDDFT?

- TDDFT is an extension of DFT; it is a DFT with time-dependent external potential:

$$v(r) \rightarrow v(r,t)$$

- Milestones of TDDFT:
  - Runge, Gross (1984): rigorous basis of TDDFT.
  - Gross, Kohn (1985): TDDFT in Linear Response.

DFT vs TDDFT

Hohenberg-Kohn:

$v(r) \Leftrightarrow \rho(r)$

The Total Energy:

$\langle \Phi | \hat{H} | \Phi \rangle = E[\rho]$

Runge-Gross:

$v(r,t) \Leftrightarrow \rho(r,t)$

The Action:

$\int_{t_0}^{t_1} dt \, \langle \Phi(t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \Phi(t) \rangle = A[\rho]$

are unique functionals of the density.

The stationary points of:

the Total Energy

$\frac{\delta E[\rho]}{\delta \rho(r)} = 0$

the Action:

$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0$

give the exact density of the system:

$\rho(r)$

$\rho(r,t)$

DFT vs TDDFT

Kohn-Sham:

$$\begin{cases} \rho(r) = \sum_{i=1}^{N} \left|\phi_i^{\mathrm{KS}}(r)\right|^2 \\ v_{\mathrm{KS}}(r) = v(r) + \int dr' \, \frac{\rho(r')}{|r-r'|} + \frac{\delta Exc[\rho]}{\delta\rho(r)} \\ H_{\mathrm{KS}}(r)\phi_i^{\mathrm{KS}}(r) = \epsilon_i^{\mathrm{KS}}\phi_i^{\mathrm{KS}}(r) \end{cases}$$

Runge-Gross:

$$\begin{cases} \rho(r,t) = \sum_{i=1}^{N} \left|\phi_i^{\mathrm{KS}}(r,t)\right|^2 \\ v_{\mathrm{KS}}(r,t) = v(r,t) + \int dr' \, \frac{\rho(r',t)}{|r-r'|} + \frac{\delta Axc[\rho]}{\delta\rho(r,t)} \\ i\frac{\partial}{\partial t}\phi_i^{\mathrm{KS}}(r,t) = H_{\mathrm{KS}}(r,t)\phi_i^{\mathrm{KS}}(r,t) \end{cases}$$

TDDFT in Linear Response

Gross and Kohn (1985)

If:

$$v_{\text{ext}}(r,t) = v_{\text{ext}}(r) + \delta v_{\text{ext}}(r,t)$$

with:

$$\delta v_{\text{ext}}(r,t) \ll v_{\text{ext}}(r)$$

then:

$$\boxed{\text{TDDFT} = \text{DFT} + \text{Linear Response}}$$

(to the time-dependent perturbation δv_{ext})

Hohenberg-Kohn Theorem for Linear Response TDDFT

DFT: $v_{\text{ext}}(r) \Leftrightarrow \rho(r)$

TDDFT: $v_{\text{ext}}(r,t) \Leftrightarrow \rho(r,t)$ Runge-Gross theorem

LR-TDDFT: $v_{\text{ext}}(r) + \delta v_{\text{ext}}(r,t) \Leftrightarrow \rho(r) + \delta\rho(r,t)$

$$\Downarrow$$

$$\delta v_{\text{ext}}(r,t) \Leftrightarrow \delta\rho(r,t)$$

Linear Response TDDFT calculation scheme

1. Ordinary DFT calculation:

$$v_{\rm ext}(r) \Rightarrow \rho(r), \epsilon^{\rm KS}, \phi^{\rm KS}(r)$$

2. Linear Response calculation:

$$\delta v_{\rm ext}(r,t) \Rightarrow \delta\rho(r,t)$$

Polarizability χ

δv_{ext} external perturbation

$\delta\rho$ induced density

Definition of the *polarizability* χ:

$$\boxed{\delta\rho = \chi\delta v_{\text{ext}}}$$

Variation in the Total Potential

The variation in the density induces a variation in the Hartree and in the exchange-correlation potentials which screen the external perturbation:

$$\delta v_{\mathrm{H}} = \frac{\delta v_{\mathrm{H}}}{\delta \rho} \delta\rho = v_c \delta\rho$$

$$\delta v_{\mathrm{xc}} = \frac{\delta v_{\mathrm{xc}}}{\delta \rho} \delta\rho = f_{\mathrm{xc}} \delta\rho$$

so that the variation in the total potential (external + screening) is

$$\delta v_{\mathrm{tot}} = \delta v_{\mathrm{ext}} + \delta v_{\mathrm{H}} + \delta v_{\mathrm{xc}}$$

Exchange-Correlation Kernel f_{xc}

The *exchange-correlation kernel* is defined:

$$\boxed{f_{\mathrm{xc}} \stackrel{\mathrm{def}}{=} \frac{\delta v_{\mathrm{xc}}}{\delta \rho}}$$

LR-TDDFT Kohn-Sham scheme:

the Independent Particle Polarizability $\chi^{(0)}$

Let's introduce a ficticious s, Kohn-Sham non-interacting system such that:

$$\delta\rho_s = \delta\rho$$

Then, instead of calculating χ, we can more easily calculate the polarizability $\chi^{(0)}$ (also χ_s or χ^{KS}) of this non-interacting system, called *independent particle polarizability* and defined:

$$\boxed{\delta\rho = \chi^{(0)}\delta v_{\mathrm{tot}}}$$

Independent Particle Polarizability $\chi^{(0)}$

By variation δv_{tot} $(= \delta v_s = \delta v^{\mathrm{KS}})$ of the Kohn-Sham equations, one obtains the Linear Response variation of the density $\delta\rho$ and then an expression for $\chi^{(0)}$ in terms of the Kohn-Sham energies and wavefunctions:

$$\chi^{(0)}(r, r', \omega) = 2\sum_{i \neq j}(f_i - f_j)\frac{\phi_i(r)\phi_j^*(r)\phi_i^*(r')\phi_j(r')}{\epsilon_i - \epsilon_j - \omega - i\eta} \qquad \text{(Adler and Wiser)}$$

In Frequency Reciprocal space:

$$\chi^{(0)}_{GG'}(q, \omega) = 2\sum_{i \neq j}(f_i - f_j)\frac{\langle\phi_j|e^{-i(q+G)r}|\phi_i\rangle\langle\phi_i|e^{i(q+G')r}|\phi_j\rangle}{\epsilon_i - \epsilon_j - \omega - i\eta}$$

χ as a function of $\chi^{(0)}$

From:

$$\begin{cases} \delta\rho = \chi \delta v_{\mathrm{ext}} \\ \delta\rho = \chi^{(0)} \delta v_{\mathrm{tot}} \end{cases}$$

the polarizability in term of the independent particle polarizability is:

$$\chi = (1 - \chi^{(0)} v_c - \chi^{(0)} f_{\mathrm{xc}})^{-1} \chi^{(0)}$$

Dielectric Function ε

Definition of the *dielectric function*:

$$\boxed{\delta v_{\text{tot}} = \varepsilon^{-1} \delta v_{\text{ext}}}$$

$$\varepsilon^{-1} = 1 + v_c \chi$$

In a periodic system it has this form:

$$\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$$

Macroscopic Dielectric Function

Definition:

$$\varepsilon_{\mathrm{M}}(\mathbf{q},\omega) \stackrel{\mathrm{def}}{=} \frac{1}{\varepsilon^{-1}_{\mathbf{00}}(\mathbf{q},\omega)}$$

Approximation: Neglecting Local Fields:

$$\varepsilon^{\mathrm{NLF}}_{\mathrm{M}}(\mathbf{q},\omega) = \varepsilon_{\mathbf{00}}(\mathbf{q},\omega)$$

Macroscopic dielectric constant:

$$\varepsilon_{\infty} = \lim_{\mathbf{q}\to 0} \varepsilon_{\mathrm{M}}(\mathbf{q},\omega = 0)$$

Local Fields

Effect of non-diagonal elements (inhomogeneities):

$$\delta v_{\mathbf{G}}^{\mathrm{tot}} = \sum_{\mathbf{G}'} \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1} \delta v_{\mathbf{G}'}^{\mathrm{ext}}$$

LR-TDDFT Calculation Scheme Résumé

$$
\begin{tikzcd}
\rho^{\mathrm{DFT}} \arrow[dr, squiggly] & & \phi_{\mathrm{KS}}^{\mathrm{DFT}} \arrow[dl, squiggly] \arrow[dr] & & \epsilon_{\mathrm{KS}}^{\mathrm{DFT}} \arrow[dl] \\
& f_{\mathrm{xc}} \arrow[drr, bend right=10] & & \chi^{(0)} \arrow[d] & \\
& & & \chi \arrow[d] & \\
& & & \varepsilon \arrow[d] & \\
& & & \varepsilon_{\mathrm{M}} &
\end{tikzcd}
$$

the *dp* code

- Definition: **Linear-Response TDDFT** code in **Frequency-Reciprocal** space on a **PW** basis
- Purposes: DP calculates **Dielectric and Optical Properties** (Absorption, Reflectivity, Refraction indices, EELS, IXSS, CIXS, etc.) for Bulk systems, Surfaces, Cluster, Moleculs, Atoms (through Supercells) made of Insulator, Semiconductor and Metallic elements.
- Approximations: **RPA**, **ALDA**, **GW-RPA**, **LRC**, non-local kernels, **Mapping Theory**, etc., with and without **Local Fields** (**LF**)
- Languages: Fortran90 with C insertions (shell, parser, some libraries); Vectorialized and Partially Parallelized (MPI)
- Machines: PC-Linux IFC, Compaq/HP True64, IBM AIX, SG IRIX, NEC SX5, Fujitsu
- Libraries: BLAS, Lapack, FFTW, CXML, ESSL, ASL, Nag, Goedecker, MFFT
- Interfaces: LSI-CP, ABINIT, PWSCF, FHIMD

DP Flow Diagram

$$
\begin{tikzcd}
\epsilon_i^{\mathrm{KS}} \arrow[ddddrr] & & \phi_i^{\mathrm{KS}}(G) \arrow[d, "\mathrm{FFT}^{-1}"] & & \text{interface} \\
& & \phi_i^{\mathrm{KS}}(r) \arrow[d] & & \\
& & \tilde{\rho}_{ij}(r) = \phi_i^*(r)\phi_j(r) \arrow[d, "\mathrm{FFT}"] & & \\
& & \tilde{\rho}_{ij}(G) \arrow[d] & & \\
& & \chi^{(0)}_{GG'}(q,\omega) = \sum_{ij}(f_i - f_j)\frac{\tilde{\rho}_{ij}(G)\tilde{\rho}^*_{ij}(G')}{\epsilon_i - \epsilon_j - \omega} \arrow[d, "\mathrm{INV}"] & & \\
f_{\mathrm{xc}} \arrow[rr] & & \chi_{GG'}(q,\omega) \arrow[d] & & \\
& & \varepsilon^{-1}_{GG'}(q,\omega) \arrow[dll] \arrow[drr] & & \\
\varepsilon_{\mathrm{M}}^{\mathrm{LF}}(q,\omega) & & & & \varepsilon_{\mathrm{M}}^{\mathrm{NLF}}(q,\omega)
\end{tikzcd}
$$

DP Tricks

If we only need $\varepsilon^{-1}_{00} = 1 - v_0 \chi_{00}$, that is only χ_{00}

then, instead of solving (inverting a full matrix):

$$\chi_{GG'} = \left(1 - \chi^{(0)} v_c - \chi^{(0)} f_{\text{xc}}\right)^{-1}_{GG''} \chi^{(0)}_{G''G'}$$

we solve the **linear system** for only the first column of $\chi_{G'0}$:

$$\left(1 - \chi^{(0)} v_c - \chi^{(0)} f_{\text{xc}}\right)_{GG'} \chi_{G'0} = \chi^{(0)}_{G0}$$

DP Performances:
CPU scaling and Memory usage

- CPU scaling for $\chi^{(0)}$: $N_G^2 \cdot N_k \cdot N_b \cdot N_r \log N_r$
- CPU scaling for ε^{-1}: $N_G^2 \cdot N_\omega$
- Memory occupation: $N_G^2 \cdot N_\omega + N_r \cdot N_k \cdot N_b \quad [\mathrm{sizeofcomplex}]$

Exchange-Correlation Kernel f_{xc} and its Approximations

Definition of the exchange-correlation kernel:

$$f_{\mathrm{xc}} \stackrel{\mathrm{def}}{=} \frac{\delta v_{\mathrm{xc}}}{\delta \rho}$$

RPA Approximation

Random Phase Approximation (RPA) = Neglect of the exchange-correlation effects:

$$\boxed{\text{RPA:} \quad f_{\text{xc}} = 0}$$

$$\varepsilon_{\text{RPA}} = 1 - v_c \chi^{(0)}$$

ALDA Approximation (TDLDA)

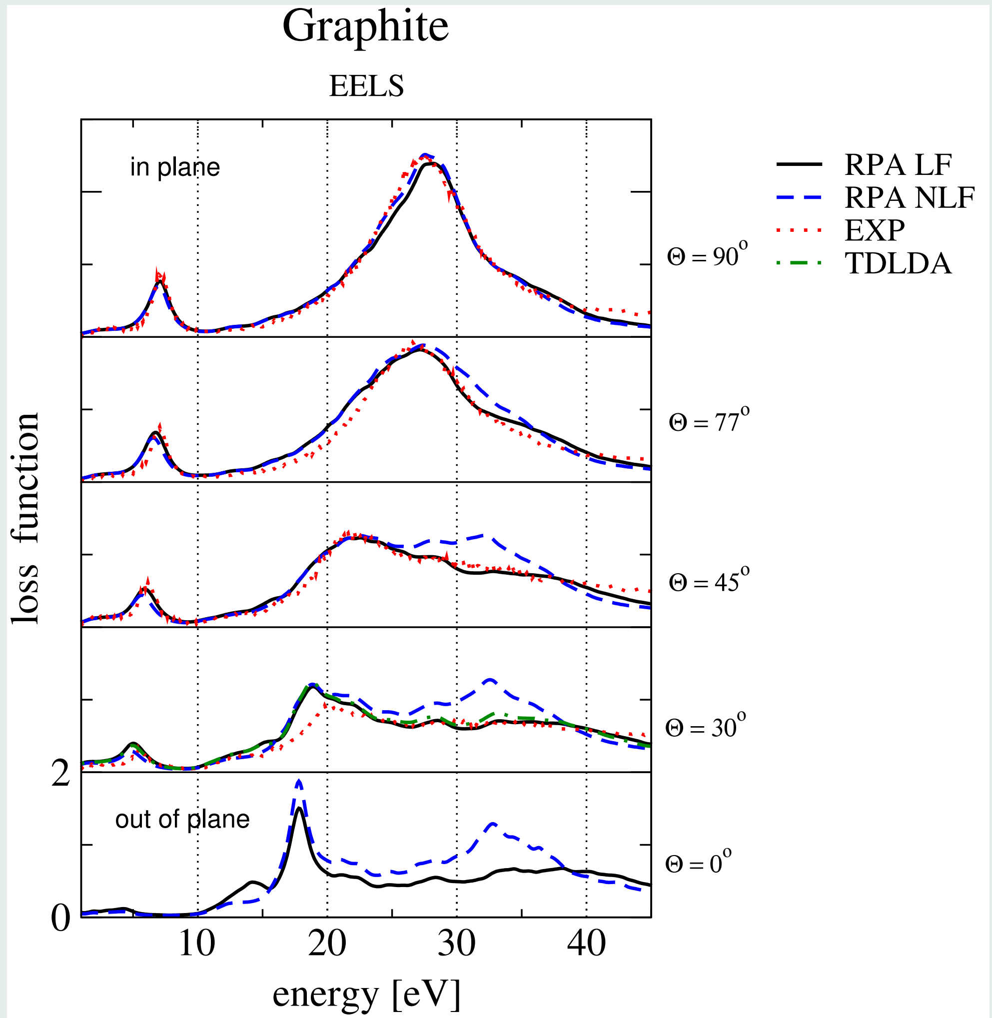
Adiabatic Local Density Approximation:

$$\boxed{\text{ALDA:} \quad f_{\text{xc}}^{\text{ALDA}} = \left.\frac{\delta v_{\text{xc}}^{\text{LDA}}}{\delta \rho}\right|_{\omega=0}}$$

$$f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}') = A(\mathbf{r})\delta(\mathbf{r}, \mathbf{r}') \quad \text{local in } r\text{-space}$$

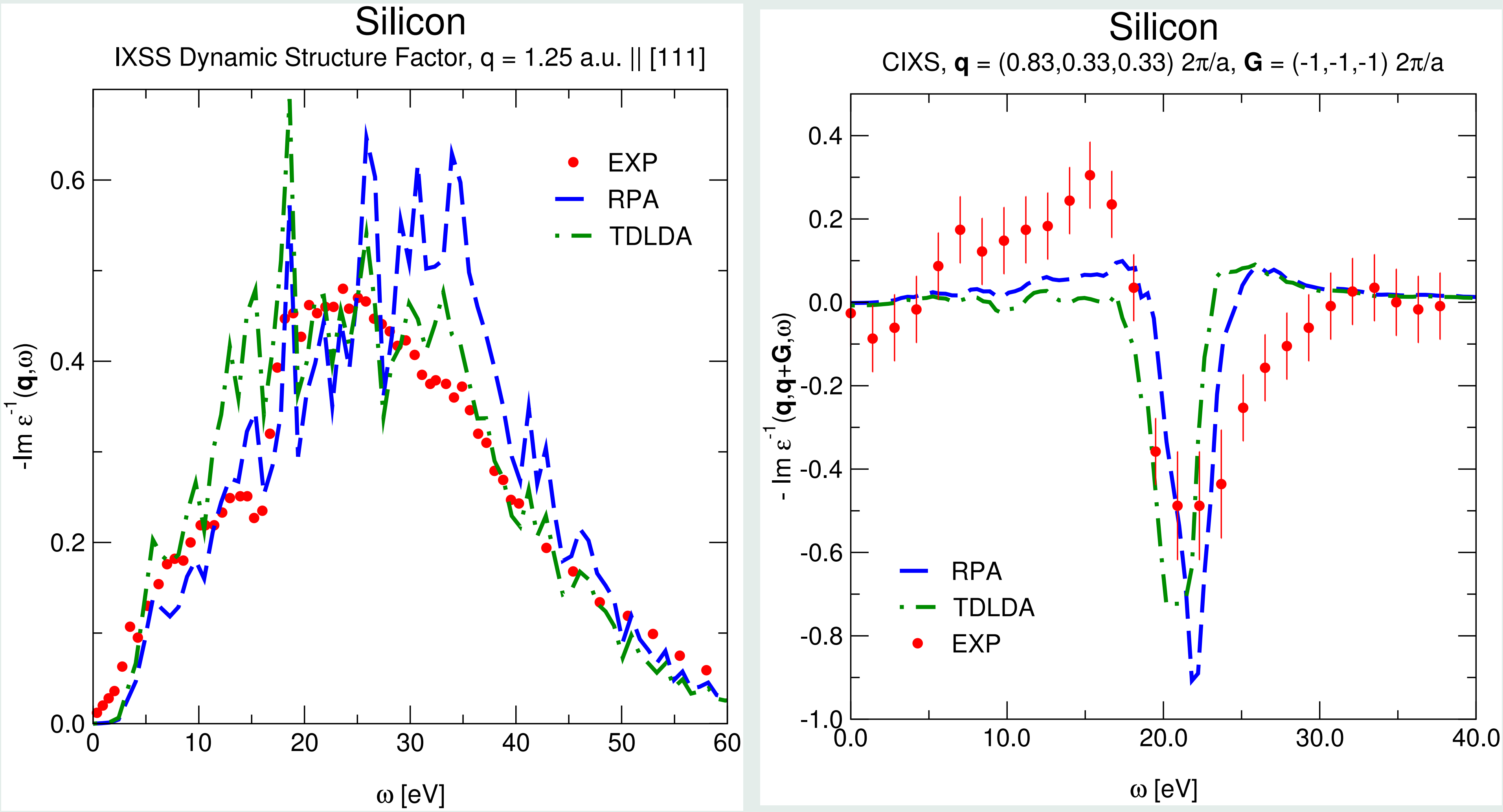
$$f_{\text{xc}\,\mathbf{GG}'}^{\text{ALDA}}(\mathbf{q}) = B(\mathbf{G} - \mathbf{G}')$$

Results on EELS



A. Marinopoulos et al., Phys. Rev. B **69**, 245419 (2004).

Results on IXSS and CIXS

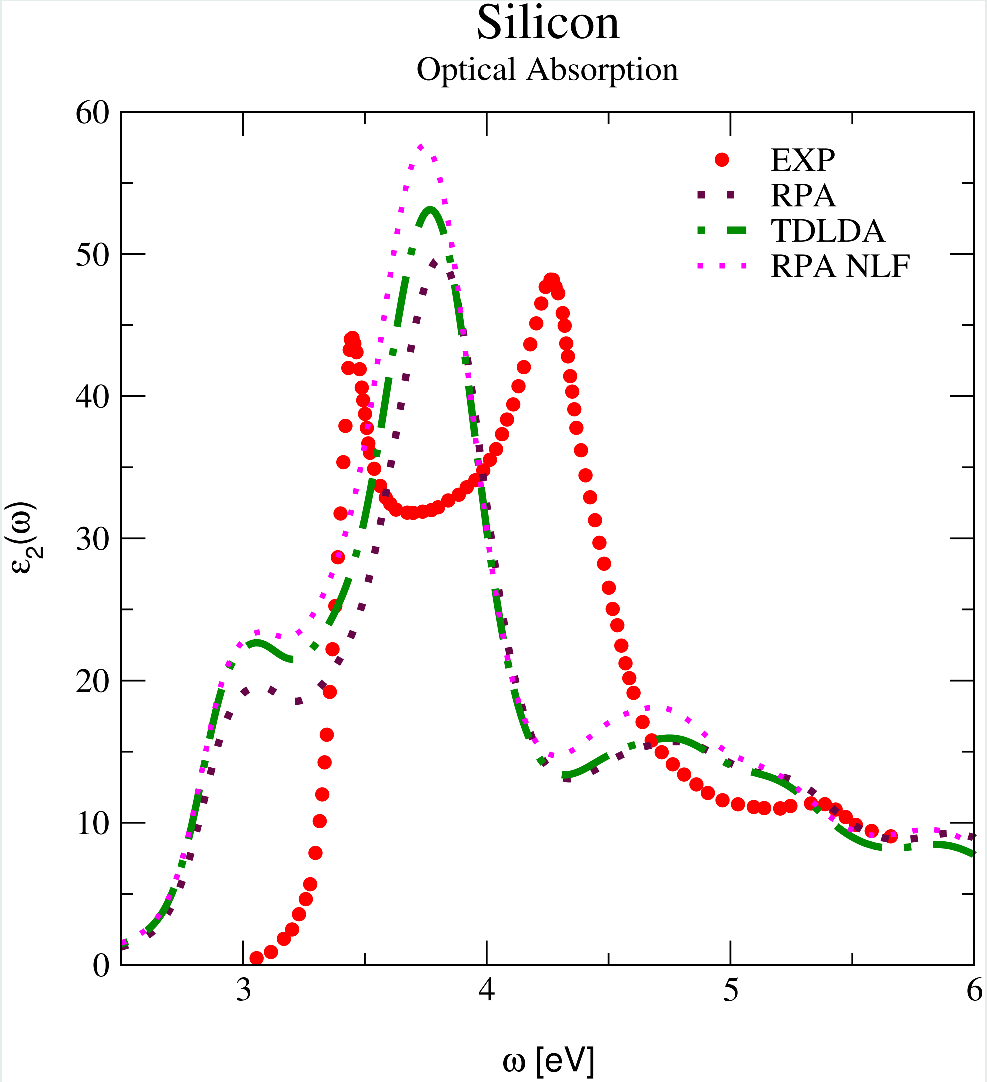


V. Olevano, PhD thesis (1999).

Conclusions on EELS

- RPA is good but with LF (Local Fields)
- ALDA does not improve unambigously

Results on ABS



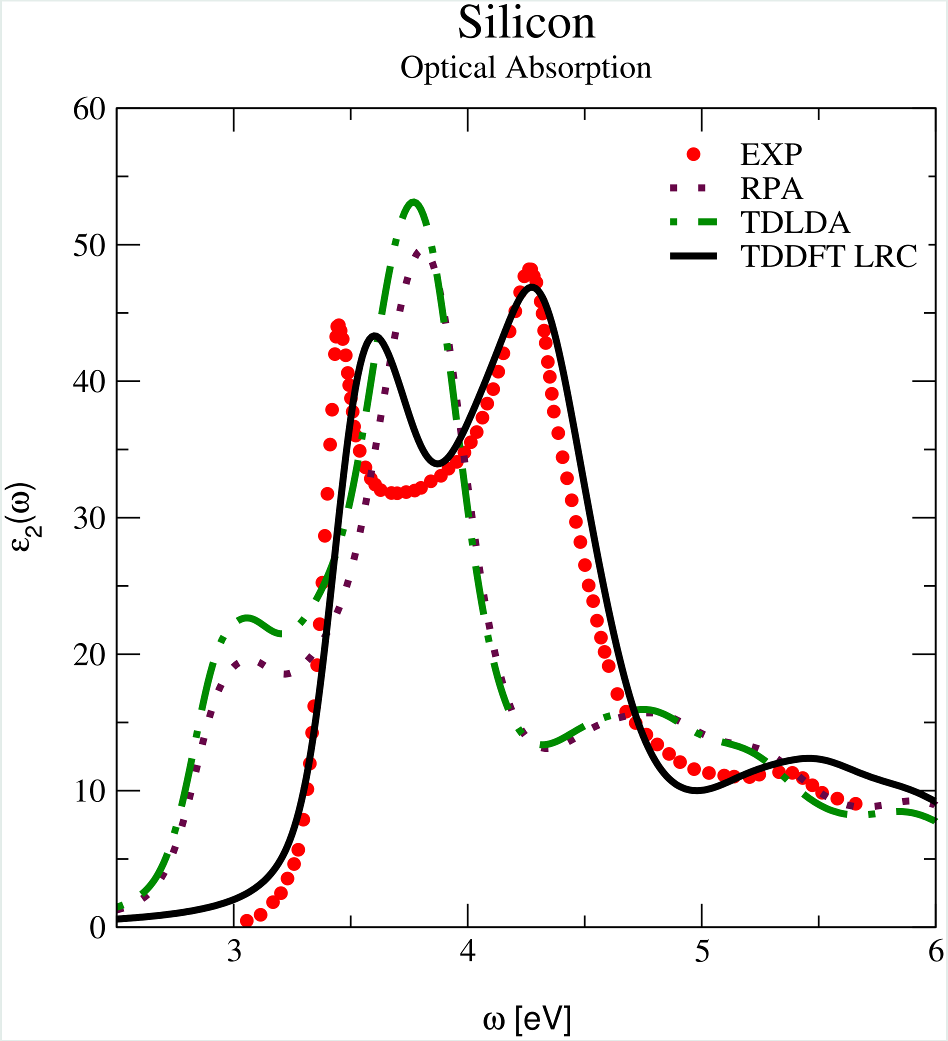
LRC Approximation

Long-Range Contribution only:

$$f_{\mathrm{xc}}^{\mathrm{LRC}} = -\frac{\alpha}{(q+G)^2}$$

$$\alpha = 4.6\varepsilon_{\infty}^{-1} - 0.2$$

Results on ABS



L. Reining et al., Phys. Rev. Lett. **88**, 066404 (2002).

Mapping Theory (MT)

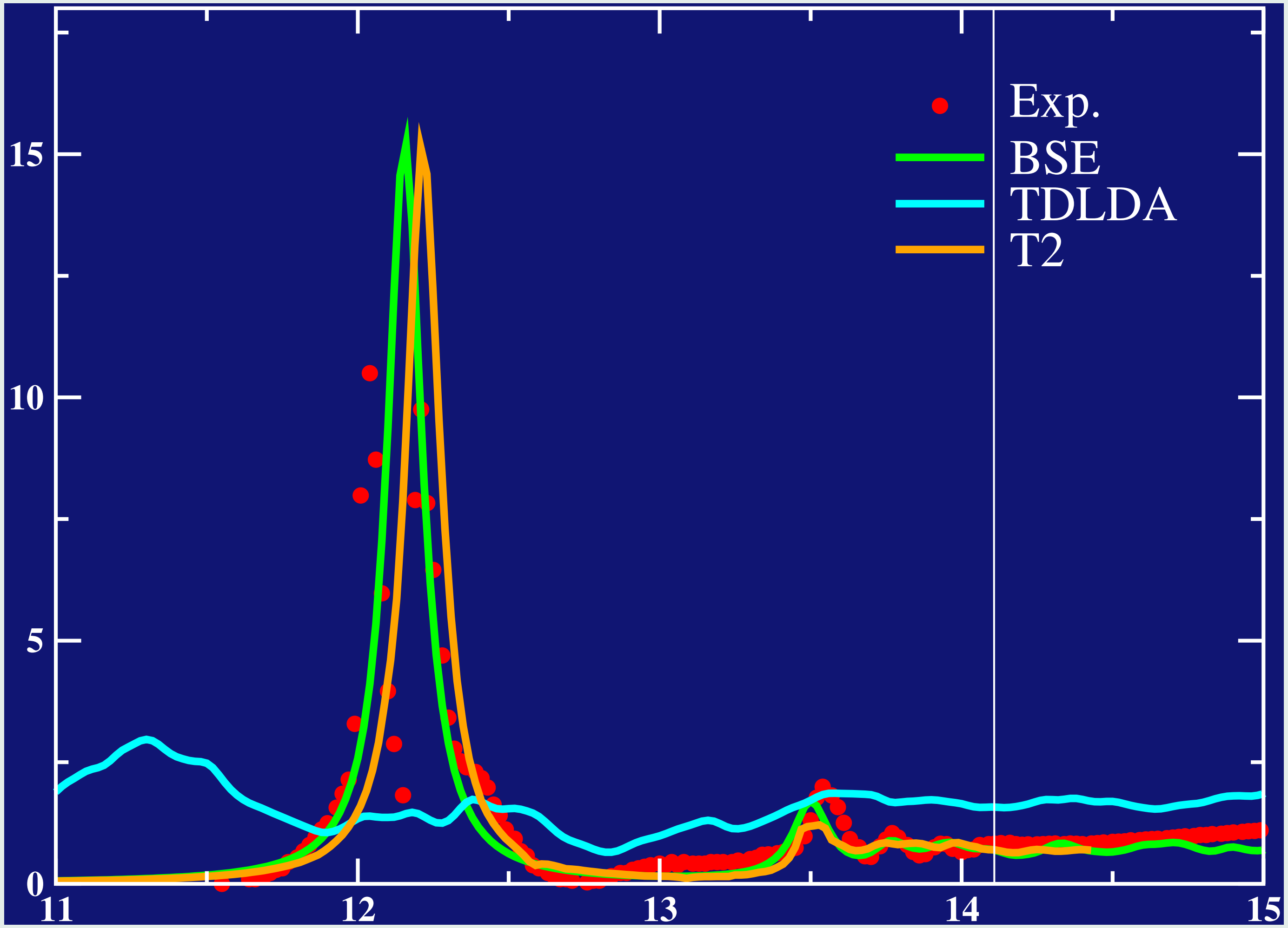
Mapping BSE on TDDFT:

$$f_{\mathrm{xc}}^{\mathrm{MP}}[\{\phi_i\},\{\epsilon_i\}]$$

$$\chi = \chi^{(0)}\left(\chi^{(0)} - \chi^{(0)} v_c \chi^{(0)} - T[\{\phi_i\},\{\epsilon_i\}]\right)^{-1}\chi^{(0)}$$

$$T = \chi^{(0)} f_{\mathrm{xc}} \chi^{(0)}$$

Results on Solid Argon ABS



F. Sottile et al., to be published

Conclusions on Optical Properties

- RPA and ALDA fail
- LRC already reproduces small Excitonic Effects
- Mapping Theory should be used for Strong Excitons

DP licence

- DP costed 7 years human full-time to the authors: is GNU/GPL going to reduce the charge on the central?

- developping software is a job in itself!

- who is going to pay for this? are private companies interested in this software? not yet!

- if the scientific community is interested and recognize the importance, then it must hire people to develop these codes!

- International, European or even National institutions must be setup to manage scientific codes interesting for the whole international scientific community.

DP licence and ETSF

IF ( )

THEN

= OpenSource GNU/GPL