Introduction to TDDFT

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

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Résumé

- Motivation
- TDDFT
- Linear-Response TDDFT
- Frequency-Reciprocal space TDDFT
- TDDFT on a Plane Waves basis: the DP code
- Approximations: RPA, ALDA, new kernels
- Results
- Conclusions

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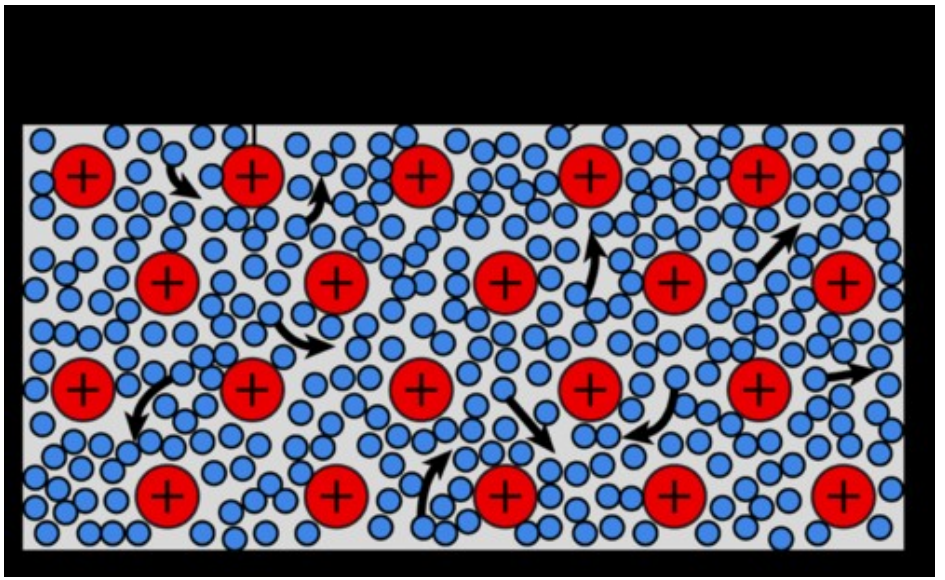
Condensed Matter: a Formidable Many-Body Problem

- Well known interaction: electromagnetic (like in QED)
- All our ignorance in Cond-Mat has roots into the many-body problem.



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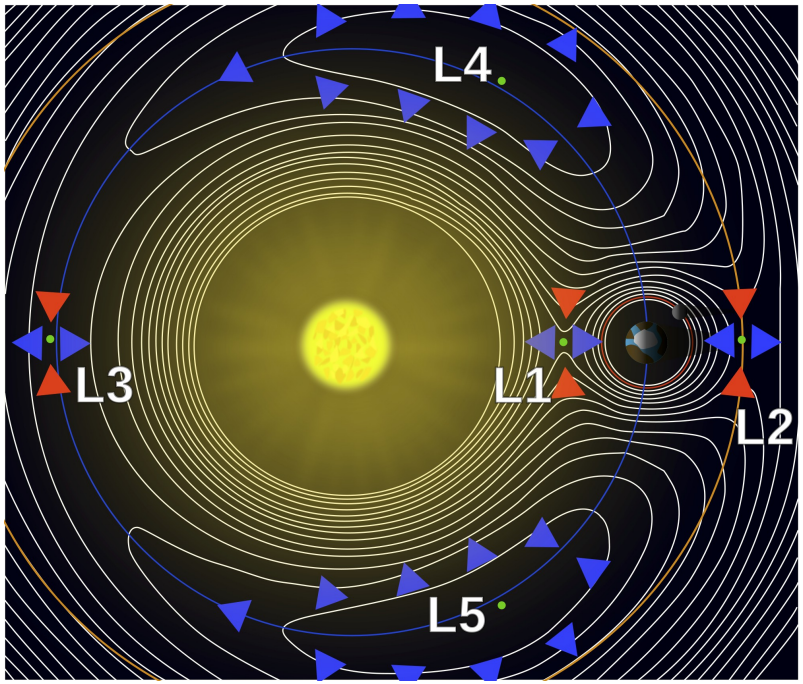
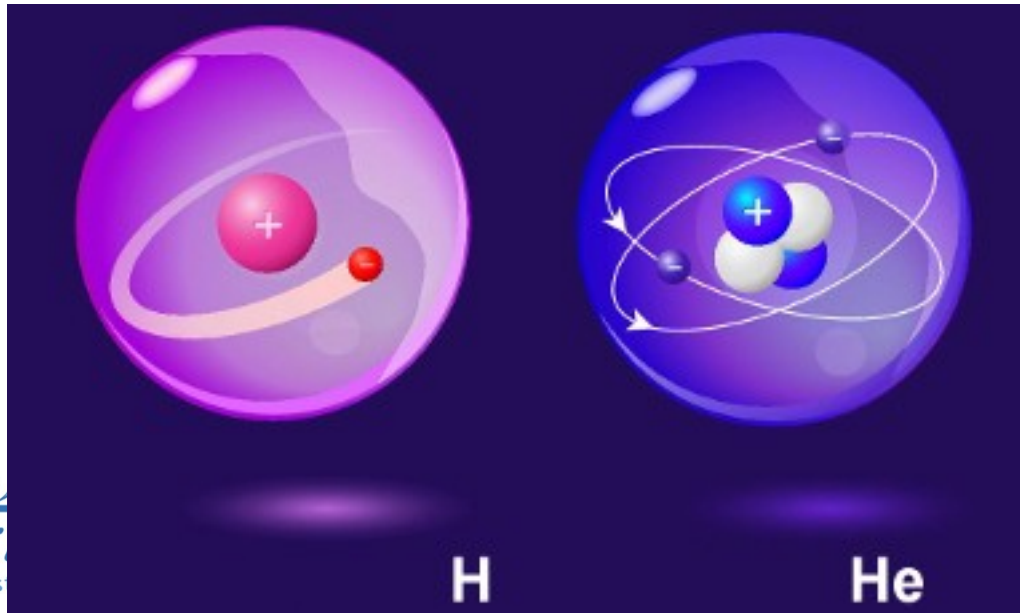
the Many-Body Problem

- Already a problem in Classical Physics: 3-body problem (Euler, Lagrange, …) and on
- In Quantum Mechanics even 2 bodies is a problem



$$H = -\frac{\partial_{r_1}^2}{2} - \frac{\partial_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_2 - r_1|}$$



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The Many-Body problem

$$H = -\frac{1}{2}\sum_{n=1}^{N}\partial_{r_n}^2 + \sum_{n=1}^{N} v(r_n) + \frac{1}{2}\sum_{n\neq m=1}^{N}\frac{1}{|r_n - r_m|}$$

kinetic

e-ions interaction

many-body e-e interaction

where N can be up to the Avogadro number 10^{23}!!!

$$H\Phi(r_1, r_2, \ldots, r_N) = E\Phi(r_1, r_2, \ldots, r_N)$$

many-body wavefunction

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The Many-Body problem

$$H = -\frac{1}{2}\sum_{n=1}^{N}\partial_{r_n}^2 + \sum_{n=1}^{N} v(r_n) + \frac{1}{2}\sum_{n\neq m=1}^{N}\frac{1}{|r_n - r_m|}$$

$$H = \sum_{n=1}^{N} h(r_n) \qquad h(r) = -\frac{1}{2}\partial_r^2 + v(r)$$ Factorizable Hamiltonian

$$h\,\phi_i(r) = \epsilon_i \phi_i(r)$$ Solvable single-particle Schrödinger equation

$$E_0 = \sum_{n=1}^{N} \epsilon_i$$ Many-body ground-state total energy

Total many-body ground state wavefunction

$$\Phi(r_1, r_2, \ldots, r_N) = \phi_1(r_1)\cdot\phi_2(r_2)\cdots\phi_N(r_N)$$

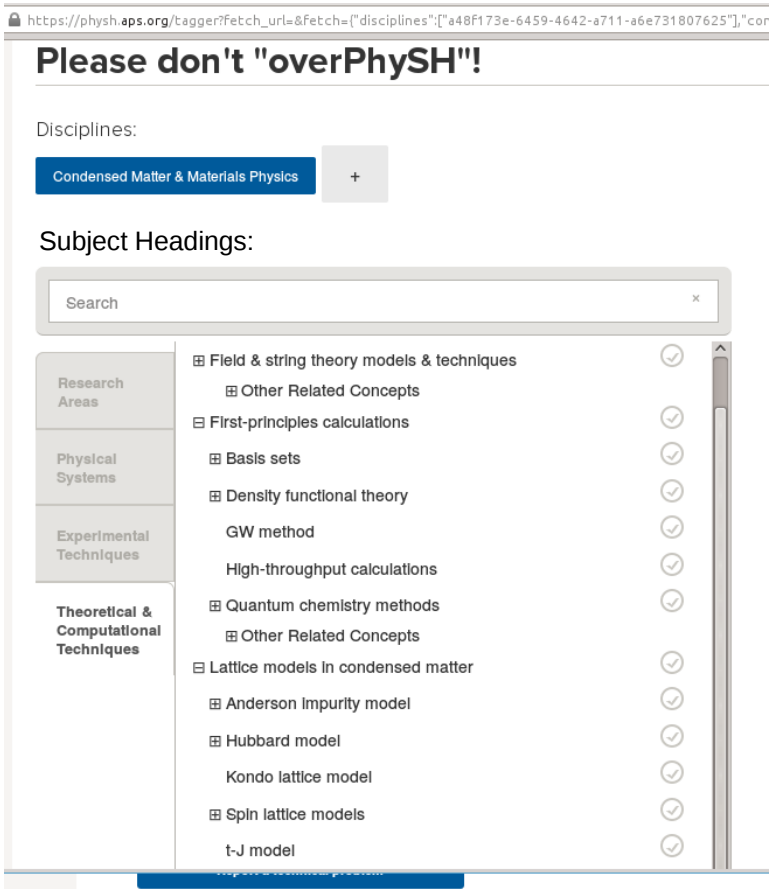
Condensed Matter Theory

Models

simplify and search (if possible)
analytical solutions

- Anderson
- Hubbard
  DMFT
- Kondo
- Ising
- Heisenberg

adjustable parameters (***U***, ***J***, ...)



Ab Initio (first principles)

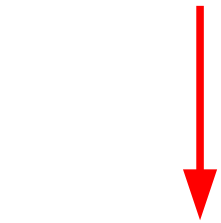
numerical solution but
microscopic Hamiltonian

- Quantum Chemistry:
  CI
  CC
  …
- **QMC**
- Density-Functional:
  DFT
  TDDFT
- Many-body Green function:
  GW
  BSE

approximations (LDA, ...)

Why do we need *ab initio* theories?

1) To understand and explain observed phenomena;
2) To offer experimentalists reference data;
3) To predict properties before the synthesis, the experiment.



Purposes of the:

ETSF
European Theoretical Spectroscopy Facility

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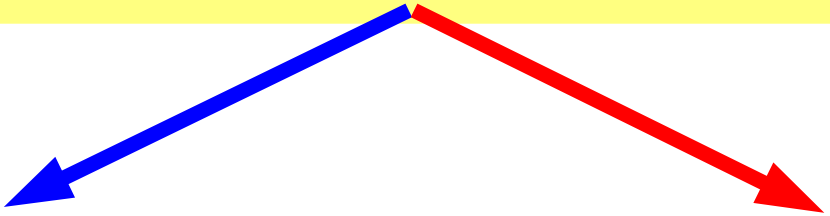
Which *ab initio* theory for which properties/spectroscopy?

Properties of Matter



Electronic **Ground State** properties:

- Total energy
- Atomic structure
- Phase stability
- Electronic density
- Magnetic order
- Elastic constant
- Phonons

Electronic **Excited States** properties:

- Electronic structure
- Band plot, gap
- Metal/Insulator char.
- Optical properties
- Dielectric properties
- Transport
- e-ph and Superconductivity

What DFT **can** predict

(normal error 1~2% in the 99% of cond-mat systems)

- Atomic Structure, Lattice Parameters (XRD)
- Total Energy, Phase Stability
- Electronic Density (SEM, XRS, STM)
- Elastic Constants
- Phonon Frequencies (IR, Neutron scattering)

that is, all **Ground State** Properties!

and this also in **Strongly Correlated** systems!:

Vanadium Oxide, VO_2

lattice parameters

M. Gatti et al., PRL 2007

	DFT-LDA nlcc	DFT-LDA semic	EXP [Longo et al.]
a	5.659 Å	5.549 Å	5.7517 ± 0.0030 Å
b	4.641 Å	4.522 Å	4.5378 ± 0.0025 Å
c	5.420 Å	5.303 Å	5.3825 ± 0.0025 Å
α	121.46	121.73°	122.646° ± 0.096

What DFT **cannot** predict

- Electronic Structure, Bandplot
- Bandgap, Metal/Insulator/Semiconductor
- Optical and Dielectric properties

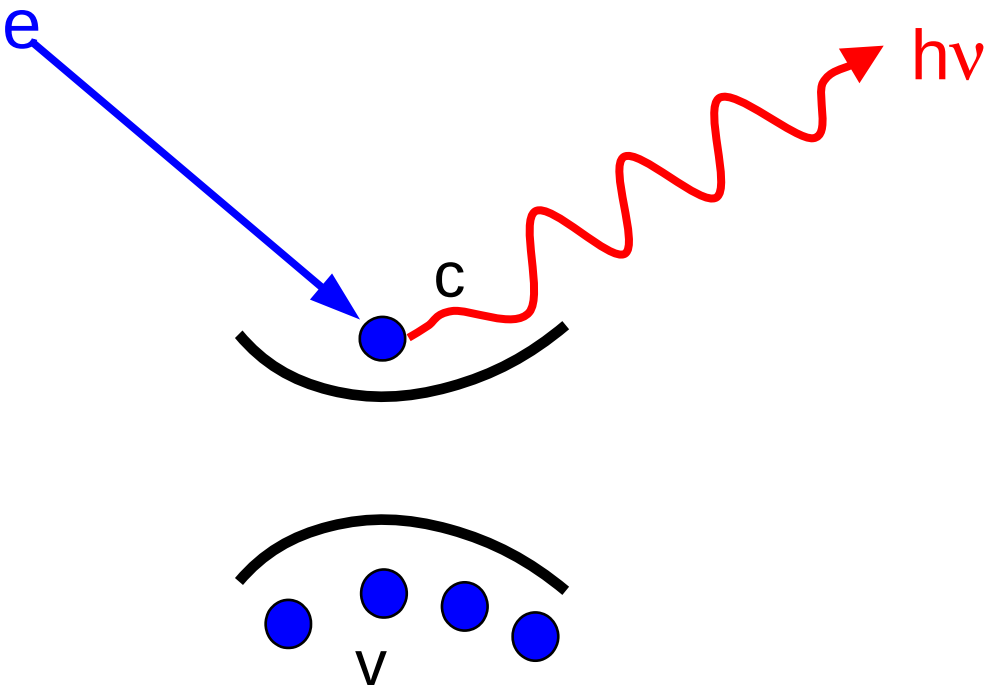
that is, all **Excited State** Properties!

You can use DFT to predict these properties,
but don't blame DFT if it fails!

Which *ab initio* theory for which excited state properties/spectroscopy

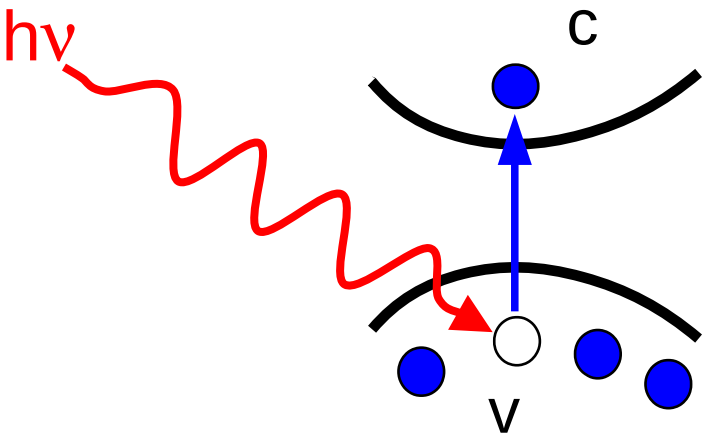
Excitations: Charged vs Neutral

Charged Excitations
N → N+1 (or N-1)
(Photoemission Spectroscopy)



Inverse Photoemission

Neutral Excitations
N → N
(Optical and Dielectric Spectroscopy)

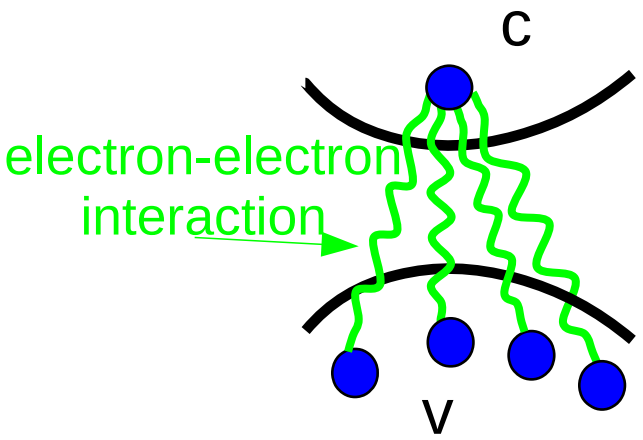


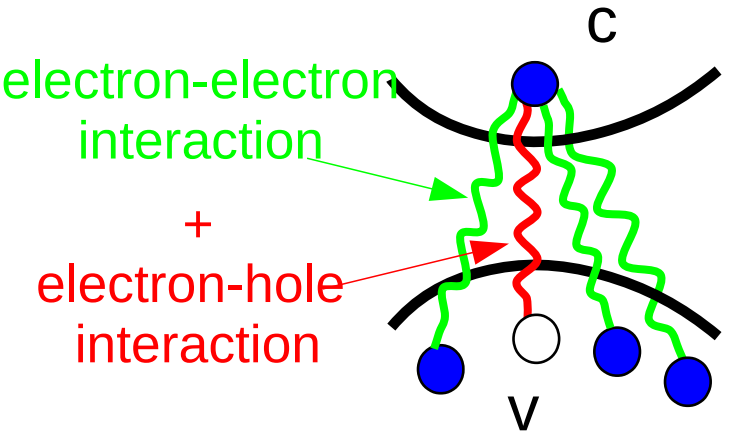
Optical Absorption

Excitations: Charged vs Neutral

Charged Excitations
N → N+1 (or N-1)

Neutral Excitations
N → N





Inverse Photoemission

Optical Absorption

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Possible *ab-initio* Theories for the Excited States

- **TDDFT** (Time-Dependent Density-Functional Theory) in the Approximations:
  - **RPA**
  - **TDLDA**
  - **beyond**

  → **Neutral** Excitations
- **MBPT** (Many-Body Theory) in the Approximations:
  - **GW** → **Charged** Excitations
  - **BSE** (Bethe-Salpeter Equation) → **Neutral** Excitations

Neutral Excitations Spectroscopies (for TDDFT)

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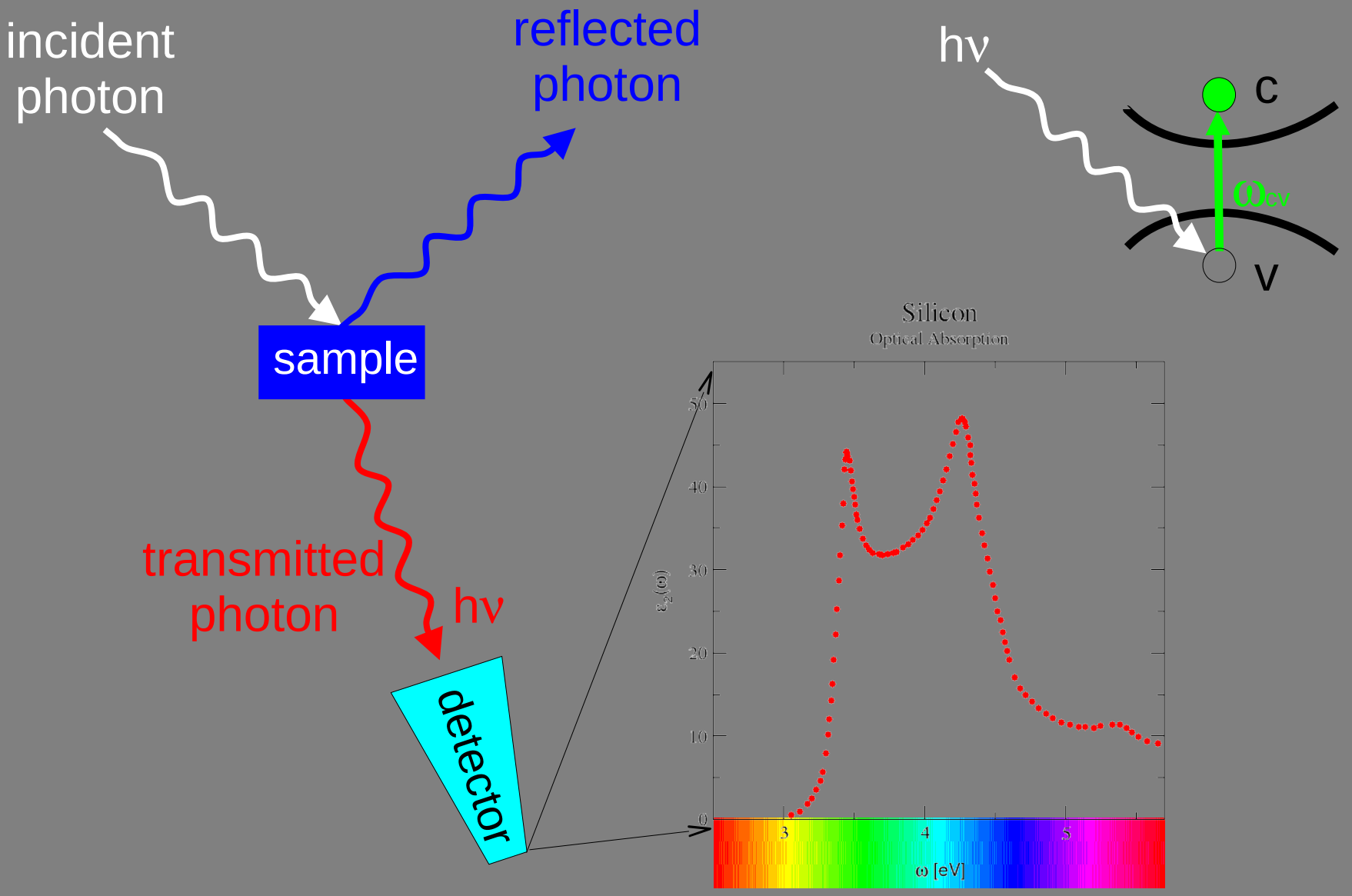
Optical Properties



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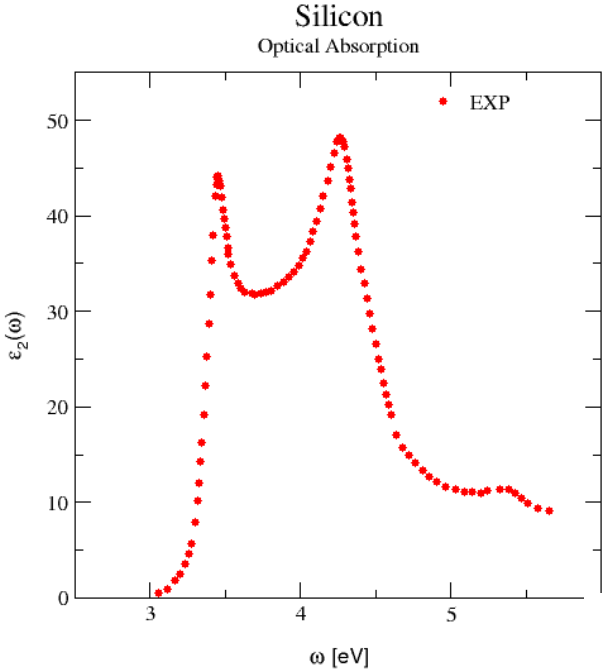
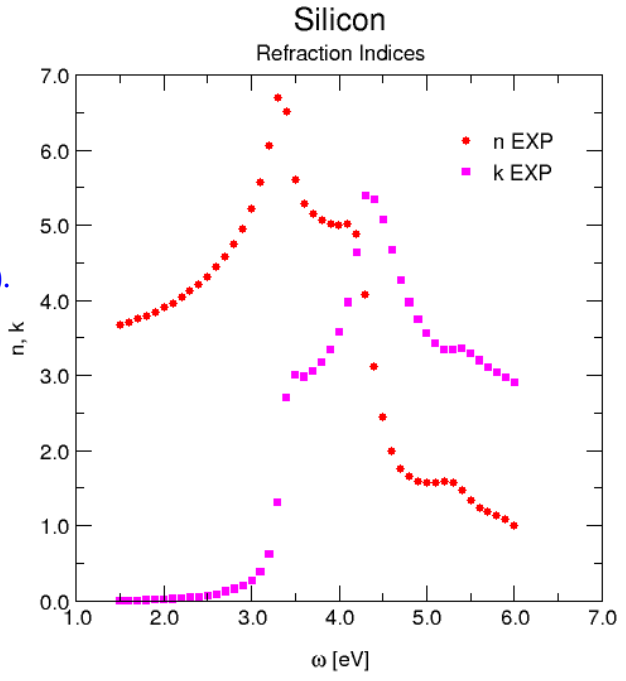
Optical Spectroscopies



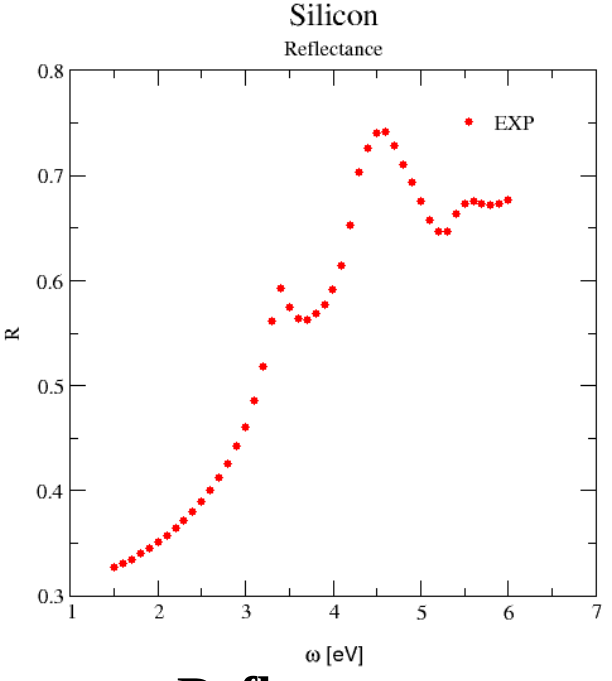
Lautenschlager et al.
PRB **36**, 4821 (1987).

Optical Absorption



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

Refraction Index



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

Reflectance

Dielectric Properties (EELS)

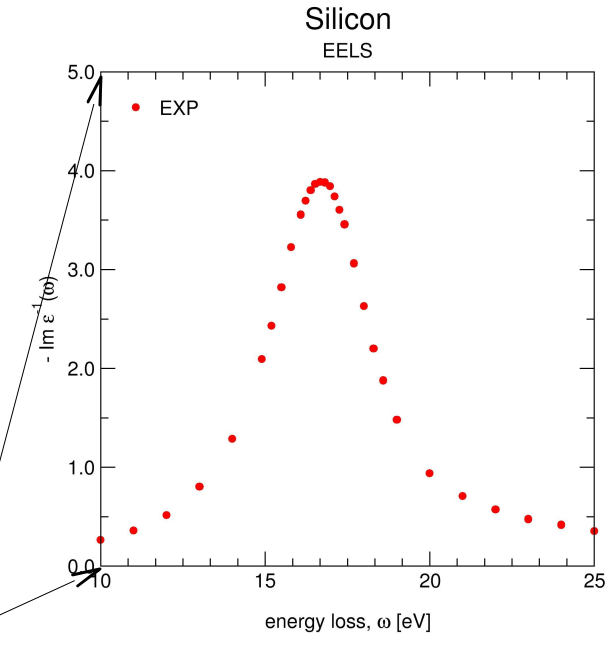
electrons

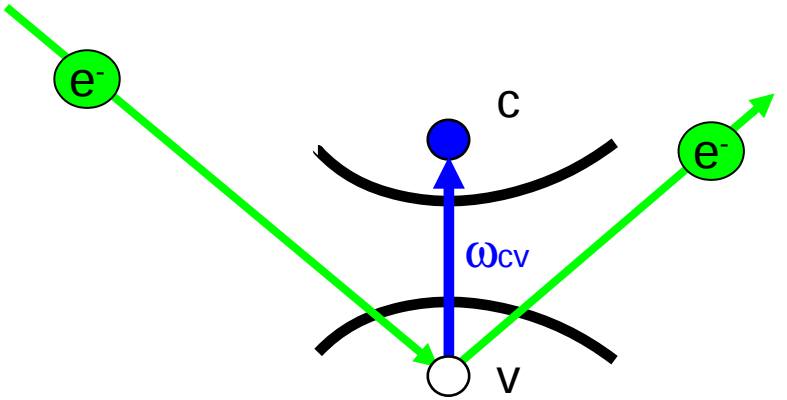
e-

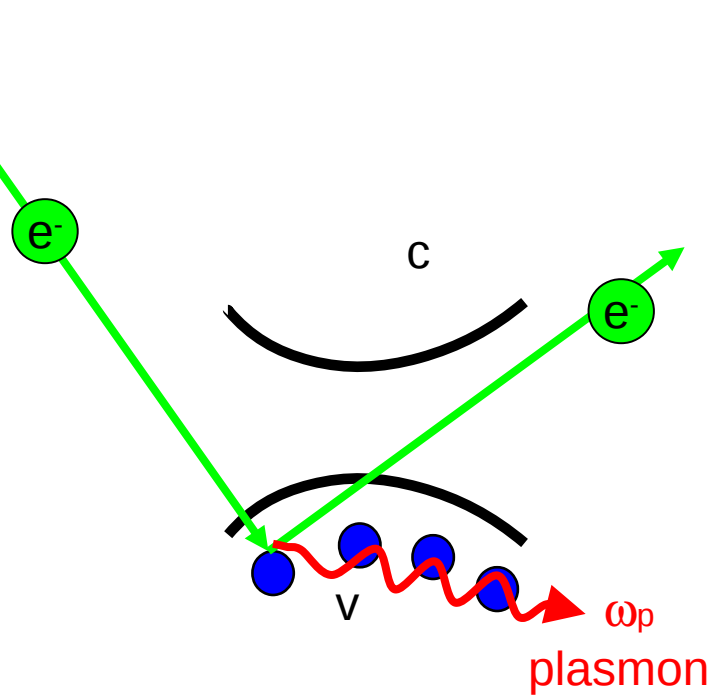
sample

e-

detector







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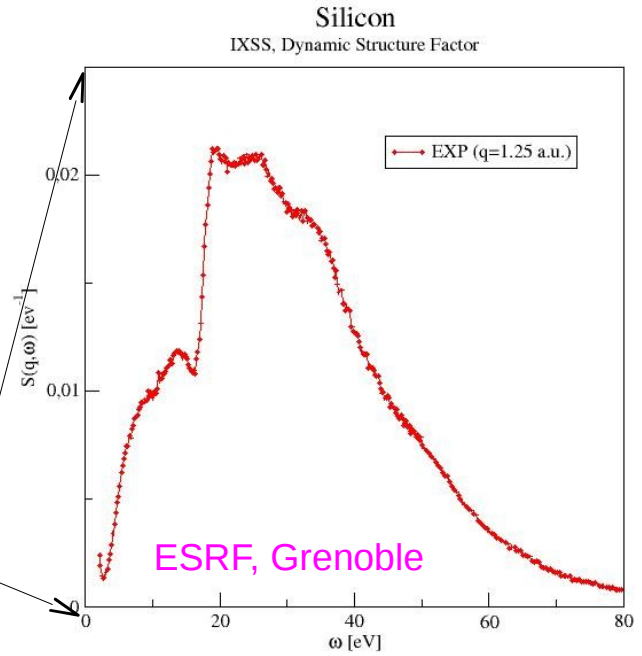
Synchrotron Radiation (IXSS)

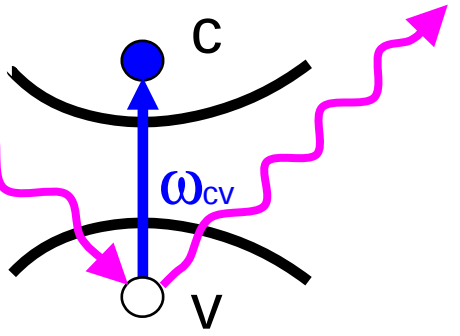
X rays

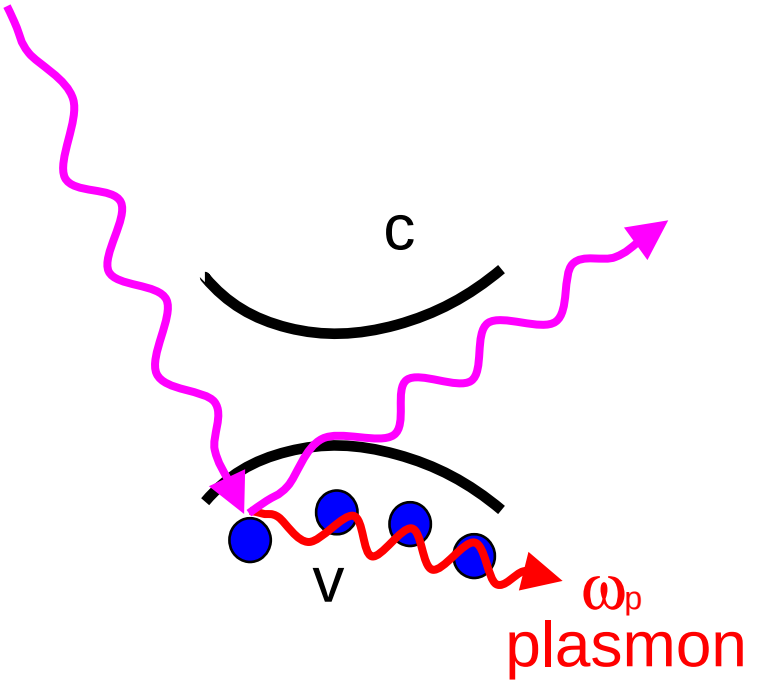
sample

detector



X





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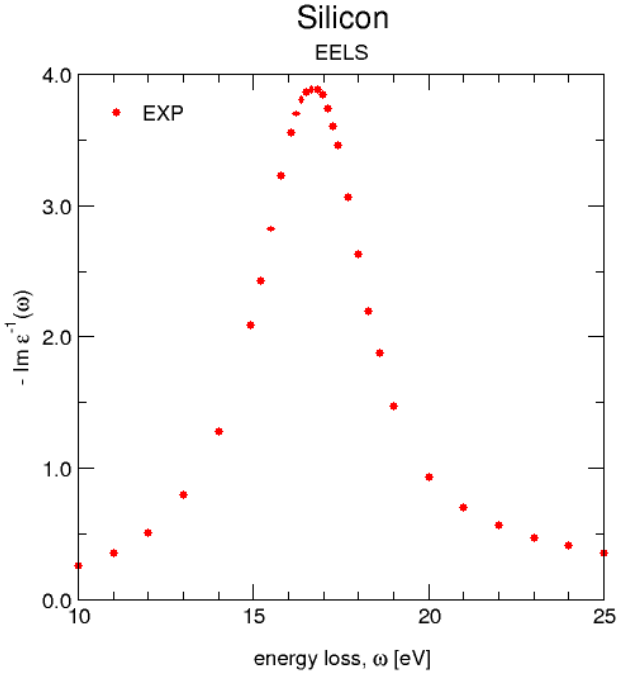
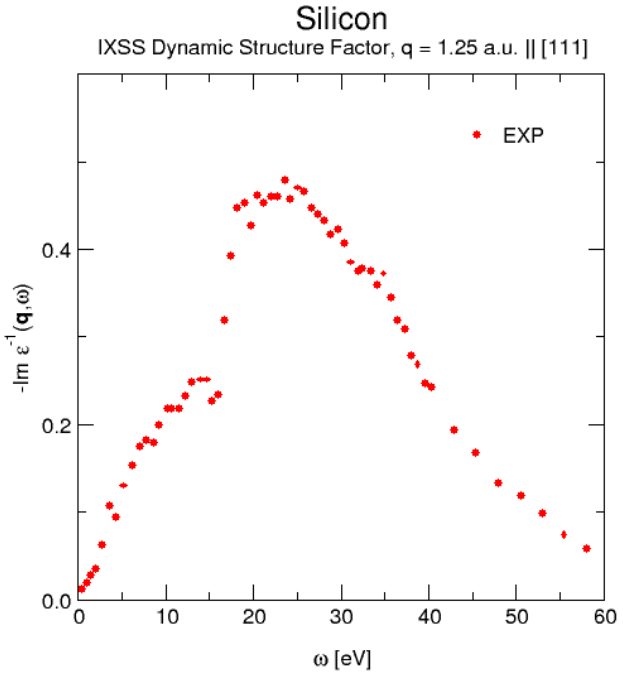
Energy-Loss Spectroscopies



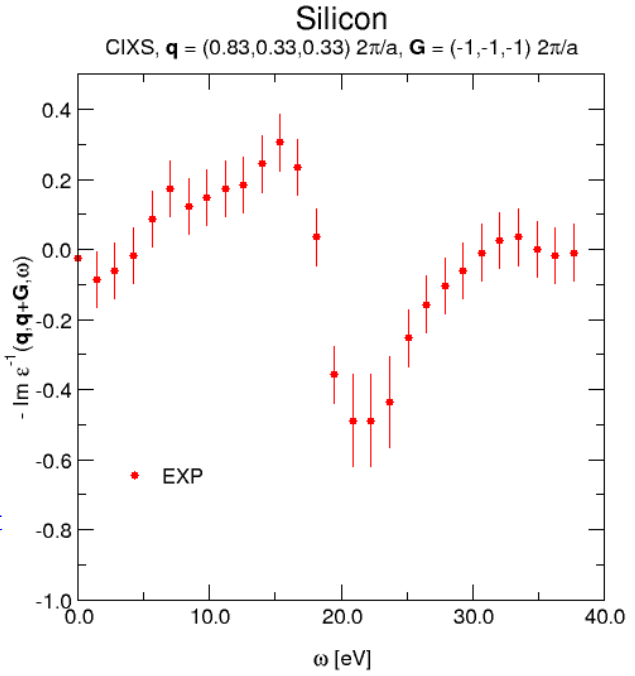
Stiebling
Z. Phys. B **31**, 355 (1978).

Energy Loss (EELS)



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

Inelastic X-ray Scattering Spectroscopy (IXSS)



Schuelke and Kaprolat
PRL **67**, 879 (1991)
(ESRF, Grenoble).

Coherent Inelastic Scattering Spectroscopy (CIXS)

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TDDFT

What is TDDFT?

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

Static Ionic Potential → $v(r) \Leftrightarrow \rho(r)$ — Hohenberg-Kohn theorem

Static Ionic Potential + External Perturbation (E.M. field) → $v(r,t) \Leftrightarrow \rho(r,t)$ — Runge-Gross theorem

- Fundamental degree of freedom:
  Time-Dependent electronic Density $\rho(r,t)$
  (instead of the total many-body wavefunction $\Psi(r_1,...,r_N,t)$)

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TDDFT milestones

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

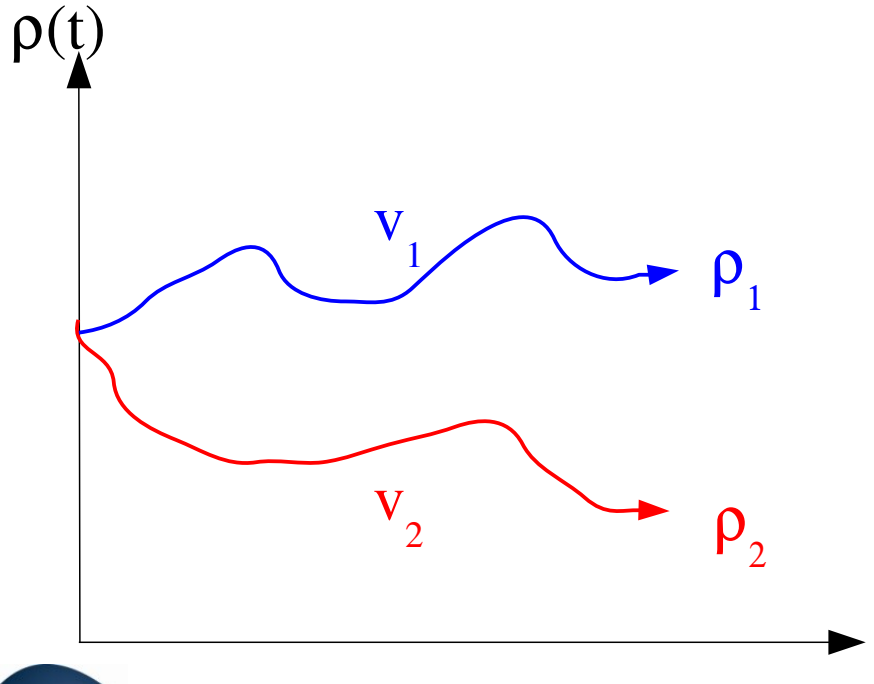
The Runge Gross theorem

PRL 52, 997 (1984)

$$i\partial_t \Psi_1(t) = (\hat{T} + \hat{V}_1(t) + \hat{W})\Psi_1(t)$$

$$i\partial_t \Psi_2(t) = (\hat{T} + \hat{V}_2(t) + \hat{W})\Psi_2(t)$$

$$v_1(t) \neq v_2(t) + c(t) \quad \Rightarrow \quad \rho_1(t) \neq \rho_2(t)$$



Any observable is functional of the (time-dependent) density:

$$\bar{o}(t) = \langle \Psi(t) | \hat{o} | \Psi(t) \rangle = o[\rho](t)$$

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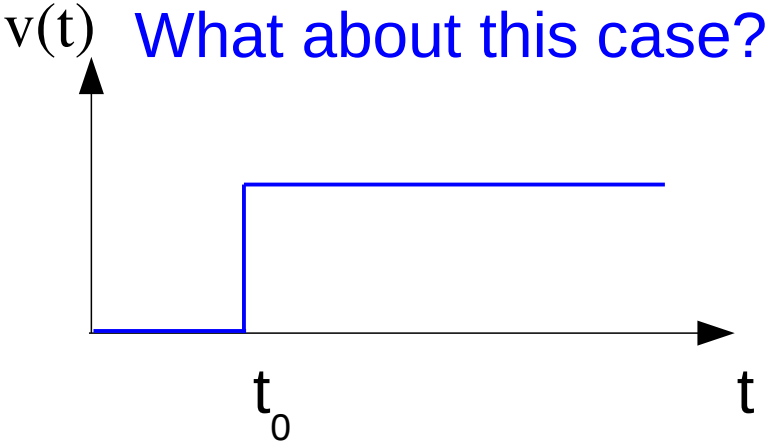
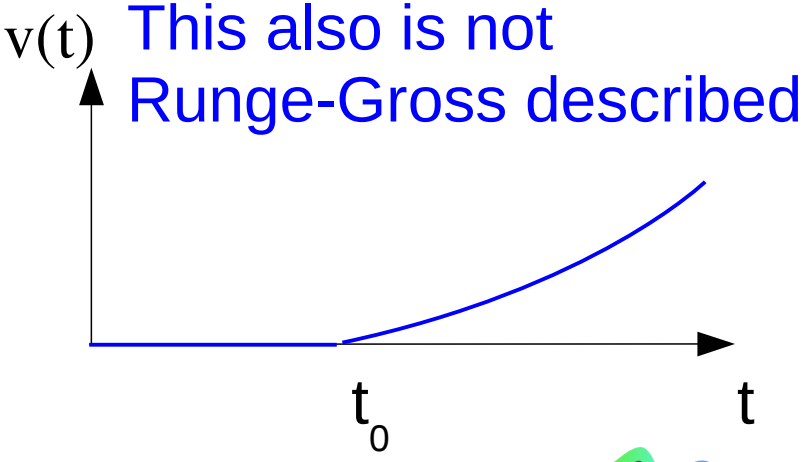
Runge Gross theorem caveats

1) Any observable is functional of the density **and of the initial state** $\Psi_0=\Psi(t_0)$

$$\bar{o}(t)=o[\rho,\Psi_0](t)$$

2) The Runge-Gross theorem is proven under the requirement of **v(t) expanded around t_0**. And if you run into problems already in describing the (non-equilibrium) initial state, you can't go on with TDDFT. Previous demonstrations required periodic v(t) or a small td perturbation (linear response), or later (Laplace transformable switch-on potentials+initial ground-state). But there is **no general proof** of the Runge-Gross theorem.





TDDFT vs DFT
Zoological Comparative Anatomy

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:

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

are unique functionals of the density.

The extrema of the:

Total Energy

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

The stationary points of 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:

$$\rho(r)=\sum_{i=1}^{N}\left|\phi_i^{KS}(r)\right|^2$$

$$v^{KS}(r)=v(r)+\int dr'\frac{\rho(r')}{|r-r'|}+\frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$$

$$H^{KS}(r)\phi_i^{KS}(r)=\epsilon_i^{KS}\phi_i^{KS}(r)$$

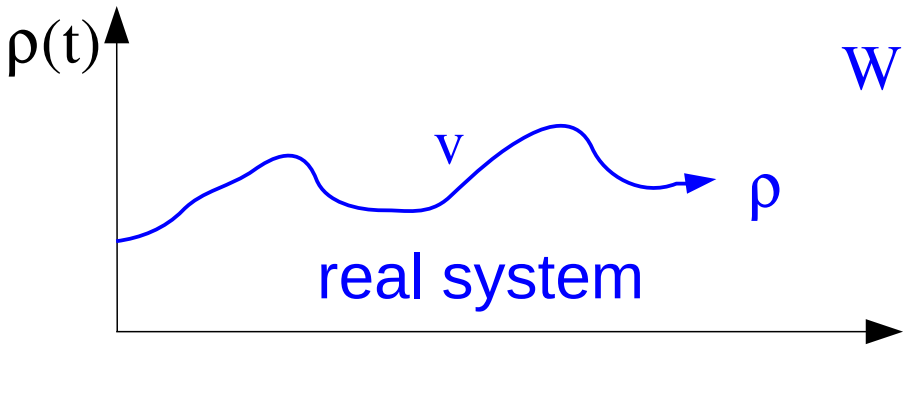
Runge-Gross:

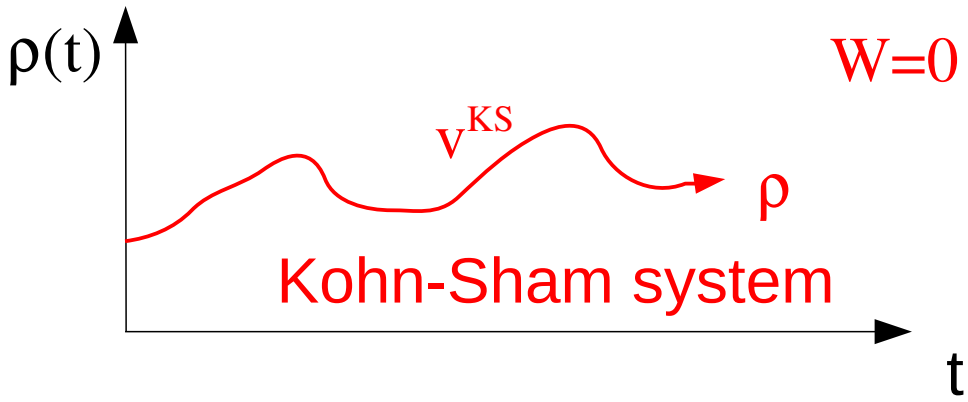
$$\rho(r,t)=\sum_{i=1}^{N}\left|\phi_i^{KS}(r,t)\right|^2$$

$$v^{KS}(r,t)=v(r,t)+\int dr'\frac{\rho(r',t)}{|r-r'|}+\frac{\delta A_{xc}[\rho]}{\delta\rho(r,t)}$$

$$i\partial_t\phi_i^{KS}(r,t)=H^{KS}(r,t)\phi_i^{KS}(r,t)$$

Kohn-Sham equations



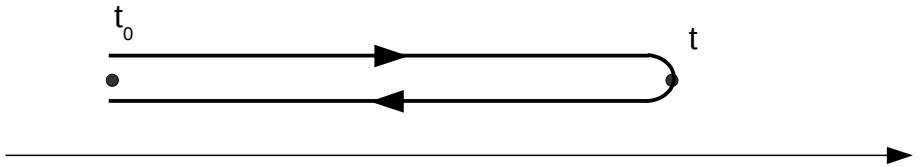


TDDFT further caveats

1) The functional $A_{xc}[\rho]$ is defined only for **v-representable densities**. It is undefined for ρ which do not correspond to some potential v → problems when variations δA[ρ] with respect to **arbitrary** densities are required in order to search for stationary points.

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

2) A functional A[ρ] with ρ(t) on the real time, is ill defined, since we would run in a **causality-symmetry paradox** → we can solve the problem by working with t on the Keldysh contour. Response functions are symmetric on the contour and become causal on physical time.



If exists $\frac{\delta A^{KS}[\rho]}{\delta\rho(r,t)}=v^{KS}(r,t)$

Then we can define the Legendre transform:

$$\tilde{A}[v]=-A[\rho]+\int dr\,dt\,\rho(r,t)v(r,t)$$

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

$$\frac{\delta \tilde{A}}{\delta v(r,t)\delta v(r't')}=\frac{\delta \rho(r,t)}{\delta v(r't')}$$

symmetric causal (=0 for t'>t)

Van Leeuwen, PRL 80, 1280 (1998).

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TDDFT in Linear Response

TDDFT in Linear Response

Gross and Kohn (1985)

- If:

$$v(r,t) = v(r) + \delta v(r,t)$$

- with:

$$\delta v(r,t) \ll v(r)$$

Strong (Laser) perturbations excluded!

TDDFT = DFT + Linear Response

(to the time-dependent perturbation)

Runge-Gross Theorem for Linear Response TDDFT

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

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

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

LR-TDDFT: $\delta v(r,t) \Leftrightarrow \delta\rho(r,t)$

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Calculation Scheme

DFT calculation (**ABINIT** code)

$$v(r) \Rightarrow \rho(r), \epsilon_i^{\mathrm{KS}}, \phi_i^{\mathrm{KS}}(r)$$

LR-TDDFT calculation (**DP** code)

$$\delta v(r,t) \Rightarrow \delta\rho(r,t), \frac{\delta\rho}{\delta v}, \mathrm{spectra}$$

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Polarizability χ

δv **External Perturbation**
(variation in the external potential)

$\delta \rho$ **Induced Density**
(variation in the density induced by δv)

implicit definition of the *polarizability* χ:

$$\delta\rho = \chi\delta v$$

Polarizability χ

Fundamental quantity associated to the cond-mat system - purpose of the TDDFT calculation

δv is also indicated as $\delta v = \delta v_{ext}$

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LR-TDDFT Kohn-Sham scheme: the Independent Particle Polarizability $\chi^{(0)}$

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

$$\delta\rho^{\mathrm{KS}} = \delta\rho$$

definition of the polarizability of the Kohn-Sham system:

$$\delta\rho = \chi^{\mathrm{KS}}\delta v^{\mathrm{KS}}$$

Kohn-Sham polarizability
(or independent-particle polarizability)

It is also indicated as $\chi^{KS} = \chi_s = \chi^{(0)} = \chi^0$

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Variation in the Kohn-Sham effective Total Potential

We write the Kohn-Sham effective potential variation δv^{KS} (= δv_s) as the external + screening, composed of an Hartree and an XC potential:

$$\delta v^{\mathrm{KS}} = \delta v + \delta v_{\mathrm{H}} + \delta v_{xc}$$

Kohn-Sham or Effective Perturbation

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

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

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

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

Exchange-Correlation Kernel definition

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

By variation δv^{KS} (= δv_s) of the Kohn-Sham equations, one obtains the Linear-Response variation of the density $\delta\rho$ and then an expression for χ^{KS} in terms of the Kohn-Sham energies and wavefunctions:

$$\chi^{\mathrm{KS}}(r,r',\omega)=\sum_{ij}(f_i-f_j)\frac{\phi_i(r)\phi_j^*(r)\phi_i^*(r')\phi_j(r')}{\omega-(\epsilon_i-\epsilon_j)-i\delta}$$

Independent-Particle Polarizability (Adler-Wiser)

In Frequency-Reciprocal space:

$$\chi^{\mathrm{KS}}_{GG'}(q,\omega)=\sum_{ij}(f_i-f_j)\frac{\langle\phi_j|e^{-i(q+G)r}|\phi_i\rangle\langle\phi_i|e^{+i(q+G')r'}|\phi_j\rangle}{\omega-(\epsilon_i-\epsilon_j)-i\delta}$$

χ as a function of χ^{KS}

From:

$$\begin{cases} \delta\rho = \chi\delta v \\ \delta\rho = \chi^{\mathrm{KS}}\delta v^{\mathrm{KS}} \end{cases}$$

The polarizability in terms of the independent-particle polarizability is:

$$\chi = \chi^{\mathrm{KS}} + \chi^{\mathrm{KS}}(v_c + f_{xc})\chi$$

Polarizability χ

Coulombian (Local-Fields)

Exchange-Correlation Kernel

Also explicitly:

$$\chi = \left(1 - \chi^{\mathrm{KS}}v_c - \chi^{\mathrm{KS}}f_{xc}\right)^{-1}\chi^{\mathrm{KS}}$$

Dielectric Function

δv_{tot}

$\delta v_{tot} = \delta v_{ext} + \delta v_H$ classical potential → test-particle

$\delta v_{tot} = \delta v_{ext} + \delta v_H + \delta v_{xc}$ quantistic potential → test-electron

$$\delta v_{tot} = \varepsilon^{-1} \delta v_{ext}$$ definition of the Dielectric Function ε

$$\boxed{\varepsilon^{-1} = 1 + v_c \chi}$$ **Test-Particle Dielectric Function**

$\varepsilon_{te}^{-1} = 1 + (v_c + f_{xc})\chi$ Test-Electron Dielectric Function

From the Microscopic to the Macroscopic Dielectric Function

$$\varepsilon_M(r,r') = \overline{\varepsilon(r,r')}$$

$$\varepsilon_M(q,\omega) = \frac{1}{\varepsilon_{00}^{-1}(q,\omega)}$$

Macroscopic Dielectric Function ε_M

$\varepsilon_{GG'}^{-1}(q,\omega)$ In a periodic system

Macroscopic Dielectric Function ε_M → **Observables** →

$$\mathrm{ABS}(\omega) = \mathrm{Im}\,\varepsilon(\omega)$$

$$\mathrm{ELF}(\omega) = -\mathrm{Im}\,\varepsilon^{-1}(\omega)$$

$$\varepsilon_M^{LF} \neq \varepsilon_{00} = \varepsilon_M^{NLF}$$

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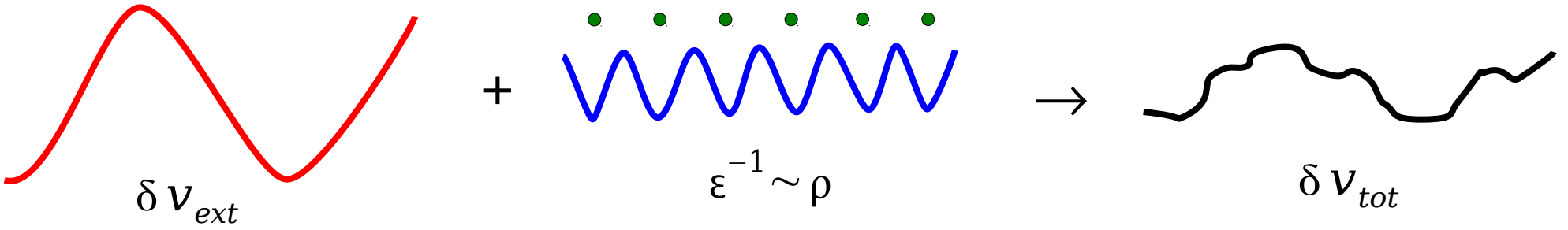
Local-Fields Effects (LF)

$$\delta v_G^{tot} = \sum_{G'} \varepsilon^{-1}_{G G'} \delta v^{ext}_{G'}$$

Effect of the ε non diagonal elements (density inhomogeneities)



$$\varepsilon_M^{NLF}(q,\omega) = \varepsilon_{00}(q,\omega)$$

Macroscopic Dielectric Function ε without local-fields effects (NLF)

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TDDFT: fundamental equations

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

Dielectric Function ε → Observables

$$\mathrm{ABS}(\omega) = \mathrm{Im}\,\varepsilon(\omega)$$

$$\mathrm{ELF}(\omega) = -\,\mathrm{Im}\,\varepsilon^{-1}(\omega)$$

$$\chi = \chi^{\mathrm{KS}} + \chi^{\mathrm{KS}}(v_c + f_{xc})\chi$$

Polarizability χ

Coulombian (Local-Fields)

Exchange-Correlation Kernel

$$\chi^{\mathrm{KS}}(r, r', \omega) = \sum_{ij}(f_i - f_j)\frac{\phi_i(r)\phi_j^*(r)\phi_i^*(r')\phi_j(r')}{\omega - (\epsilon_i - \epsilon_j) - i\delta}$$

Independent-Particle Polarizability (Adler-Wiser)

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

Exchange-Correlation Kernel

approximations required

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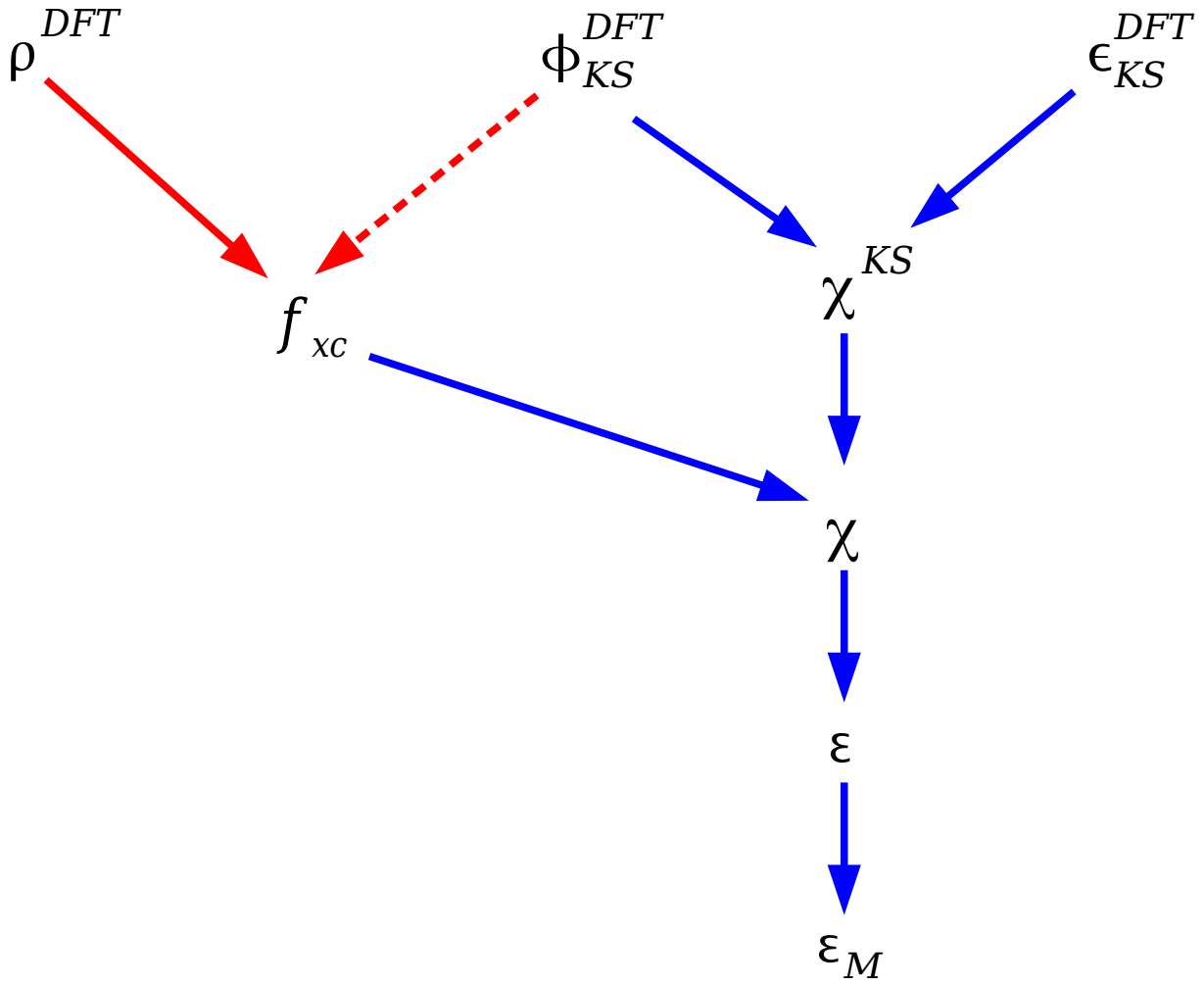
LR-TDDFT Calculation Scheme Résumé



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DP code

dp code (dielectric properties)

- The thing: **Linear-Response TDDFT** code in **Frequency-Reciprocal** Space on **PW** basis.
- Purpose: Dielectric and Optical Properties (Absorption, Reflectivity, Refraction, EELS, IXSS, CIXS,..
- Systems: bulk, surfaces, clusters, molecules, atoms (through supercells) made of insulator, semiconductor and metal elements.
- Approximations: RPA, ALDA, GW-RPA, LRC, non-local kernels, …, with and without LF (Local Fields).
- Machines: Linux and other UNIX flavours, even Windows porting.
- Libraries: BLAS, Lapack, CXML, ESSL, IMSL, ASL, Goedecker, FFTW.
- Interfaces: ABINIT

http://www.dp-code.org

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Frequency-Reciprocal space:
why and where could be convenient

- Reciprocal Space → Infinite Periodic Systems (Bulk, but also Surfaces, Wires, Tubes with the use of Supercells);
- Frequency Space → Spectra.

In the case of isolated systems (atoms, molecules) it is more convenient a real space-time approach (e.g. Octopus code)

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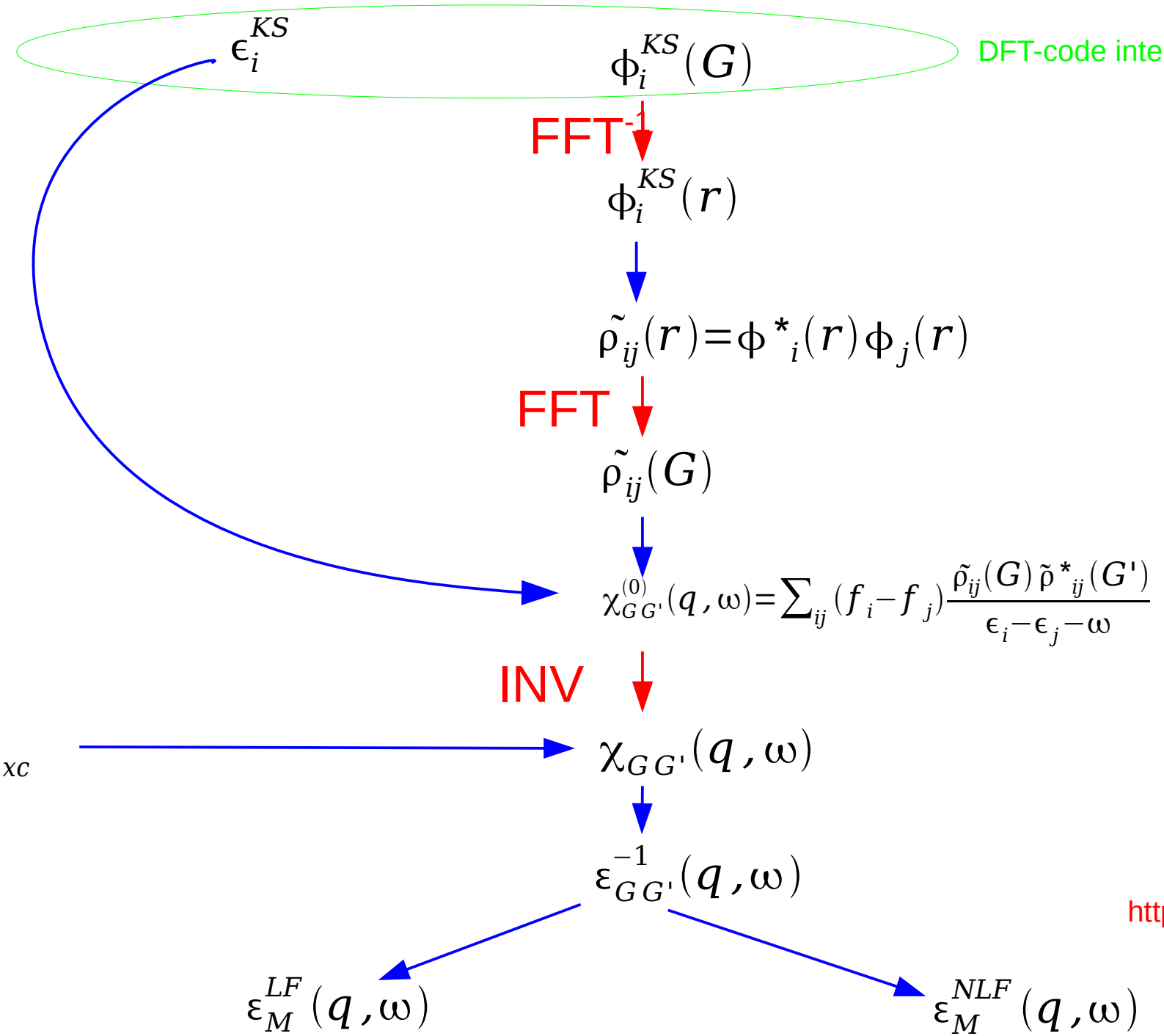
DP Flow Diagram



http://www.dp-code.org

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):

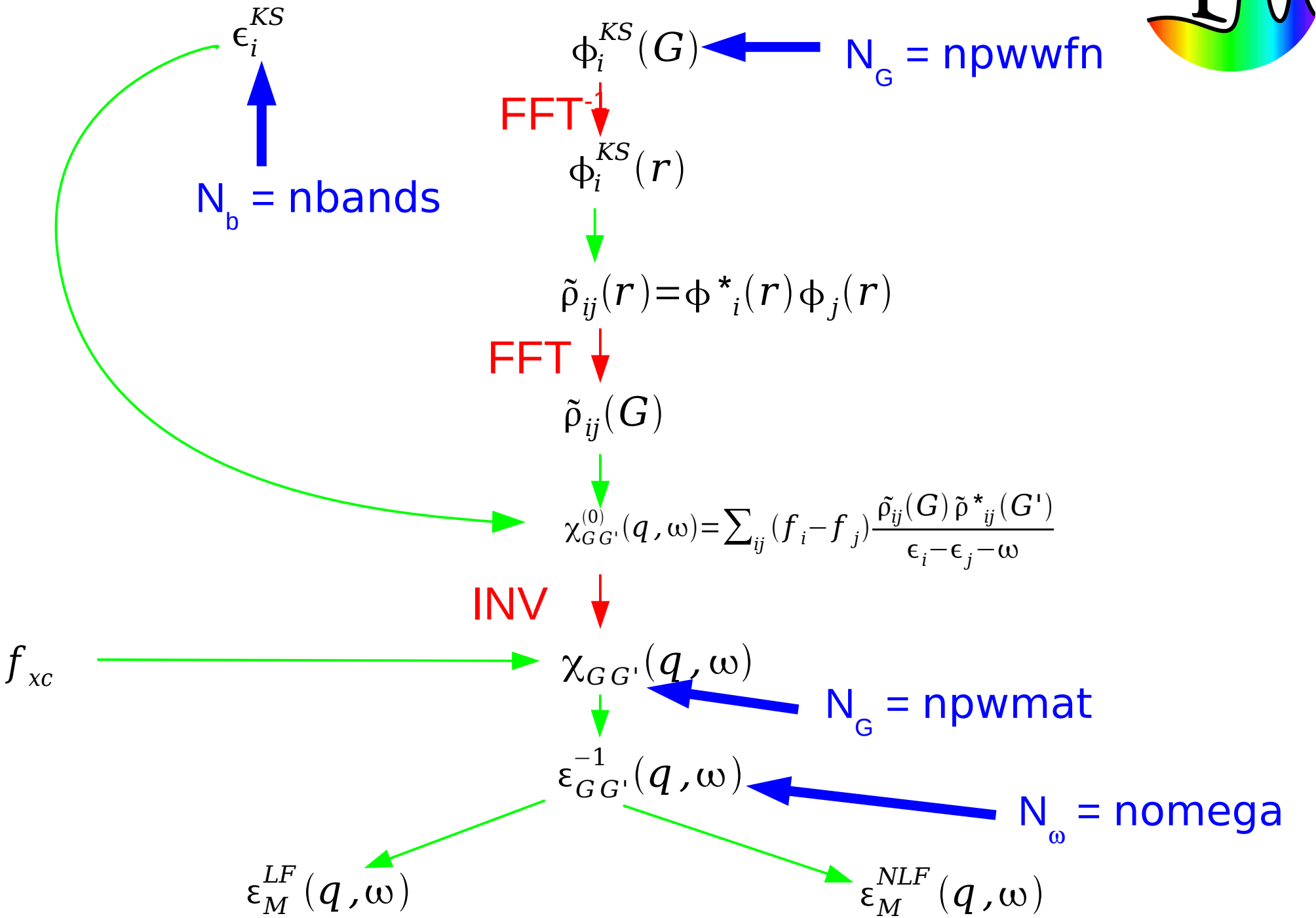
$$\chi_{G G'} = (1 - \chi^{(0)} v_c - \chi^{(0)} f_{xc})^{-1}_{G G''} \chi^{(0)}_{G'' G'}$$

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

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

$O(N^2)$ instead of $O(N^3)$

DP Parameters



DP performances: CPU scaling and Memory usage

- CPU scaling for $\chi^{(0)} \; : \; N_b N_k (N_\omega N_G^2 + N_r \log N_r)$
- CPU scaling for $\varepsilon^{-1} \; : \; N_\omega N_G^2$
- Memory occupation $N_\omega N_G^2 + N_r N_k N_b$

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XC Approximations

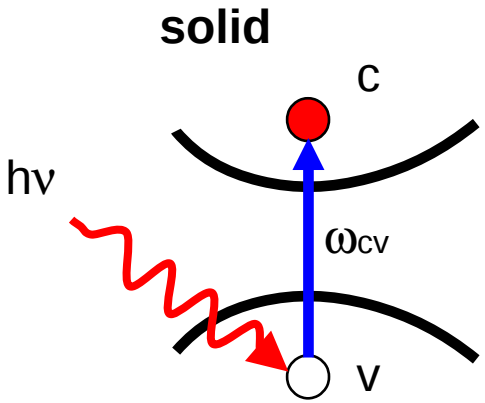
Exchange-Correlation Kernel f_{xc}: the RPA approximation

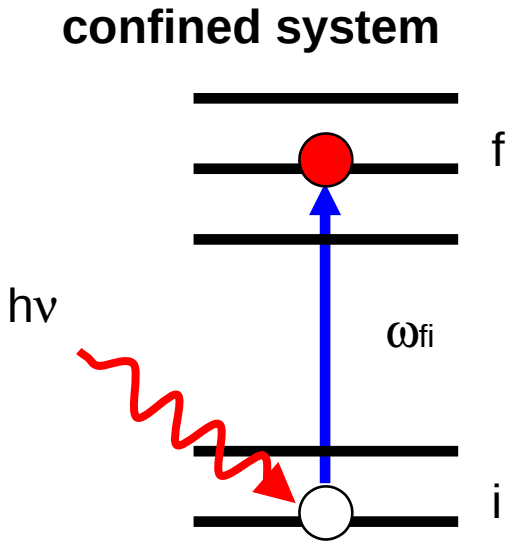
- Random Phase Approximation = neglect of the exchange-correlation effects (in the response)
  - **RPA** $$f_{xc}^{\mathrm{RPA}} = 0$$

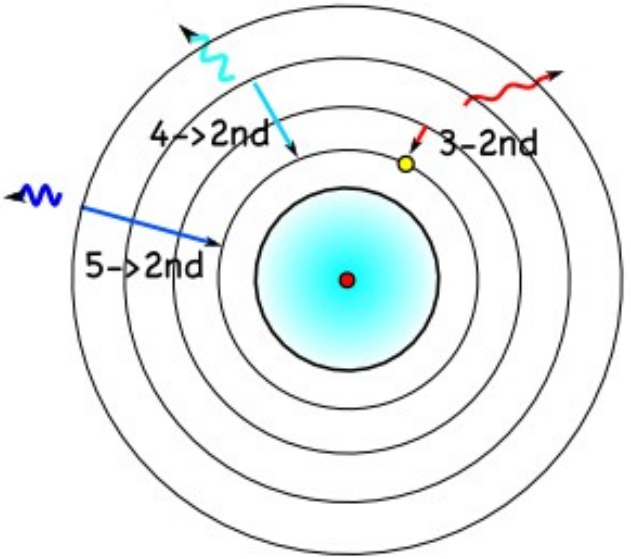
RPA Approximation

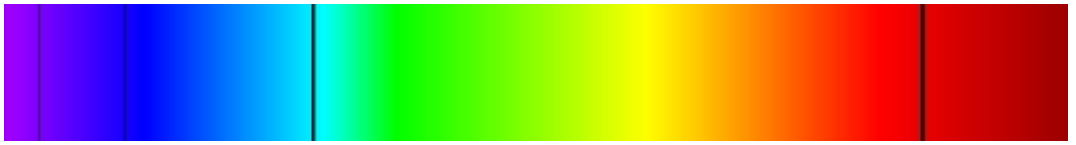
RPA (without Local Fields) = sum over independent transitions

(application of Fermi's Golden Rule to an independent particle system)









$$\mathrm{Im}\,\varepsilon^{\mathrm{RPA}}(\omega) = \sum_{vc} |\langle \phi_c | \mathbf{D} | \phi_v \rangle|^2 \delta(\omega - (\epsilon_c - \epsilon_v))$$

Fermi's Golden Rule

Optical Absorption

KS wavefunctions

KS energies

Adiabatic Local Density Approximation (TDLDA)

- The Adiabatic Local Density Approximation
  - **ALDA**

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

$$f_{xc}^{\mathrm{ALDA}}(r,r') = A(r)\delta(r,r')$$

local in r-space
static (no memory effects)

TDDFT: Results

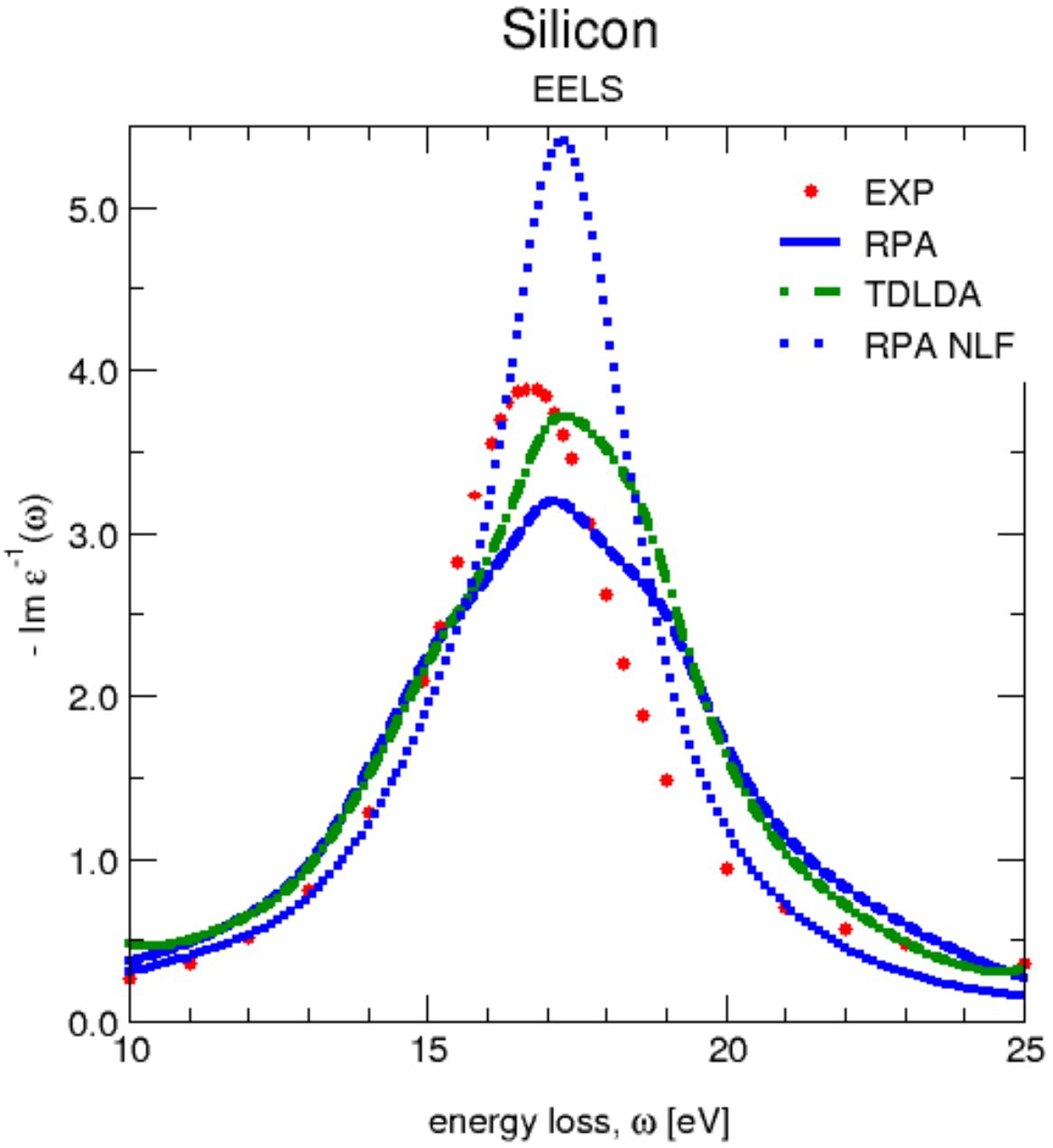
		RPA	ALDA
Isolated	Energy Loss	ok	ok
	Optical Prop	ok but..	ok but..
Solids	Energy Loss	ok	ok
	Optical Prop	no	no

Energy Loss -> $-\mathrm{Im}\ \varepsilon^{-1}$

Optical Properties -> $\mathrm{Im}\ \varepsilon$

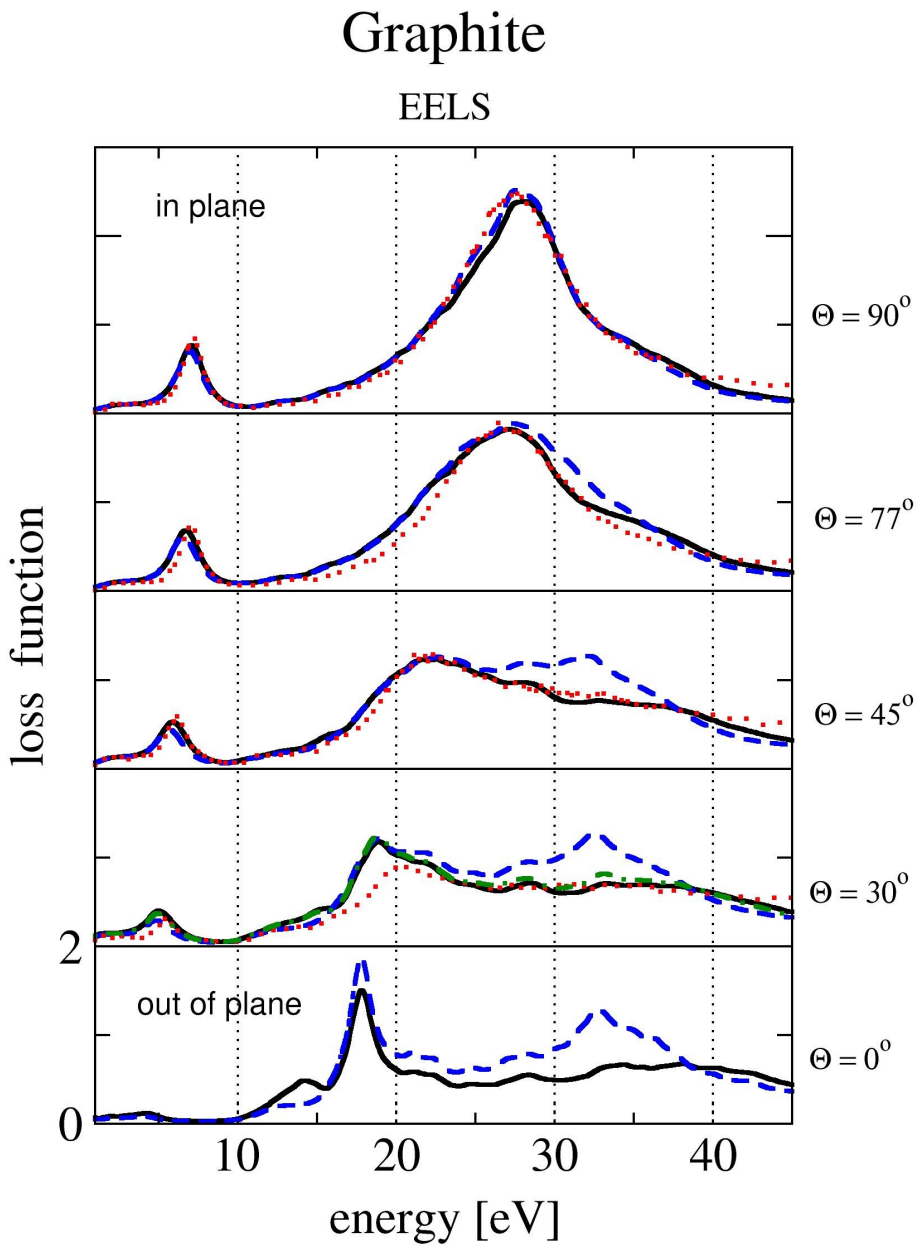
TDDFT Results: Energy Loss

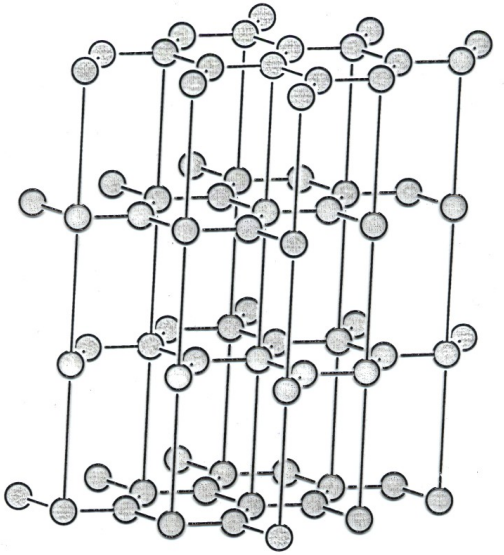
TDDFT and EELS in Solids



- TDLDA (but also RPA) in good agreement with experiment;
- Importance of Local-Field (LF) effects.

Local Field Effects in EELS

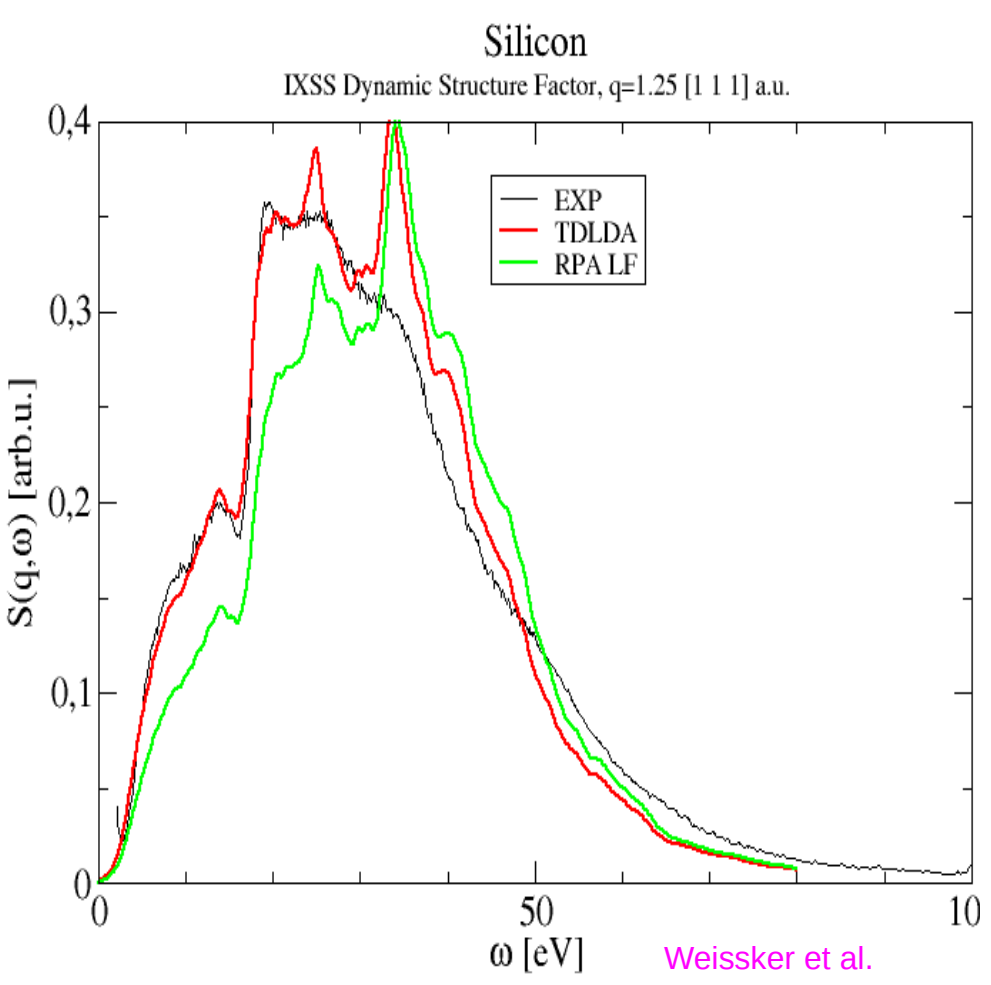




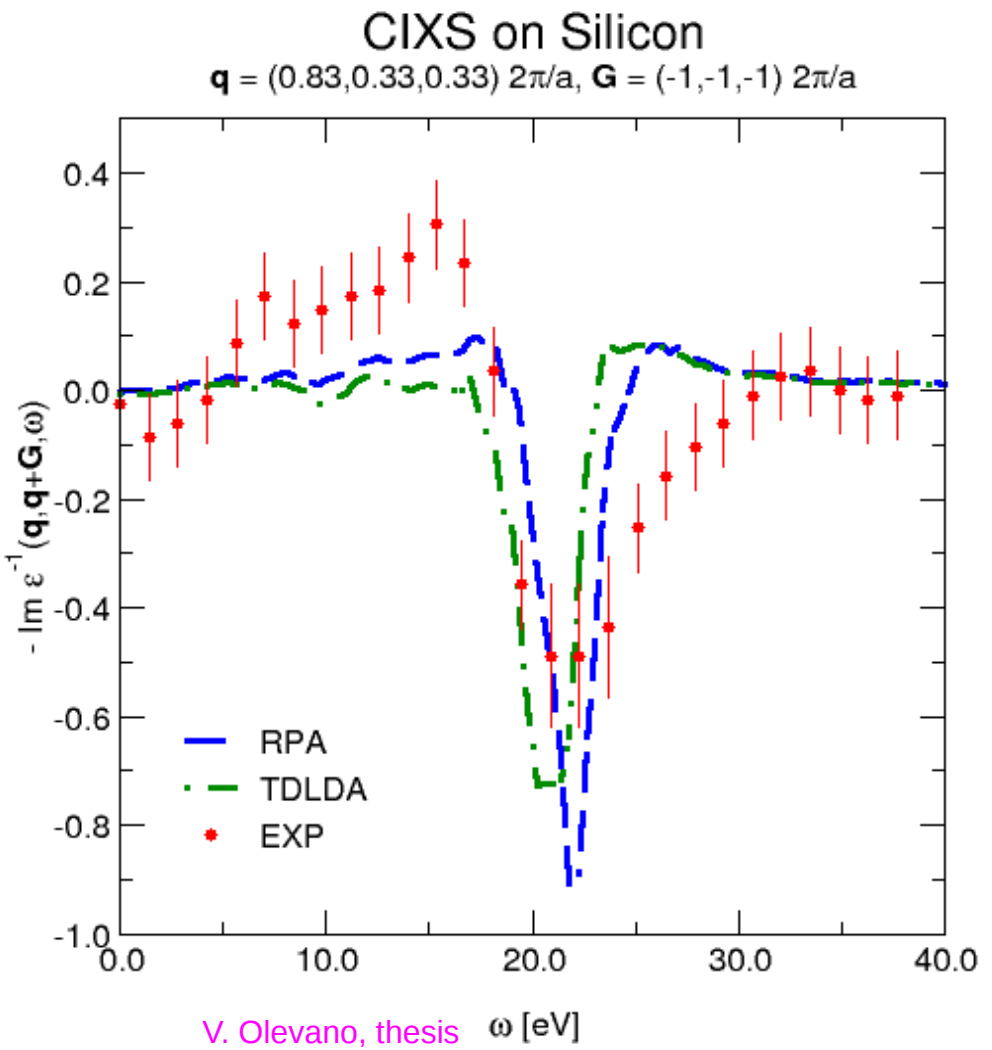
- RPA is enough. But when inhomogeneities are present, Local-Field effects should be absolutely taken into account.
- **Quantitative** Agreement

A. Marinopoulos et al. PRL **89**, 76402 (2002)

IXSS and CIXS
and other synchrotron-radiation spectroscopies



Weissker et al.



V. Olevano, thesis

- In Solids all Dielectric Properties related to the Energy-Loss function are well described by TDDFT in RPA with an improvement in ALDA.

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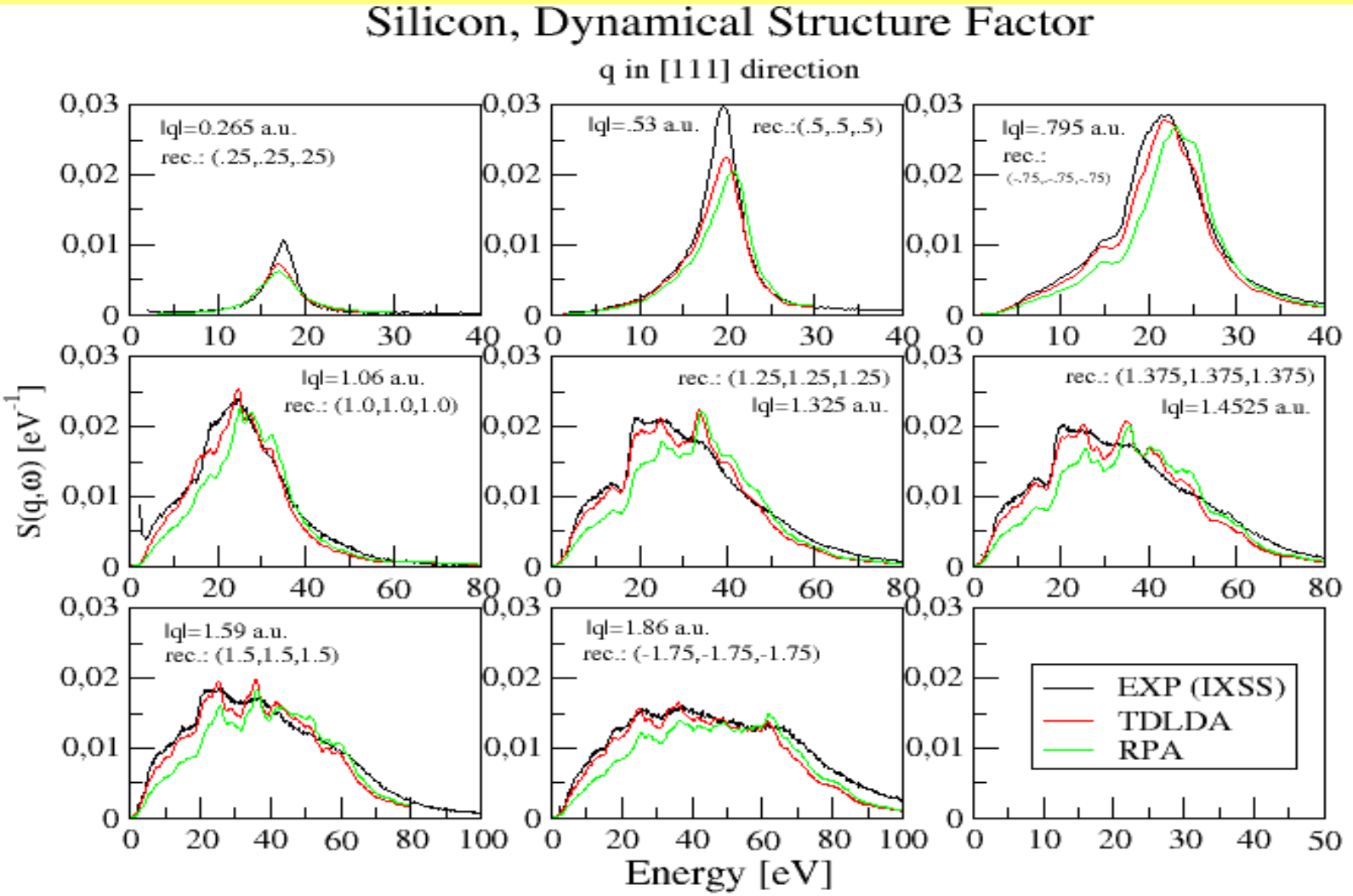
IXSS synchrotron-radiation spectroscopy

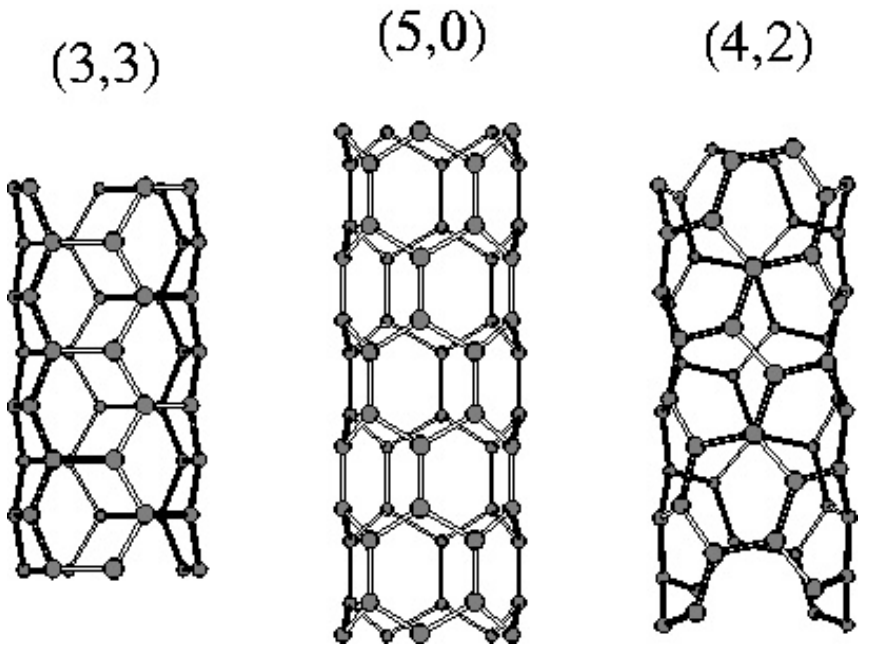


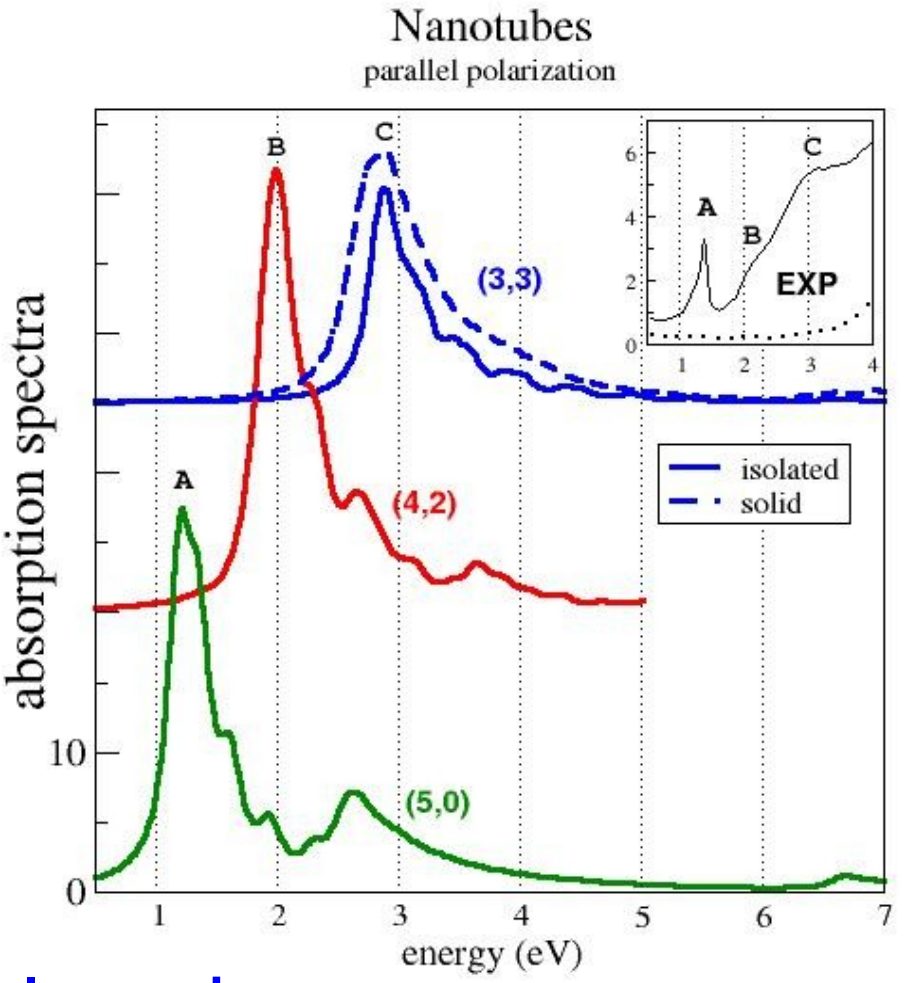
Weissker et al.

- In Solids all Dielectric Properties related to the Energy-Loss function are well described by TDDFT in RPA with an improvement in ALDA.

TDDFT Results: Optical Properties

TDDFT RPA
Optical Properties in Nanotubes





- RPA is qualitatively able to interpret observed structures in optical spectra

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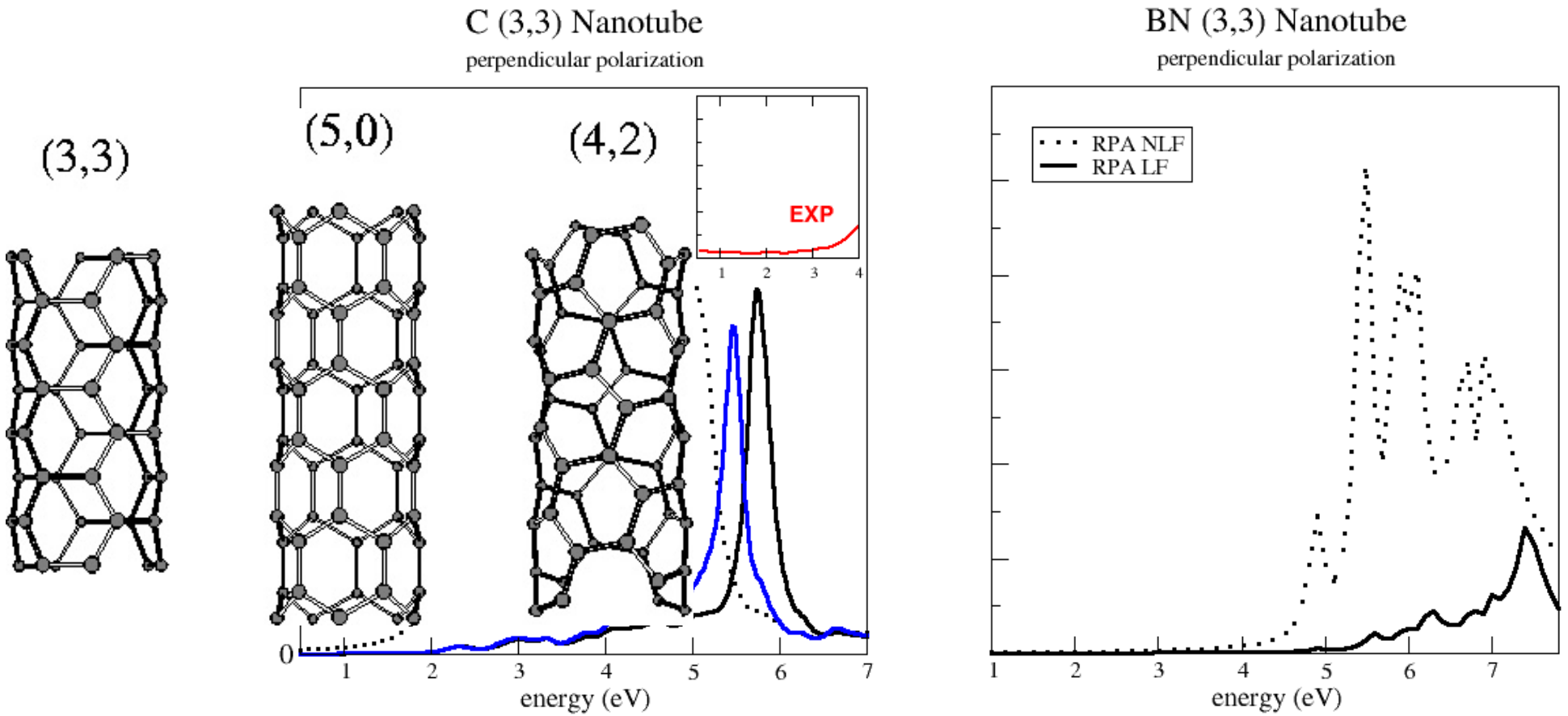
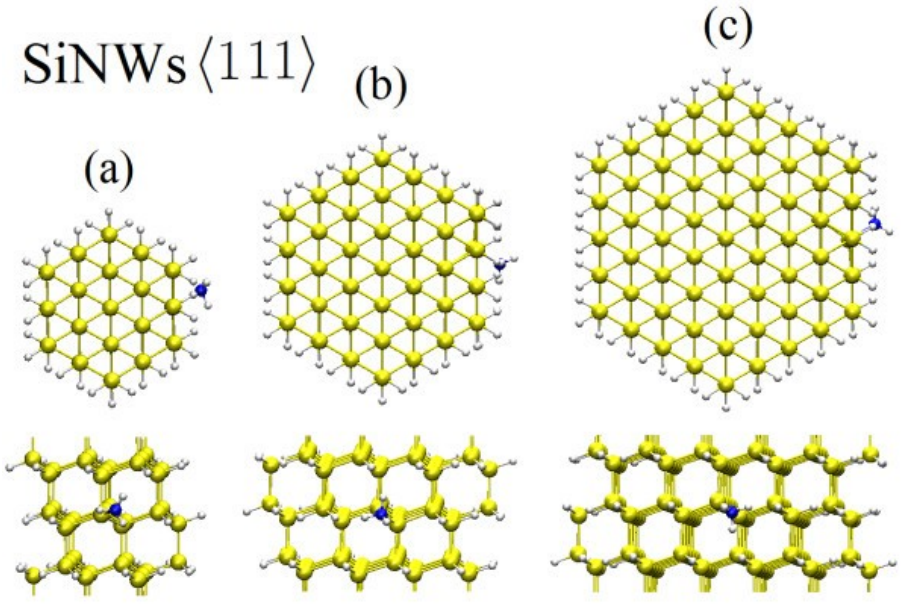
LF Effects in in C and BN Nanotubes

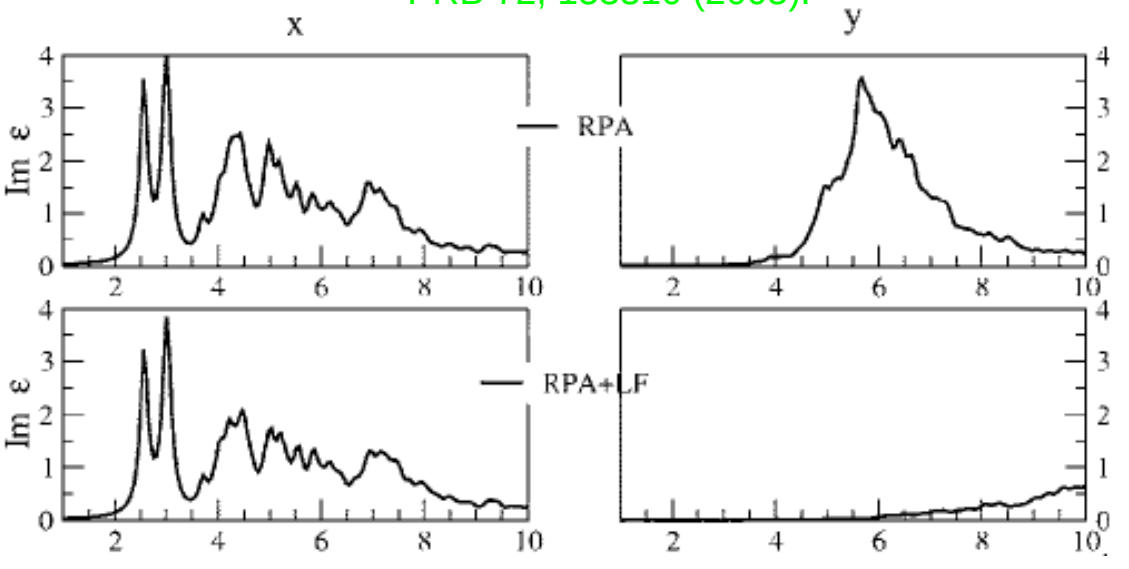


- LF explain depolarization effects both for C and BN Nanotubes in perpendicular polarization optical spectra

LF Effects in in Si Nanowires



PRB 72, 153310 (2005).



- LF explain depolarization effects for Nanowires in perpendicular polarization optical spectra

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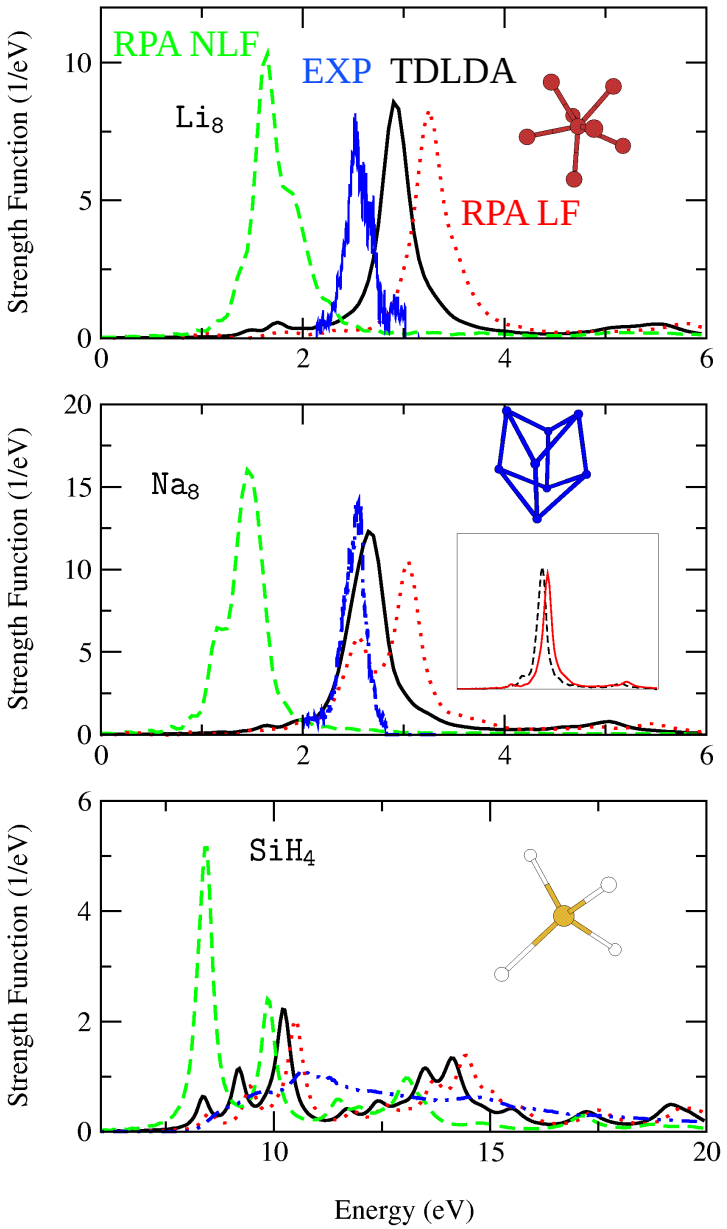
Optical Absorption in Clusters



- Fair agreement (improvable) of the TDLDA result with the Experiment.

G. Onida et al, Rev. Mod. Phys. **74**, 601 (2002).

TDDFT Excitation Energies

eigenvalues = poles of χ

$$\sum_{t'} \Omega_{tt'}(\omega = E_\lambda) A^\lambda_{t'} = E^2_\lambda A^\lambda_t$$

Casida equation
(same equation as
RPA of nuclear physics)

eigenvectors = oscillator strengths

$$\Omega_{tt'} = \omega_t^2 \delta_{tt'} + 2\sqrt{\omega_t \omega_{t'}} f^{Hxc}_{tt'}$$

$$\omega_t = \epsilon_c - \epsilon_v$$ Kohn-Sham excitation energies

$$f^{Hxc}_{tt'} = \int dr_1 dr_2 \phi^*_c(r_1)\phi_v(r_1)[v_c(r_1,r_2) + f_{xc}(r_1,r_2,\omega)]\phi^*_{v'}(r_2)\phi_{c'}(r_2)$$

4-points Hartree+xc kernel

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TDDFT Excitation Energies

eigenvalues = excitations = poles of χ

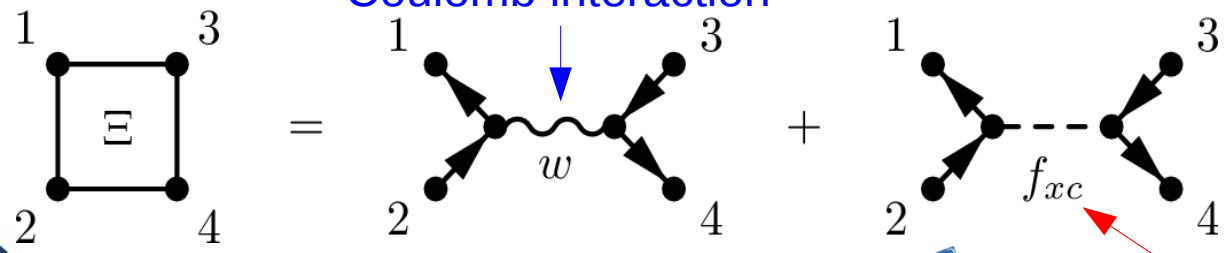
$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

Casida equation
(same equation as
RPA of nuclear physics)

eigenvectors (oscillator strengths)

$$A_{cv,c'v'} = i\Xi_{cv,c'v'} + (\varepsilon_c - \varepsilon_v)\delta_{cc'}\delta_{vv'}$$
$$B_{cv,v'c'} = i\Xi_{cv,v'c'}$$

Kohn-Sham energies



TDDFT kernel

xc-kernel
(must be approximated:
Adiabatic LDA)

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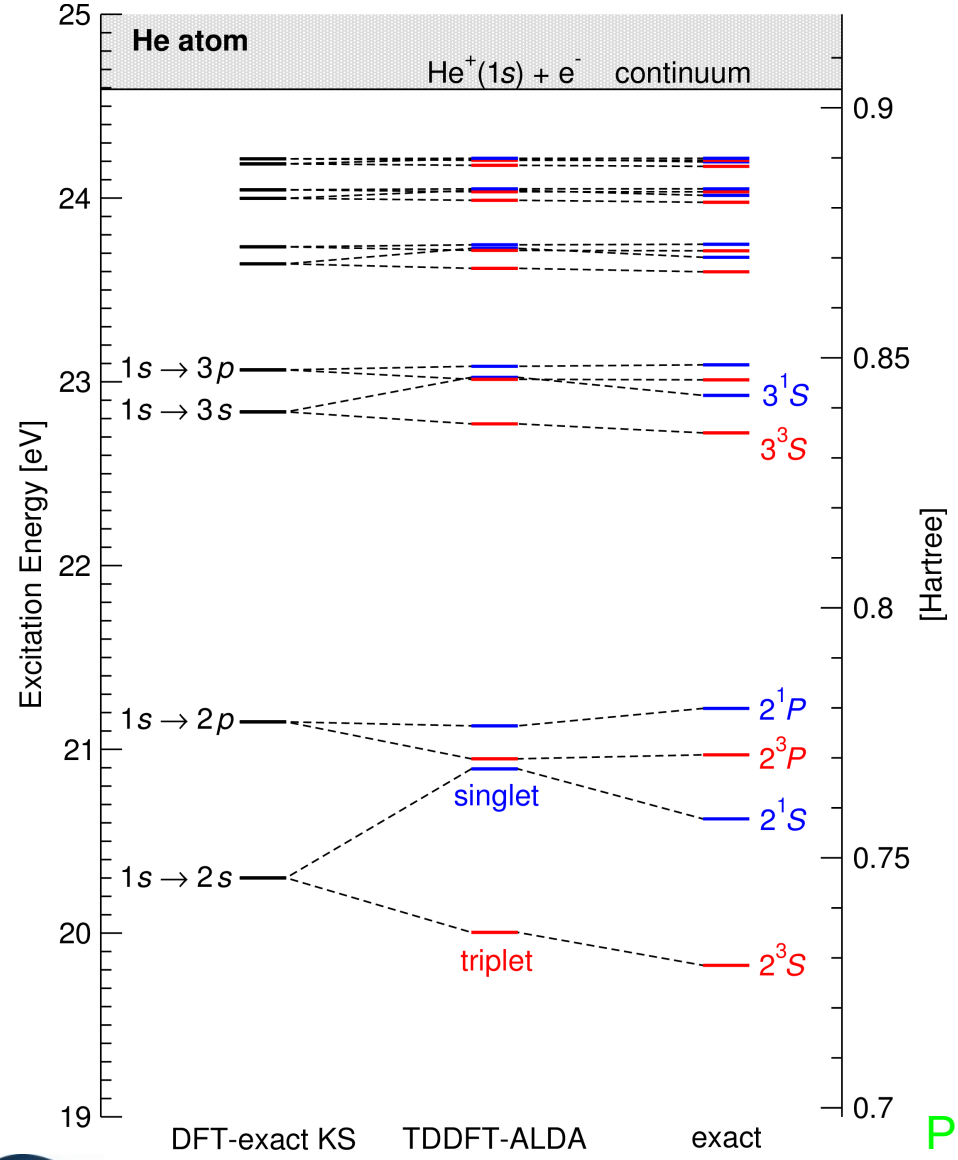
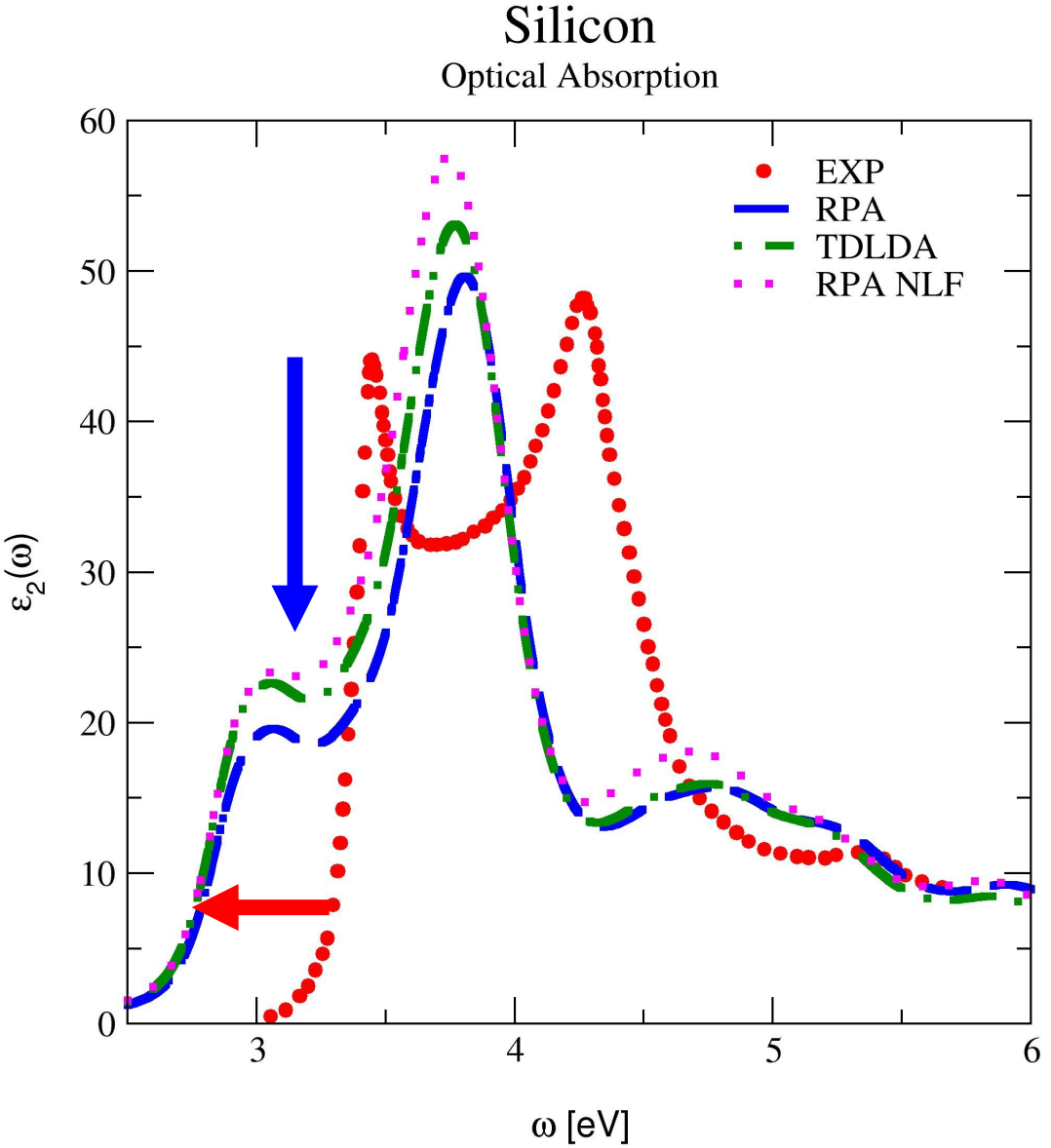
Optical Absorption on Helium atom



- Exact-DFT+Exact-TDDFT must of course reproduce the Exact result.
- Approximated TDLDA on top of Exact-DFT introduces the right singlet-triplet exchange split (but thank to the v term) and performs reasonably well.
- TDLDA performance: 0.2 eV error.

Petersilka, Gross and Burke (2000)

Optical Properties in Solids: Si

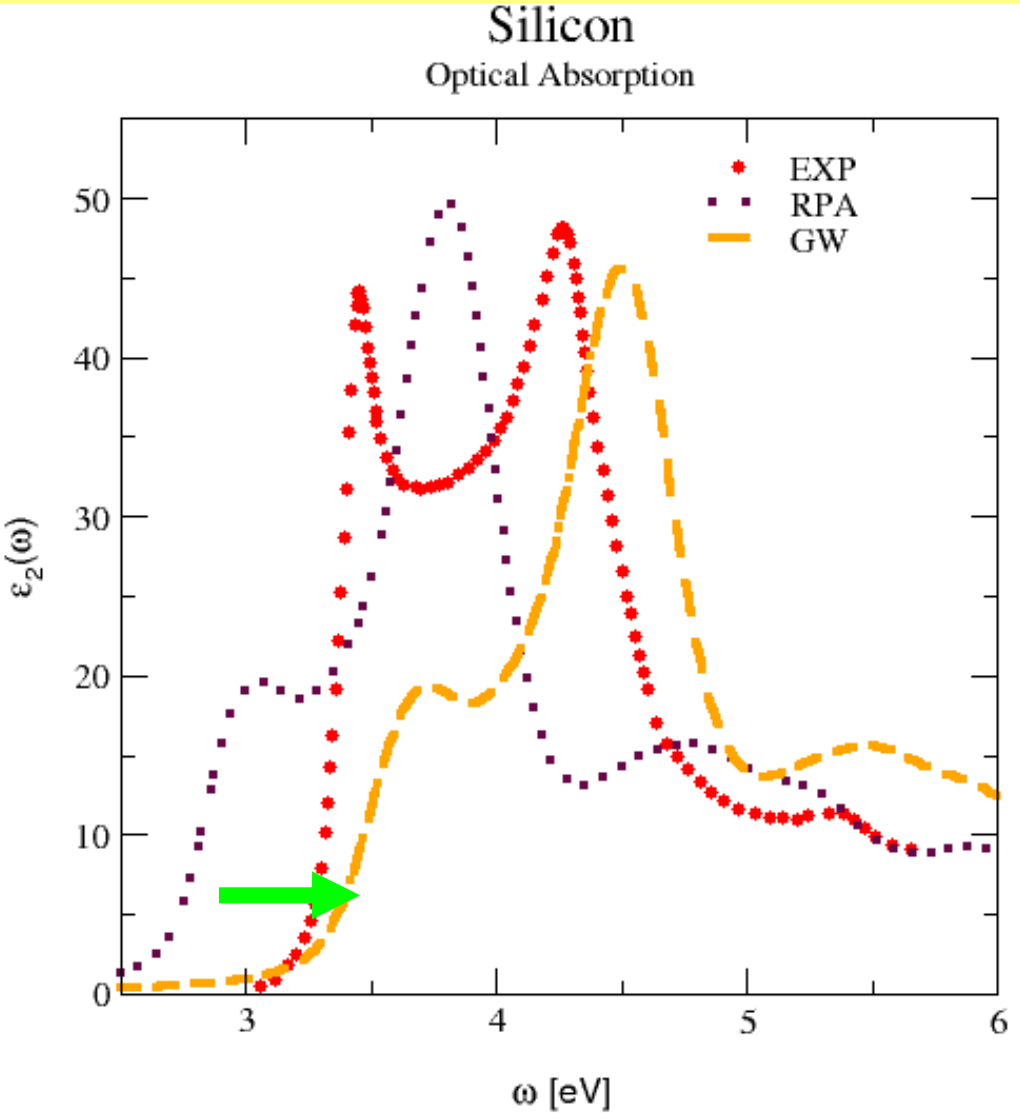


- The TDLDA **cannot** reproduce Optical Properties in Solids.
- We miss both:

1 **Self-Energy (electron-electron) effects** (red shift of the entire spectrum)

2 **Excitonic (electron-hole) effects** (underestimation of the low-energy part)

GW: optical properties in Solids



- GW corrects the red-shift but still misses the Excitonic Effects

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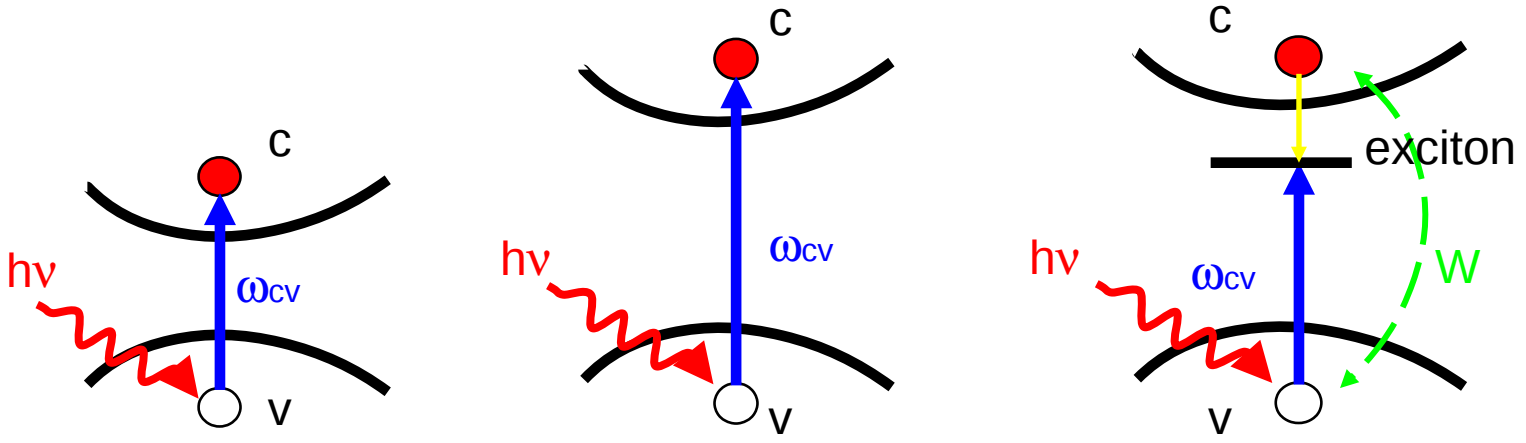
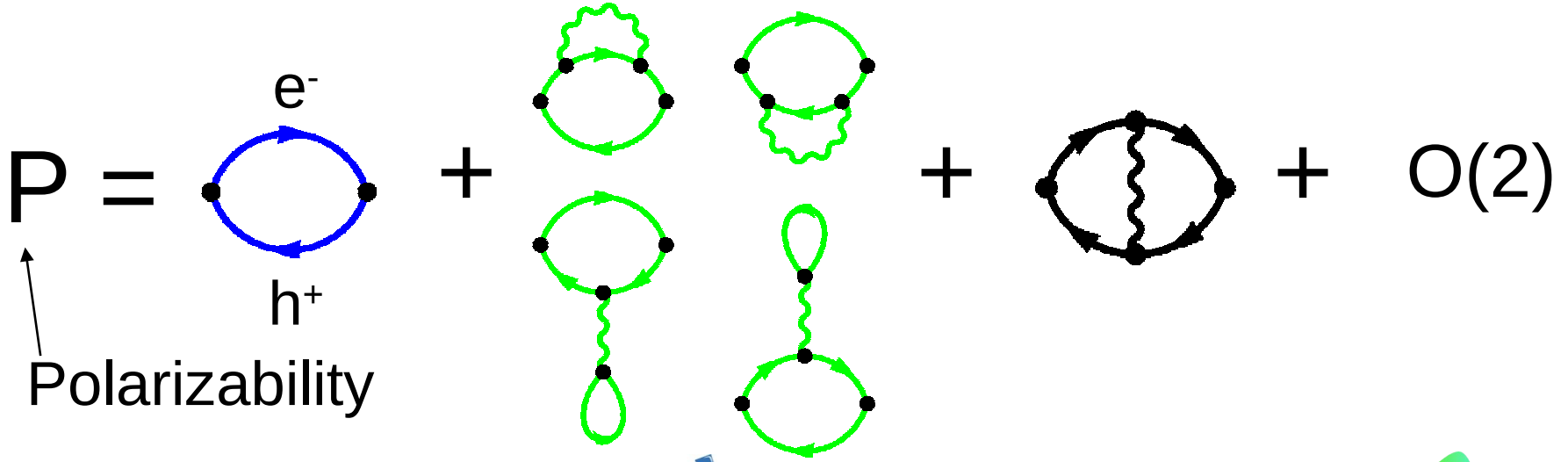
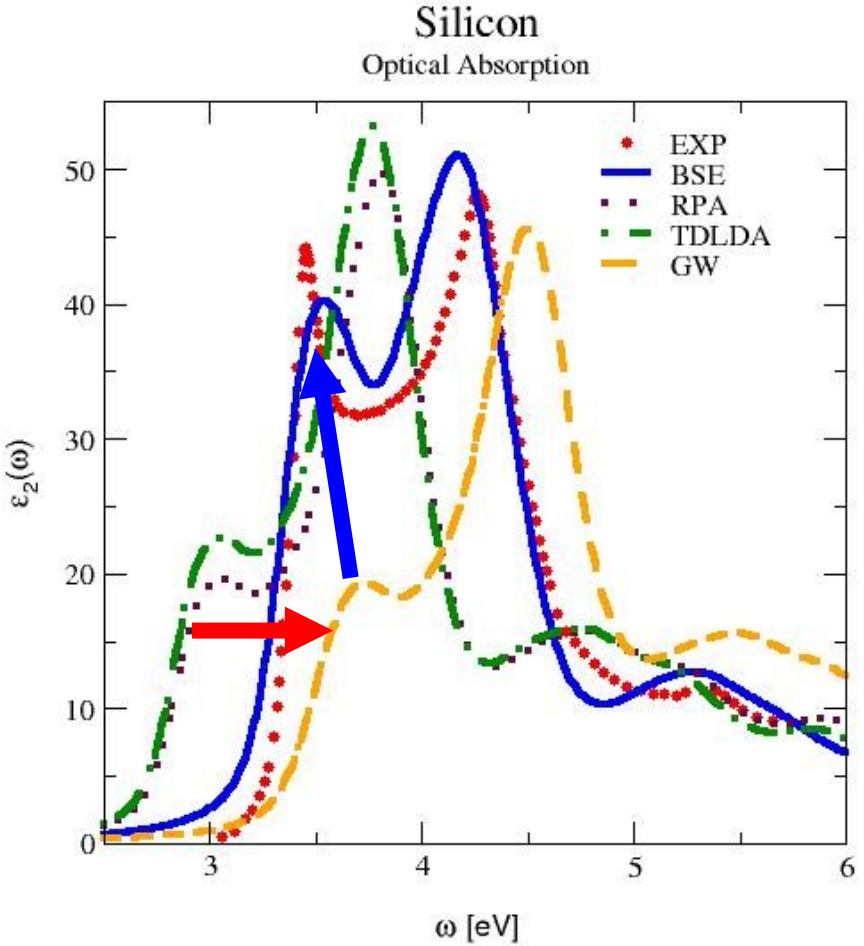
MBPT: GW, BSE and Excitonic Effects

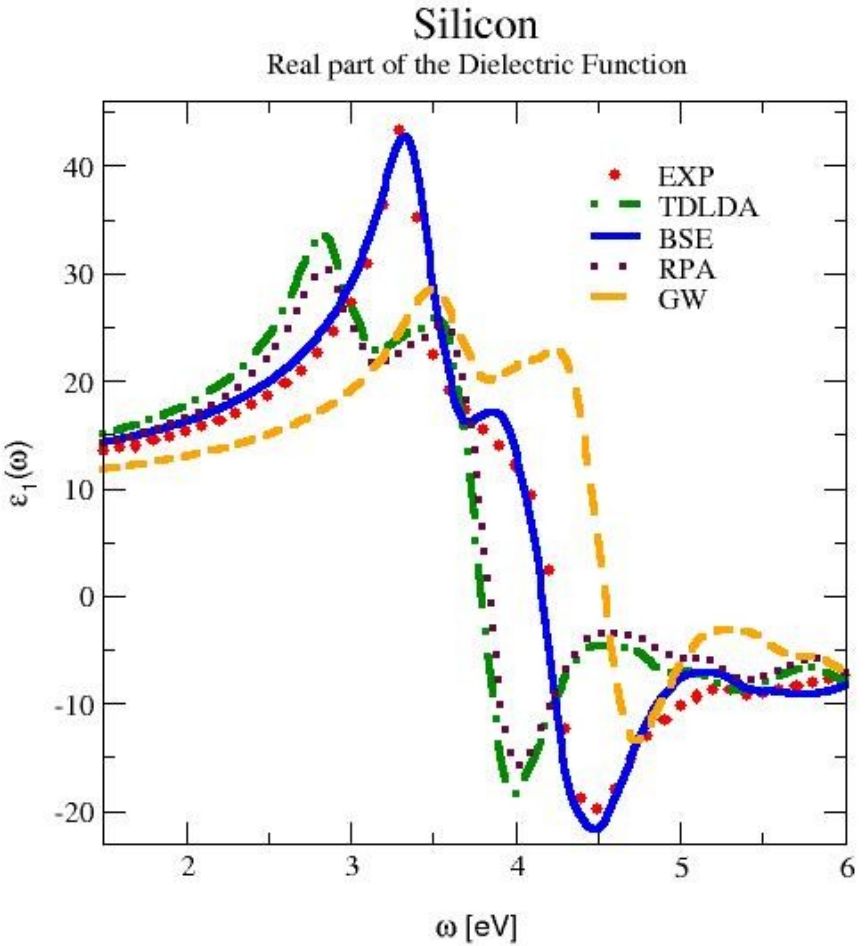


RPA GW BSE



Bethe-Salpeter Equation: optical properties in Solids





- Almost quantitative agreement BSE - experiment

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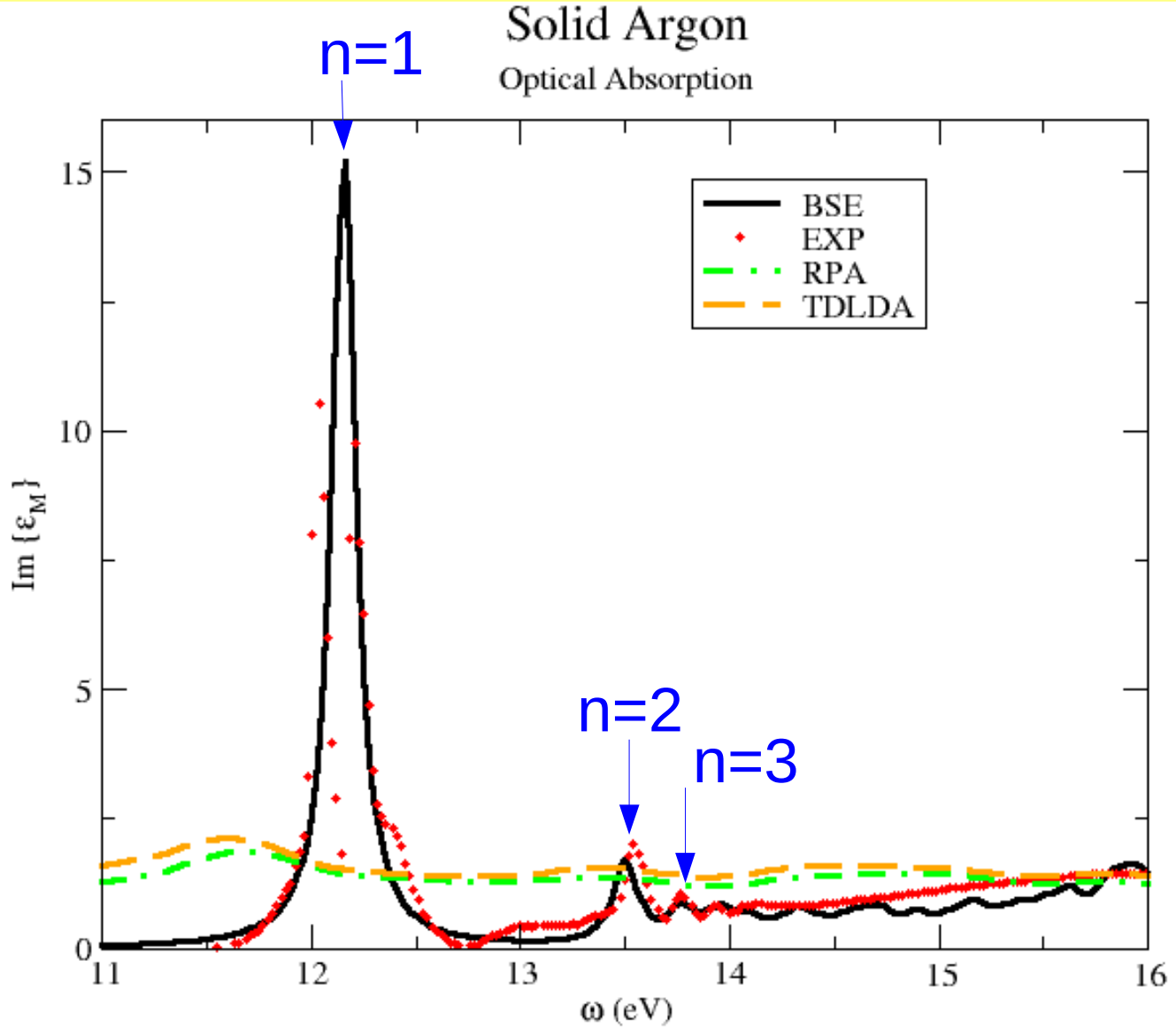
Solid Argon: Hydrogen series



- Exciton ~ Hydrogen atom → $E_n \sim 1/n^2$ Balmer-like series
- BSE can reproduce even **bound Excitons**

What can we do to solve the TDDFT kernel problem?

- If a new Approximation in TDDFT could be established, combining TDDFT's simplicity with MBPT's reliability…
- Hints for this new Approximation: compare critically MBPT with TDDFT fundamental equations.

New Approximations:

LRC

(Long Range Contribution only)

Nanoquanta kernel

(or mapping BSE on TDDFT)

JGM-based NLDA

(Jellium-with-Gap model based bi-local density approximation)

LRC Approximation

long-range coulombian

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

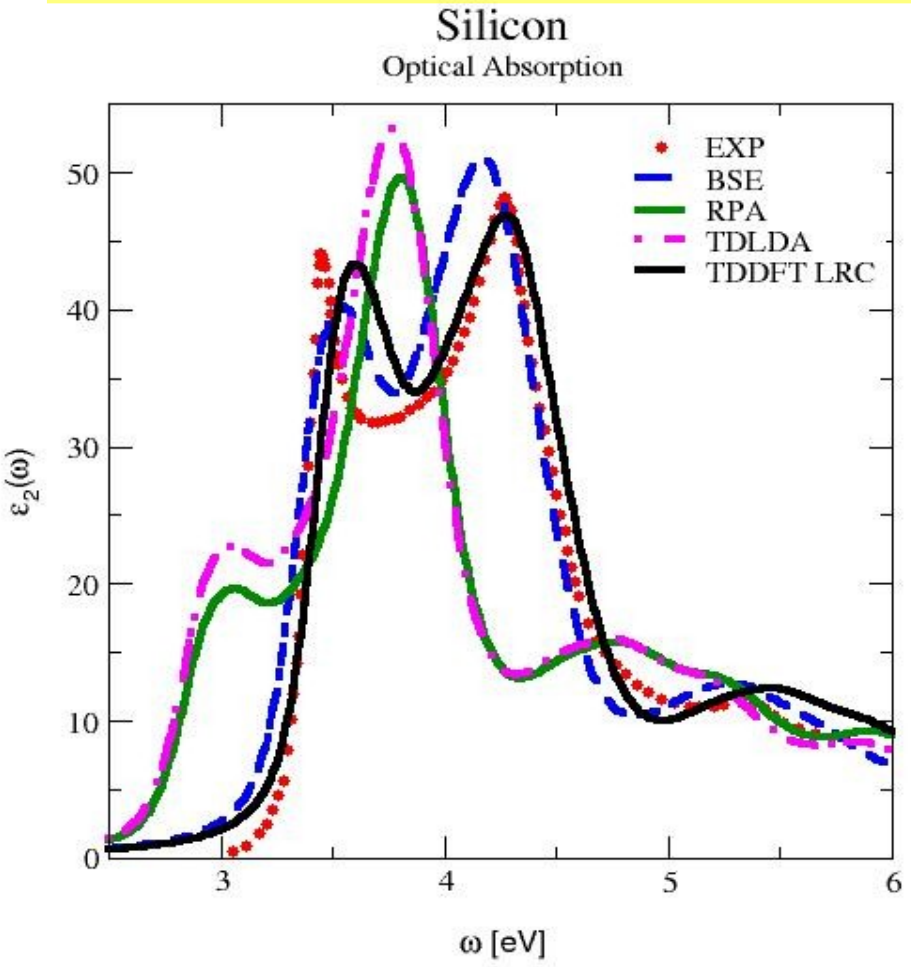
ALDA: local kernel

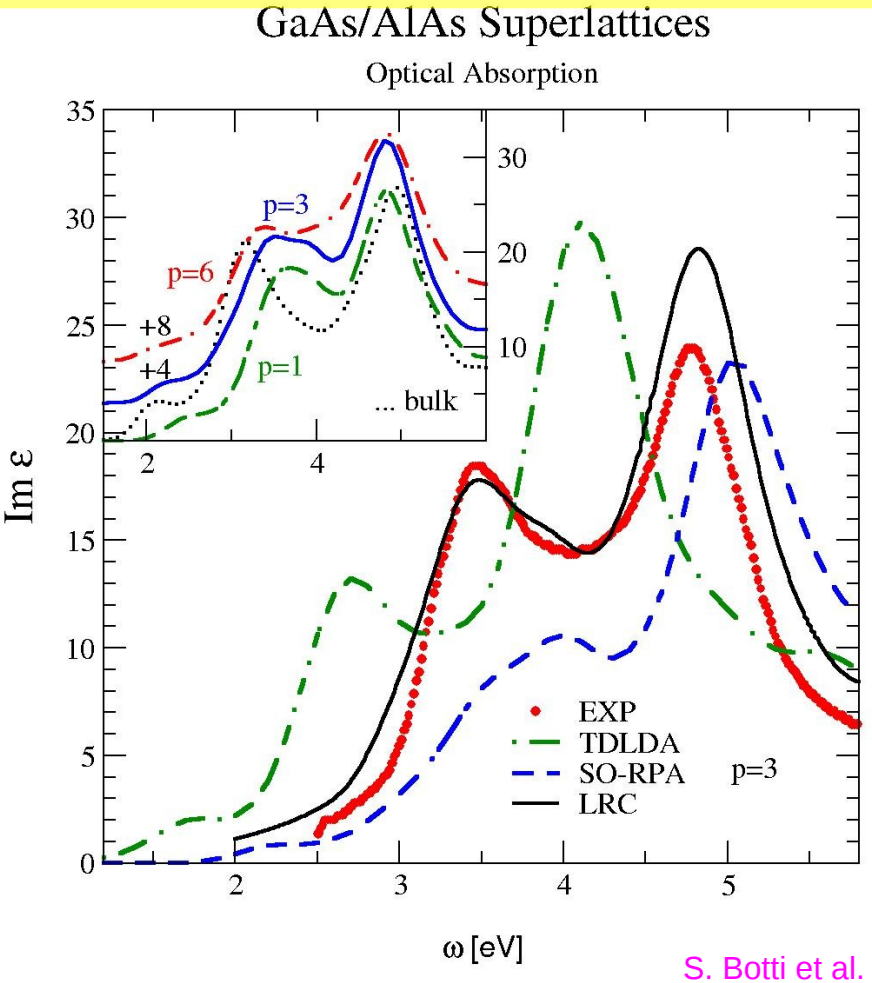
$$f_{xc}^{\mathrm{LRC}} = \frac{\alpha}{q^2}$$

Long Range Contribution only

$\alpha = -4.6\,\varepsilon_{\infty}^{-1}$ Inversely proportional to the screening

TDDFT, LRC approximation





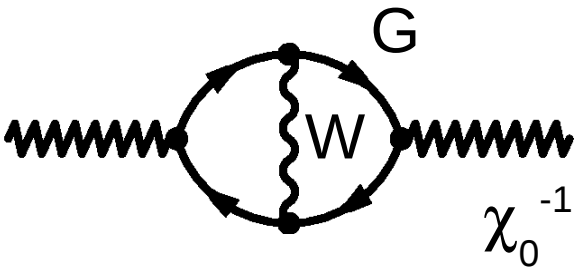
S. Botti et al.

- Thanks to the LRC approximation,

  TDDFT works also on Optical Properties in Solids

Nanoquanta kernel

$$f_{xc} =$$



L. Reining, V. Olevano, A. Rubio and G. Onida, (2001)

G. Adragna and R. Del Sole, (2001)

F. Sottile, V. Olevano and L. Reining, (2004)

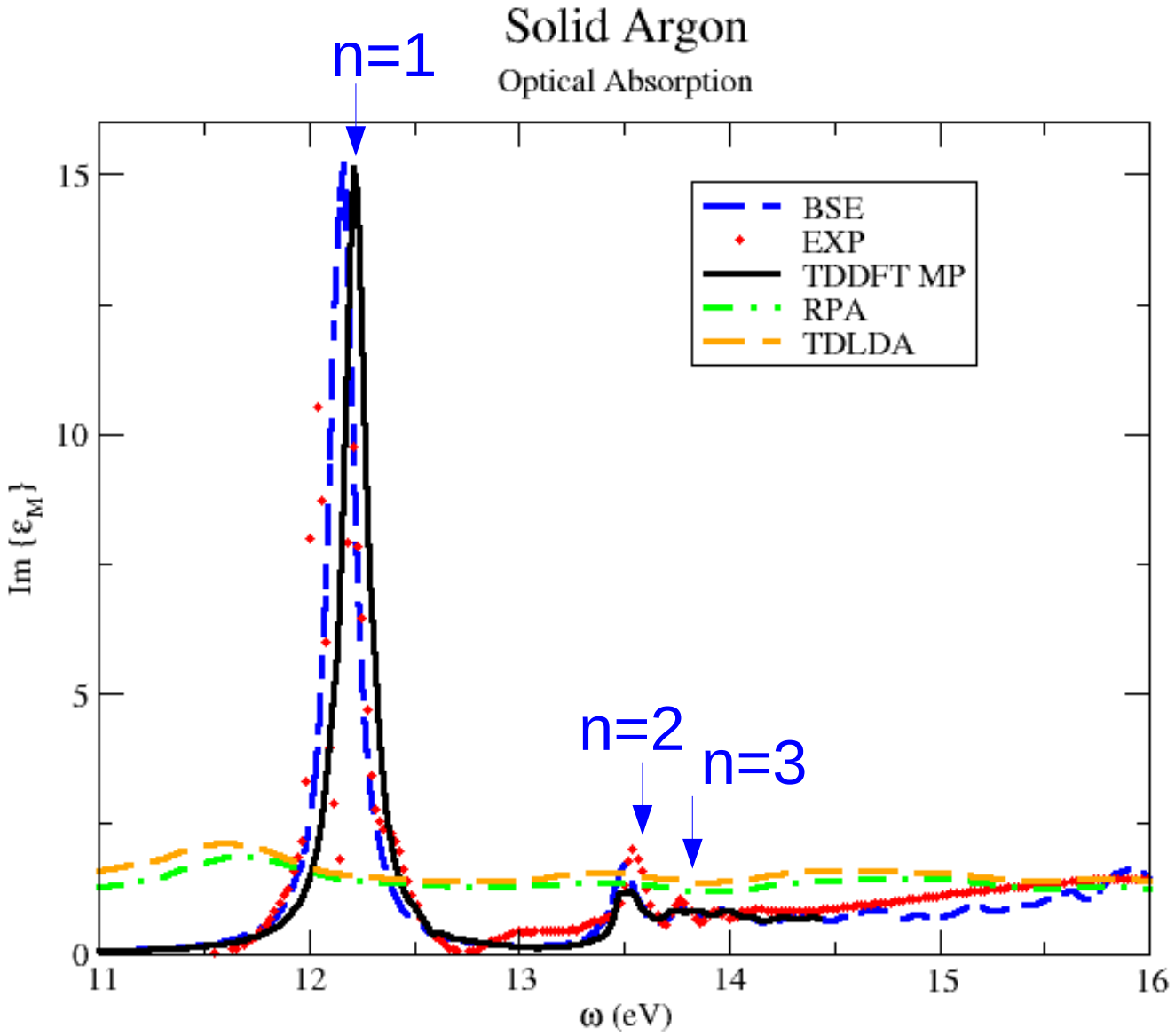
A. Marini, R. Del Sole, A. Rubio, (2004)

U. Von Barth, N. E. Dahlen, R. Van Leeuwen and G. Stefanucci, (2006)

R. Stubner, I. Tokatly and O. Pankratov, (2006)

M. Gatti,, V. Olevano, L. Reining and I. Tokatly, (2007)

Solid Argon: Bound Excitons



F. Sottile et al. 2005

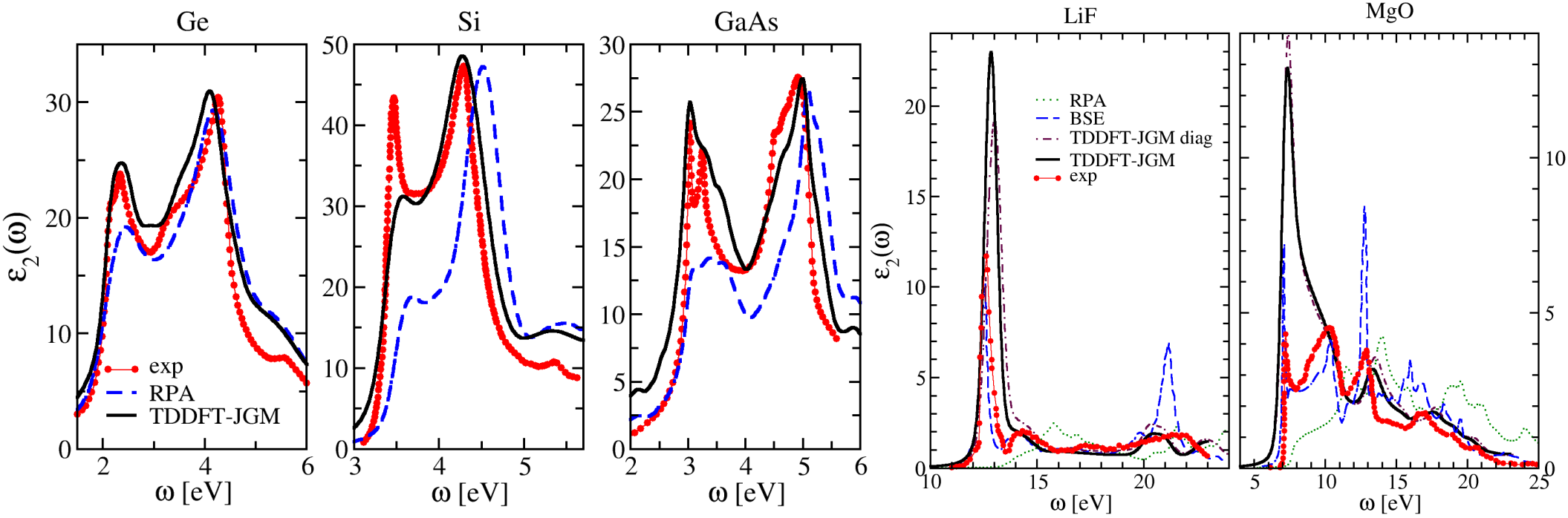
With the **Nanoquanta kernel,** TDDFT describes even **Bound Excitons**

TDDFT JGM NLDA approximation

$$f_{xc}^{\mathrm{JGM}}(q;n,E_g) = \frac{4\pi}{q^2} B'(n,E_g)[e^{-k'_{n,E_g} q^2} - 1] - \frac{4\pi}{k_F^2} \frac{C'(n,E_g)}{1+1/q^2}$$

$$f_{xc}^{\mathrm{JGM}}(q \to 0;n,E_g) \simeq -\frac{E_g^2}{nq^2}$$

P. E. Trevisanutto et al., PRB (2013).



Conclusions

- TDDFT is a valid theory of Condensed Matter Theoretical Physics to calculate from first principles excited-state properties;
- The agreement with the experiment is good, but the choice of the right xc-approximation with respect to the given spectroscopy is crucial:
  - **RPA** with **LF** is able to reproduce **EELS** spectra at q=0;
  - **TDLDA** improves upon **RPA** on **EELS** (and also **IXSS**, **CIXS**) spectra at high q;
  - **TDLDA** seems also to improve upon **RPA** on optical spectra in finite systems;
  - More refined kernels (**LRC**, **Nanoquanta**) are required to reproduce optical spectra in solids, especially in presence of strong excitonic effects and bound excitons.
- Perspectives:
  - Improve the algorithms, simplify the orbital expressions of the kernel.

Thank you for your attention!

Non-Linear Optics

Second Order Independent-Particle Polarizability χ^2_{KS}

$$\chi^2_{KS}(2\mathrm{q},q,q,\omega,\omega)=\sum_{ijl}\frac{\rho_{ij}(2\mathrm{q})\,\rho_{jl}(-q)\,\rho_{li}(-q)}{2\omega-(\epsilon_j-\epsilon_i)}\left[\frac{(f_i-f_l)}{\omega-(\epsilon_l-\epsilon_i)}-\frac{(f_l-f_j)}{\omega-(\epsilon_j-\epsilon_l)}\right]$$

Where:

$$\rho_{ij}(q)=\langle\Phi_i|e^{-iqr}|\Phi_j\rangle$$

$$i=n,k$$
$$j=n',k+2\mathrm{q}$$
$$l=n'',k+q$$