Time Dependent Density Functional Theory

An introduction

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Palaiseau, 7 February 2012

Outline

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The name of the game: TDDFT

DFT

Hohenberg-Kohn theorem 1

The ground-state expectation value of any physical observable of a many-electrons system is a unique functional of the electron density $n(\mathbf{r})$

$$\langle \varphi^0 | \, \widehat{O} \, | \varphi^0 \rangle = O[n]$$

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Phys.Rev. **136**, B864 (1964)

(Fermi, Slater)

TDDFT

Runge-Gross theorem

The expectation value of any physical time-dependent observable of a many-electrons system is a unique functional of the **time-dependent** electron density $n(\mathbf{r}, t)$ and of **the initial state** $\varphi^0 = \varphi(t = 0)$

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Static problem

Second-order differential equation
Boundary-value problem.

$$H\varphi(\mathbf{r}_1,..,\mathbf{r}_N) = E\varphi(\mathbf{r}_1,..,\mathbf{r}_N)$$

TDDFT

Time-dependent problem

First-order differential equation
Initial-value problem

$$H(t)\varphi(\mathbf{r}_1,..,\mathbf{r}_N;t) = \imath\hbar\frac{\partial}{\partial t}\varphi(\mathbf{r}_1,..,\mathbf{r}_N;t)$$

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What about infinite systems?

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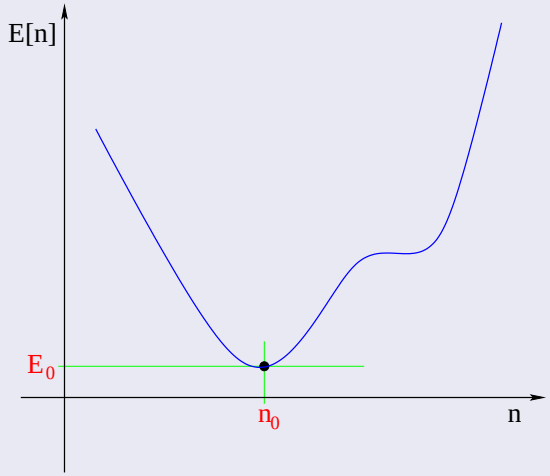
The total energy functional has a minimum, the ground-state energy E_0, corresponding to the ground-state density n_0.



Runge-Gross theorem - No minimum

Time-dependent Schrödinger eq. (initial condition $\varphi(t=0)=\varphi_0$), corresponds to a **stationary** point of the Hamiltonian action

$$A = \int_{t_0}^{t_1} dt \, \langle \varphi(t) | \, \imath \frac{\partial}{\partial t} - H(t) \, | \varphi(t) \rangle$$

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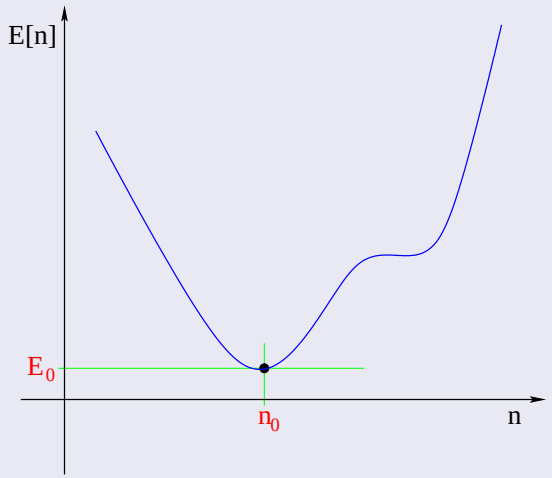

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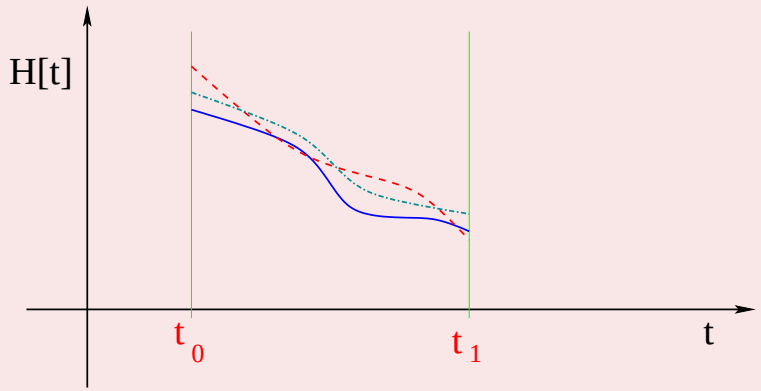

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Kohn-Sham equations

$$\left[-\frac{1}{2}\cdot\nabla_i^2 + V_{tot}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$V_{tot}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}'\, v(\mathbf{r},\mathbf{r}')n(\mathbf{r}') + V_{xc}\left([n],\mathbf{r}\right)$$

$$V_{xc}\left([n],\mathbf{r}\right) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Unknown exchange-correlation potential.
V_{xc} functional of the density.

TDDFT

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Demonstrations, further readings, etc.

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First Approach: Time Evolution of KS equations

$$[H_{KS}(t)]\,\phi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_i^{occ} |\phi_i(\mathbf{r},t)|^2$$

$$\phi(t) = \hat{U}(t,t_0)\phi(t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau H(\tau)\hat{U}(\tau,t_0)$$

A. Castro *et al.* J.Chem.Phys. **121**, 3425 (2004)

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First Approach: Time Evolution of KS equations

Photo-absorption cross section σ

$$\sigma(\omega) = \frac{4\pi\omega}{c}\mathrm{Im}\alpha(\omega)$$

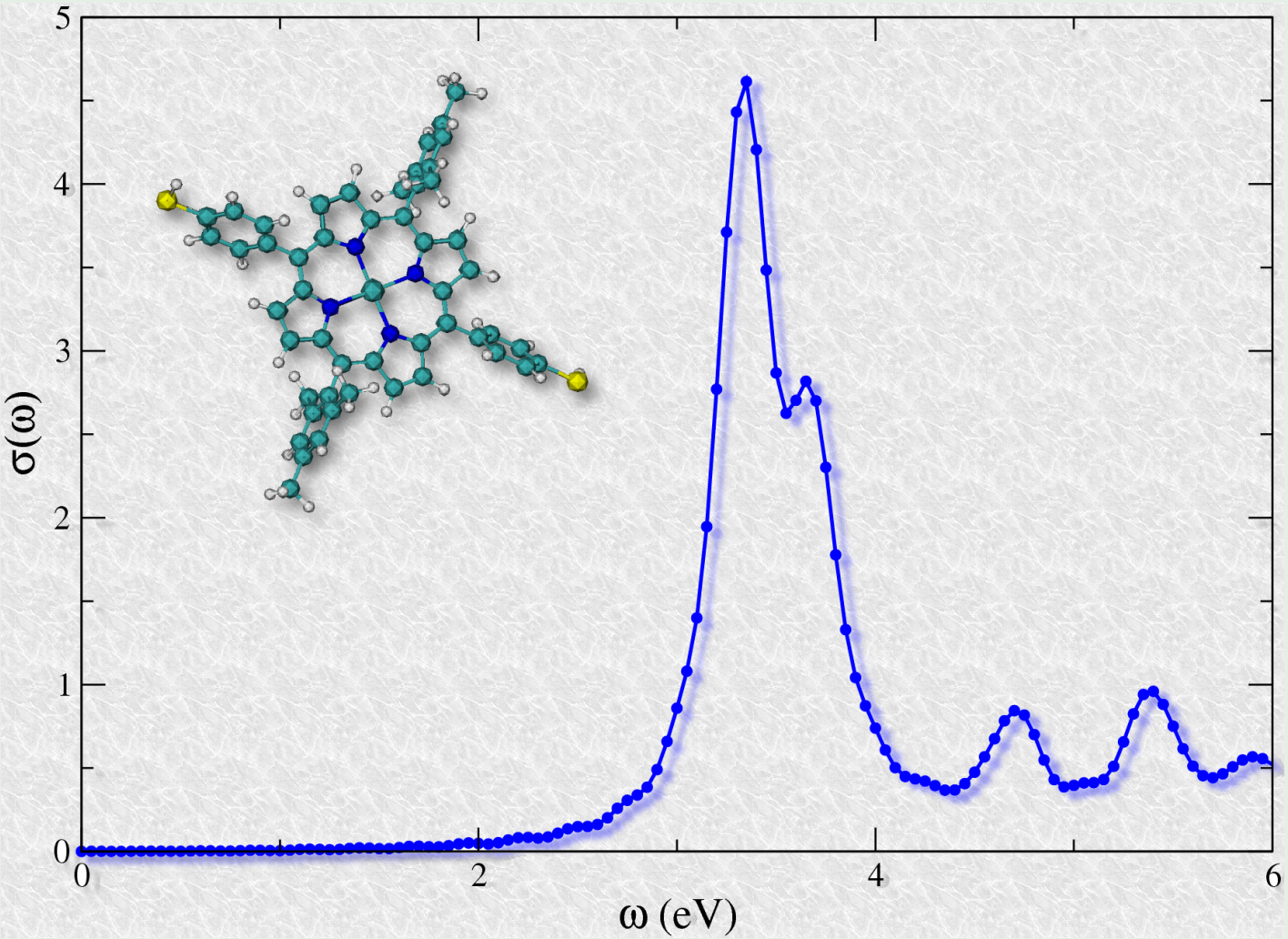
$$\alpha(t) = -\int d\mathbf{r}\, V_{ext}(\mathbf{r},t) n(\mathbf{r},t)$$

in dipole approximation ($\lambda \ggg$ dimension of the system)

$$\sigma_{zz}(\omega) = -\frac{4\pi\omega}{c}\mathrm{Im}\ \alpha(\omega) = -\frac{4\pi\omega}{\mathrm{c}}\mathrm{Im}\int \mathrm{d}\mathbf{r}\ \mathrm{z}\ \mathrm{n}(\mathbf{r},\omega)$$

First Approach: Time Evolution of KS equations

Photo-absorption cross section σ: porphyrin



First Approach: Time Evolution of KS equations

Other observables

Multipoles

$$M_{lm}(t) = \int d\mathbf{r} r^l Y_{lm}(r) n(\mathbf{r}, t)$$

Angular momentum

$$L_z(t) = -\sum_i \int d\mathbf{r} \phi_i(\mathbf{r}, t)\, \imath\, (\mathbf{r} \times \nabla)_z\ \phi_i(\mathbf{r}, t)$$

First Approach: Time Evolution of KS equations

Advantages

- Direct application of KS equations
- Advantageous scaling
- Optimal scheme for finite systems
- All orders automatically included

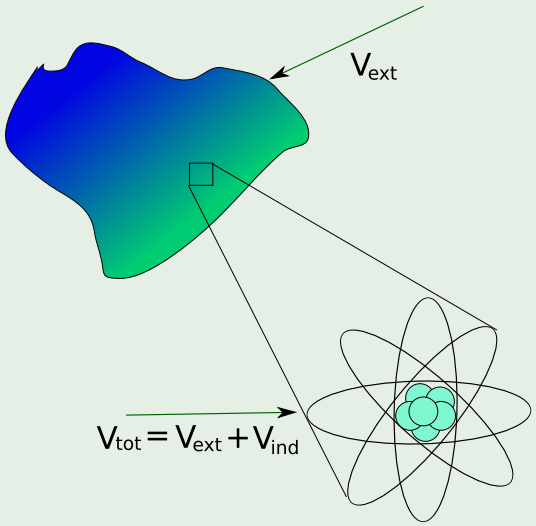
Shortcomings

- Difficulties in approximating the $V_{xc}[n](\mathbf{r}, t)$ functional of the history of the density
- Real space not necessarily suitable for solids
- Does not explicitly take into account a "small" perturbation. Interesting quantities (excitation energies) are contained in the linear response function!

Outline

Linear Response Approach

System submitted to an external perturbation



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$$\mathbf{E} = \varepsilon^{-1} \mathbf{D}$$

Dielectric function ε

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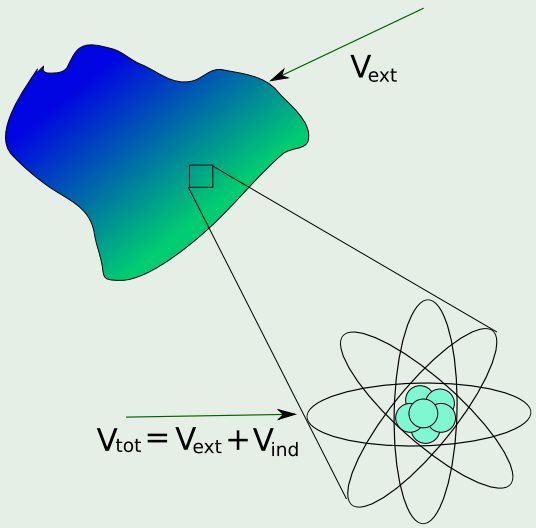

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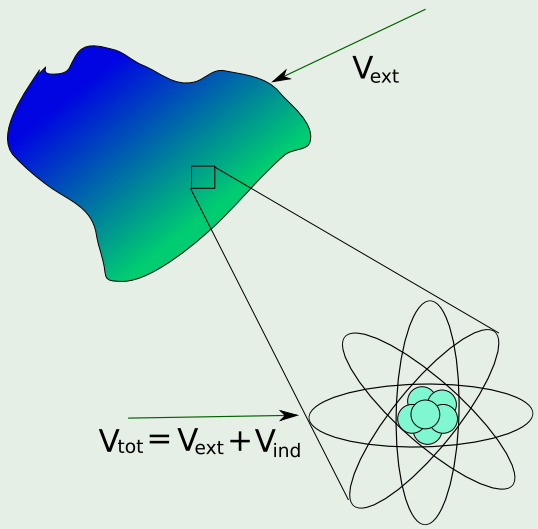

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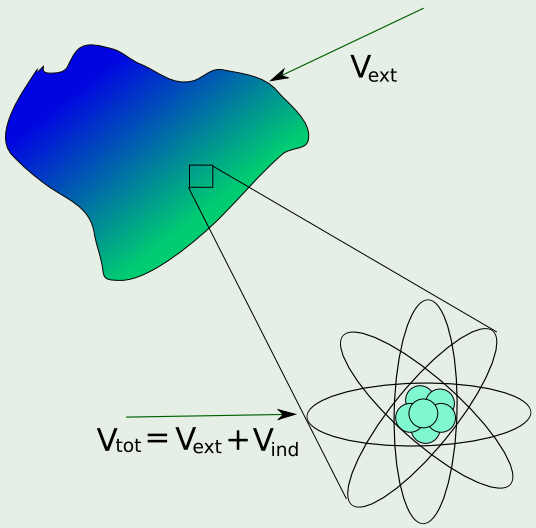

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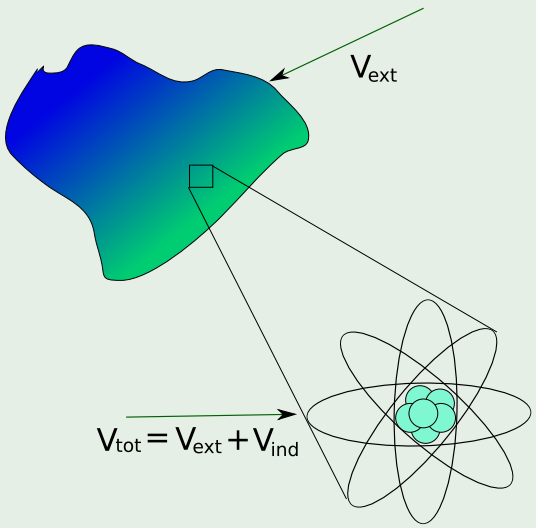

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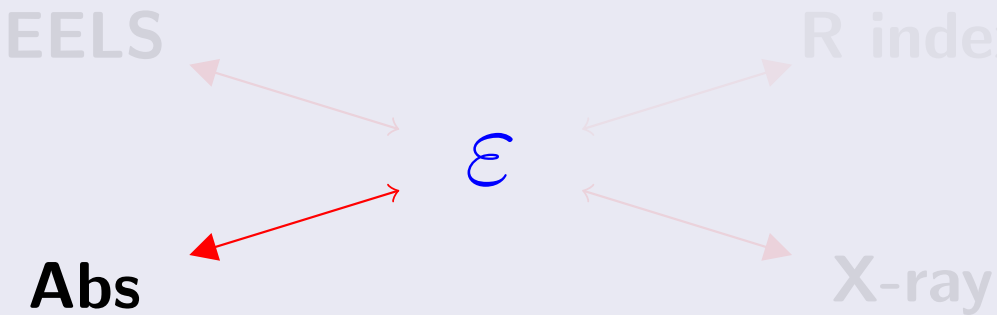

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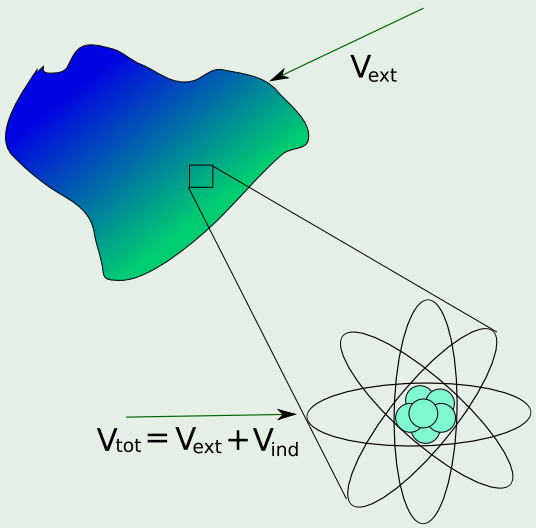

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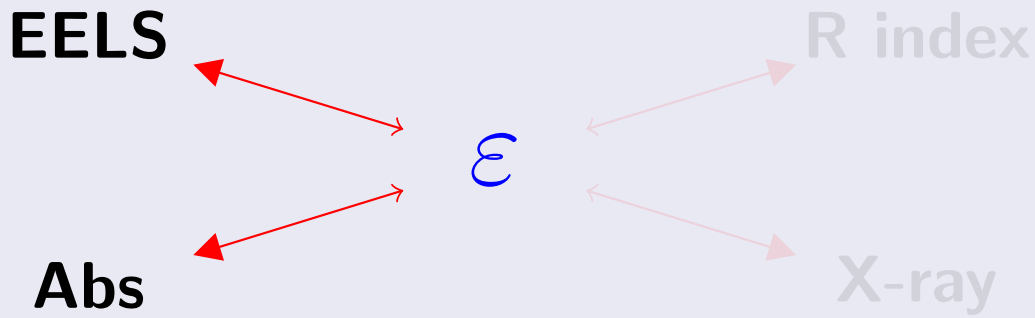

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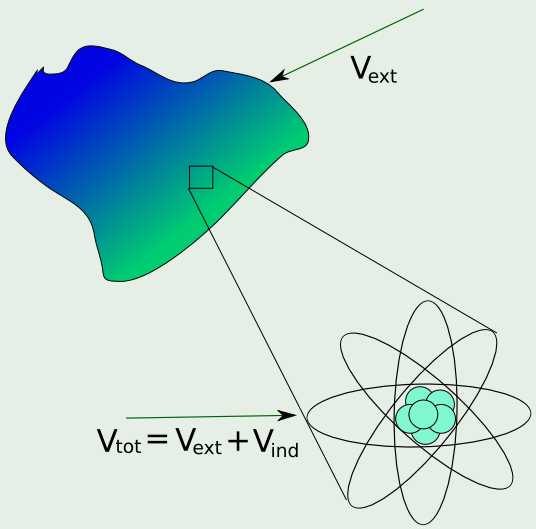

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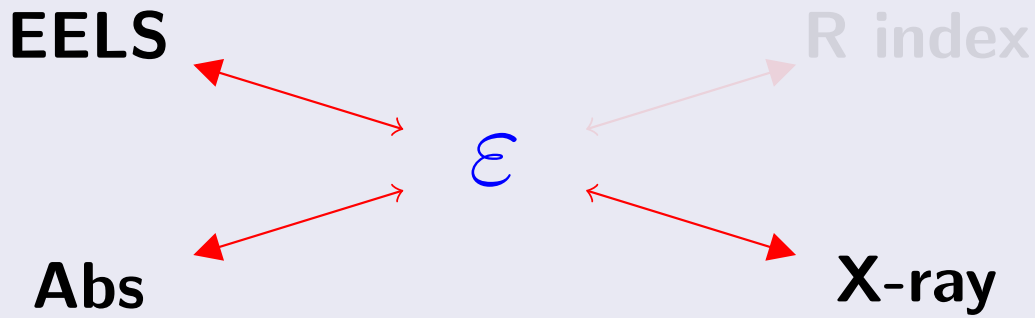

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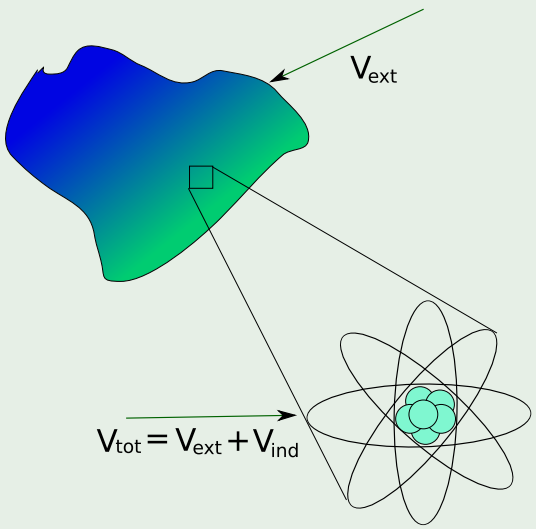

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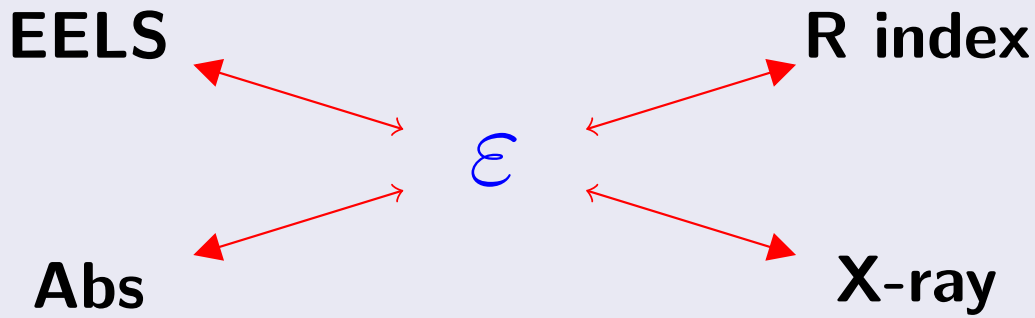

Linear Response Approach

Definition of polarizability

$$\begin{array}{lcccl} \text{not polarizable} & \Rightarrow & V_{tot} = V_{ext} & \Rightarrow & \varepsilon^{-1} = 1 \\ \text{polarizable} & \Rightarrow & V_{tot} \neq V_{ext} & \Rightarrow & \varepsilon^{-1} \neq 1 \\ & & & & \varepsilon^{-1} = 1 + v\chi \end{array}$$

χ is the polarizability of the system

Linear Response Approach

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Linear Response Approach

Polarizability

$$\text{interacting system} \quad \delta n = \chi \delta V_{ext}$$

$$\text{non-interacting system} \quad \delta n_{n-i} = \chi^0 \delta V_{tot}$$

Linear Response Approach

Polarizability

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Single-particle polarizability

$$\chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$$

hartree, hartree-fock, dft, etc.

G.D. Mahan *Many Particle Physics* (Plenum, New York, 1990)

Linear Response Approach

Polarizability

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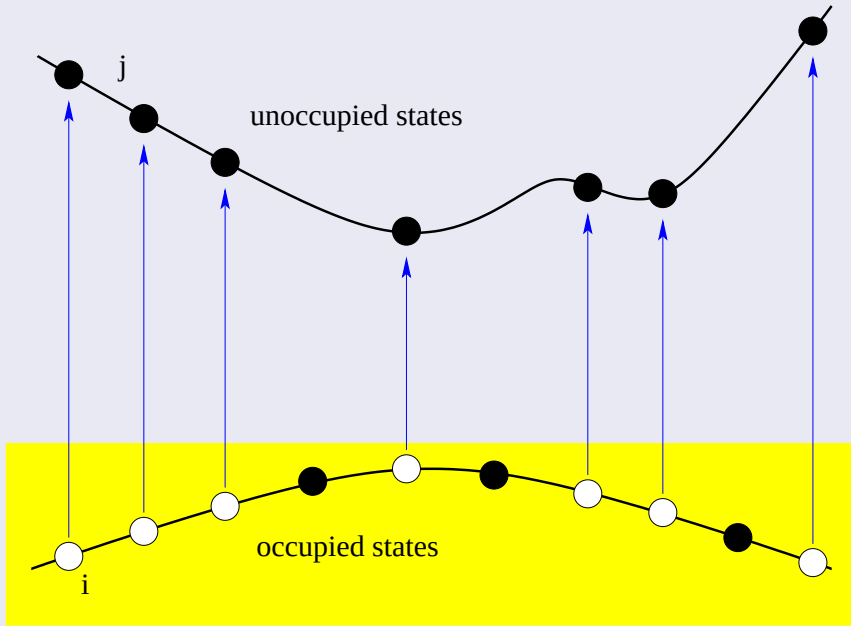

Linear Response Approach

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$$\Updownarrow$$

Density Functional Formalism

$$\delta n = \delta n_{n-i}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_H + \delta V_{xc}$$

Linear Response Approach

Polarizability

$$\chi \delta V_{ext} = \chi^0 \left(\delta V_{ext} + \delta V_H + \delta V_{xc} \right)$$

$$\chi = \chi^0 \left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}} \right)$$

$$\frac{\delta V_H}{\delta V_{ext}} = \frac{\delta V_H}{\delta n} \frac{\delta n}{\delta V_{ext}} = v\chi$$

$$\frac{\delta V_{xc}}{\delta V_{ext}} = \frac{\delta V_{xc}}{\delta n} \frac{\delta n}{\delta V_{ext}} = f_{xc}\chi$$

with f_{xc} = exchange-correlation kernel

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Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\rightarrow \quad \phi_i, \epsilon_i \qquad [V_{xc}]$
2. $\phi_i, \epsilon_i \quad \rightarrow \quad \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$
3. $\left.\begin{array}{l} \frac{\delta V_H}{\delta n} = v \\ \frac{\delta V_{xc}}{\delta n} = f_{xc} \end{array}\right\}$ variation of the potentials
4. $\chi = \chi^0 + \chi^0 (v + f_{xc})\, \chi$

A comment

- $f_{xc} = \left\{ \begin{array}{l} \frac{\delta V_{xc}}{\delta n} \\ \text{“any” other function} \end{array} \right.$

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Photo-absorption cross spectrum

$$\sigma(\omega) = \frac{4\pi\omega}{c}\mathrm{Im}\alpha(\omega)$$

$$\alpha(\omega) = -\int d\mathbf{r}d\mathbf{r}' V_{ext}(\mathbf{r},\omega)\chi(\mathbf{r},\mathbf{r}',\omega)V_{ext}(\mathbf{r}',\omega)$$

$$\sigma_{zz}(\omega) = -\frac{4\pi\omega}{c}\mathrm{Im}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\mathrm{z}\chi(\mathbf{r},\mathbf{r}',\omega)\mathrm{z}'$$

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Periodic Systems

A better representation: Fourier space

$$\mathbf{E}(\mathbf{r},t) = \sum_{\mathbf{G}} \int \frac{d\mathbf{q}d\omega}{(2\pi)^4} \mathbf{E}(\mathbf{q}+\mathbf{G},\omega) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r} - i\omega t}$$

$$\varepsilon(\mathbf{r},\mathbf{r}',t,t') = \sum_{\mathbf{G}\mathbf{G}'} \int \frac{d\mathbf{q}d\omega}{(2\pi)^4} \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r} - i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}' - i\omega(t-t')}$$

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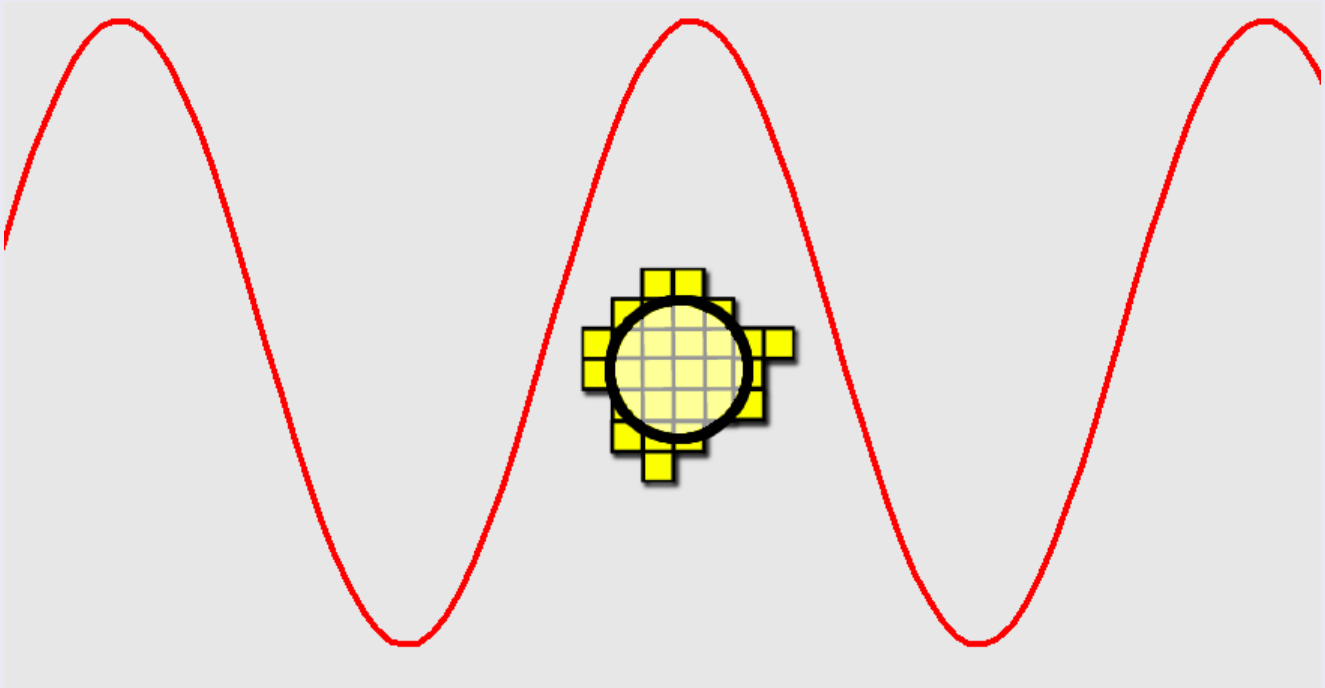
Periodic Systems

Macroscopic average



average over distance d:

- $d \ggg \Omega_R$
- $d \lll \lambda$

Macroscopic average

$$\langle f(\mathbf{r},\omega)\rangle_{\mathbf{R}} = \frac{1}{\Omega_R}\int d\mathbf{r} f(\mathbf{r},\omega)$$

$$= \frac{1}{\Omega_R}\int d\mathbf{r}\left[\int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}}\sum_{\mathbf{G}} f(\mathbf{q}+\mathbf{G},\omega)e^{i\mathbf{G}\cdot\mathbf{r}}\right]$$

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macroscopic electric field $\mathbf{E}(\mathbf{q}+\mathbf{0},\omega) = \mathbf{E}(\mathbf{q},\omega)$

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Absorption coefficient

General solution of Maxwell's equation

$$\text{in vacuum} \quad \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(x/c-t)}$$

$$\text{in a medium} \quad \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(Nx/c-t)}$$

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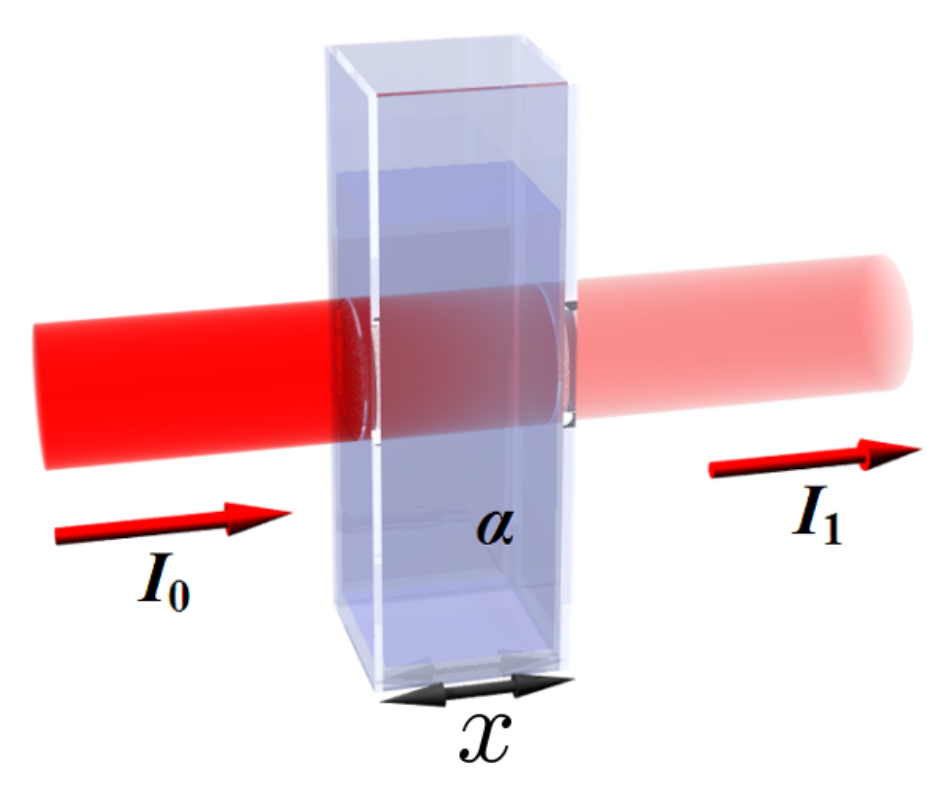

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complex (macroscopic) refractive index N

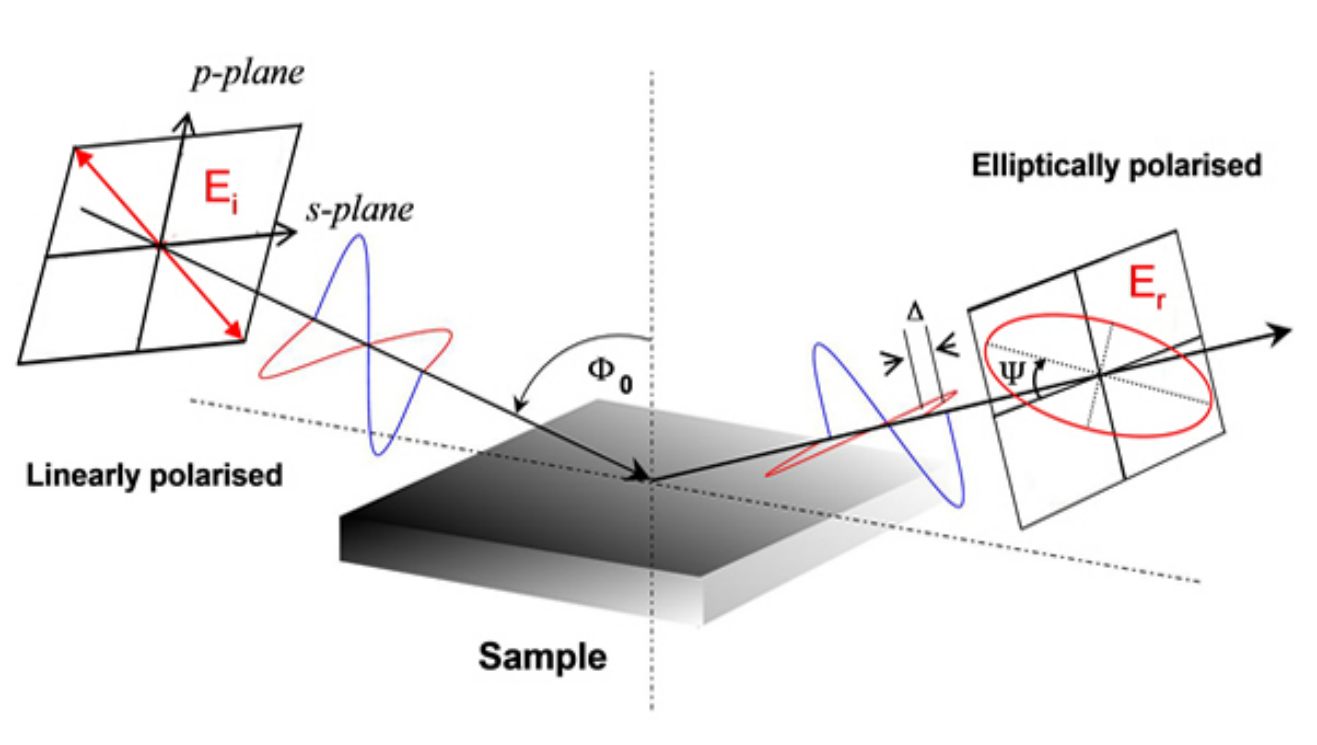
$$N = \sqrt{\varepsilon_M} = \nu + i\kappa \quad ; \quad \mathbf{D} = \varepsilon_M \mathbf{E}$$

absorption coefficient α (inverse distance $\left| \frac{|\mathbf{E}(x)|^2}{|\mathbf{E}_0|^2} = \frac{1}{e} \right.$)

$$\alpha = \frac{\omega \mathrm{Im}\varepsilon_\mathrm{M}}{\nu c}$$

Absorption coefficient

Ellipsometry Experiment



$$\varepsilon_M = sin^2\Phi + sin^2\Phi tan^2\Phi \left(\frac{1 - \frac{E_r}{E_i}}{1 + \frac{E_r}{E_i}} \right)$$

Dielectric Function in Crystals

Let's calculate ε_M

$$\mathbf{D} = \varepsilon_M \mathbf{E}$$

WRONG!

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The average of the product is not the product of the averages

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The Energy Loss Spectra

Imaginary part of the macroscopic inverse dielectric function

$$\text{ELS} = \text{Im}\varepsilon_{00}^{-1}$$

$$\frac{2\pi}{\mathbf{q}} = \lambda \ggg \Omega_R$$

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$$\text{ELS} = \text{Im}\varepsilon^{-1}_{00}$$

$$\frac{2\pi}{\mathbf{q}} = \lambda \ggg \Omega_R$$

Dielectric Function in Crystals

Absoprtion Spectra

$$\text{abs} = \text{Im}\varepsilon_{\text{M}} = \text{Im}\frac{1}{\varepsilon_{00}^{-1}}$$

Energy Loss Spectra

$$\text{ELS} = \text{Im}\varepsilon_{00}^{-1} = \text{Im}\frac{1}{\varepsilon_{\text{M}}}$$

Dielectric Function in Crystals

Question

ε_{00} is not the macroscopic dielectric function

What is it then ?

ε_{00} is the macroscopic dielectric function ...

without local fields.

Dielectric Function in Crystals

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Dielectric Function in Crystals

Question

ε_{00} is not the macroscopic dielectric function

What is it then ?

ε_{00} is the macroscopic dielectric function ...

without local fields.

Reciprocal space

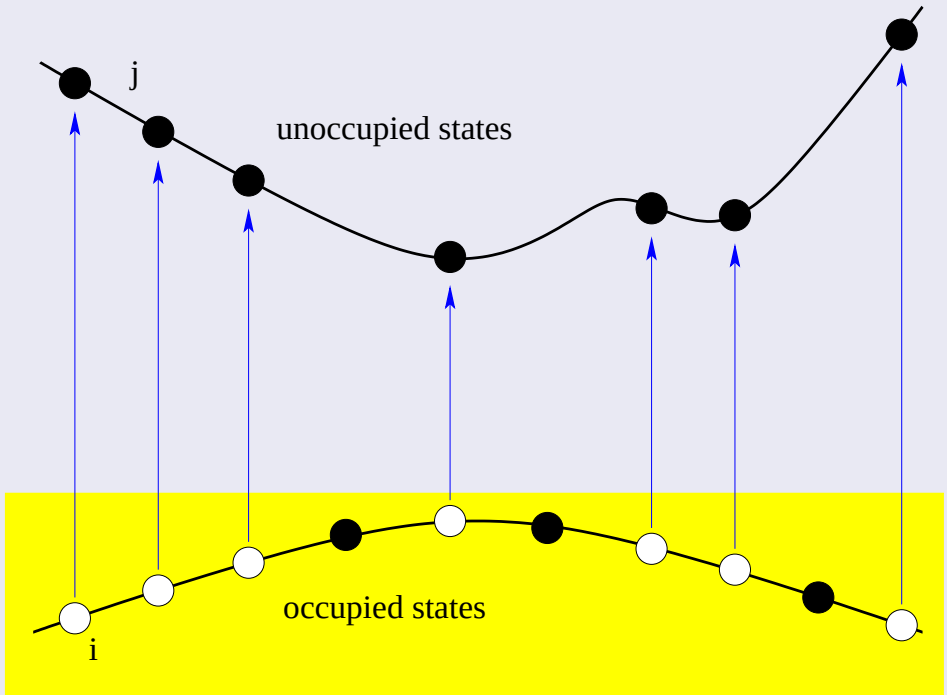
$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) \longrightarrow \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$$

G =reciprocal lattice vector

q =momentum transfer of the perturbation

Reciprocal space

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\left\langle \phi_{v\mathbf{k}} \middle| e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \middle| \phi^*_{c\mathbf{k}+\mathbf{q}} \right\rangle \left\langle \phi_{c\mathbf{k}+\mathbf{q}} \middle| e^{-\imath(\mathbf{q}+\mathbf{G}')\mathbf{r}'} \middle| \phi^*_{v\mathbf{k}} \right\rangle}{\omega - \left(\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}\right) + \imath\eta}$$



Reciprocal space

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\left\langle \phi_{v\mathbf{k}} \middle| e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \middle| \phi^*_{c\mathbf{k}+\mathbf{q}} \right\rangle \left\langle \phi_{c\mathbf{k}+\mathbf{q}} \middle| e^{-\imath(\mathbf{q}+\mathbf{G'})\mathbf{r'}} \middle| \phi^*_{v\mathbf{k}} \right\rangle}{\omega - \left(\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}\right) + \imath\eta}$$

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0 + \chi^0 \left(v + f_{xc}\right) \chi$$

$$\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

Reciprocal space

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\left\langle \phi_{v\mathbf{k}} \middle| e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \middle| \phi^*_{c\mathbf{k}+\mathbf{q}} \right\rangle \left\langle \phi_{c\mathbf{k}+\mathbf{q}} \middle| e^{-\imath(\mathbf{q}+\mathbf{G'})\mathbf{r'}} \middle| \phi^*_{v\mathbf{k}} \right\rangle}{\omega - \left(\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}\right) + \imath\eta}$$

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$$\mathrm{ELS}(\mathbf{q},\omega) = -\mathrm{Im}\left\{\varepsilon^{-1}_{00}(\mathbf{q},\omega)\right\} \;;\; \mathrm{Abs}(\omega) = \lim_{\mathbf{q}\to 0} \mathrm{Im}\left\{\frac{1}{\varepsilon^{-1}_{00}(\mathbf{q},\omega)}\right\}$$

S.L.Adler, Phys.Rev **126**, 413 (1962); N.Wiser Phys.Rev **129**, 62 (1963)

Reciprocal space

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S.L.Adler, Phys.Rev **126**, 413 (1962); N.Wiser Phys.Rev **129**, 62 (1963)

Absorption and Energy Loss Spectra $\mathbf{q} \to 0$

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$$\varepsilon_{00}^{-1}(\omega) = 1 + v_0\chi_{00}(\omega)$$

Absorption and Energy Loss Spectra $\mathbf{q} \to 0$

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$$\text{ELS}(\omega) = -v_0\text{Im}\left\{\chi_{00}(\omega)\right\} \; ; \; \text{Abs}(\omega) = -v_0\text{Im}\left\{\frac{1}{1+v_0\chi_{00}(\omega)}\right\}$$

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$$\text{ELS}(\omega) = -v_0 \; \text{Im}\left\{\chi_{00}(\omega)\right\} \quad ; \quad \text{Abs}(\omega) = -\text{v}_0 \; \text{Im}\left\{\bar{\chi}_{00}(\omega)\right\}$$

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$$\bar{v}_{\mathbf{G}} = \begin{cases} v_{\mathbf{G}} & \forall \mathbf{G} \neq 0 \\ 0 & \mathbf{G} = 0 \end{cases}$$

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Exercise

$$\text{Im}\left\{\frac{1}{\varepsilon_{00}^{-1}}\right\} = -v_0\text{Im}\left\{\bar{\chi}_{00}\right\}$$

Abs and ELS ($\mathbf{q} \to 0$) differs **only by** v_0

$$\text{ELS}(\omega) = -\text{Im}\left\{\varepsilon_{00}^{-1}(\omega)\right\} \quad ; \quad \text{Abs}(\omega) = \text{Im}\left\{\frac{1}{\varepsilon_{00}^{-1}(\omega)}\right\}$$

$$\text{ELS}(\omega) = -v_0\ \text{Im}\left\{\chi_{00}(\omega)\right\} \quad ; \quad \text{Abs}(\omega) = -\text{v}_0\ \text{Im}\left\{\bar{\chi}_{00}(\omega)\right\}$$

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microscopic components

Microscopic components $\bar{v}$

$$\bar{v} = \text{local field effects}$$

$$\bar{\chi}^{\text{NLF}} = \chi^0 + \chi^0 \left(\cancel{\bar{v}} + f_{xc} \right) \bar{\chi}^{\text{NLF}}$$

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Exercise

$$\text{Abs}^{\text{NLF}} = -v_0 \, \text{Im} \left\{ \bar{\chi}^{\text{NLF}} \right\} = \text{Im} \left\{ \varepsilon_{00} \right\}$$

Outline

TDDFT in practice

Practical schema and approximations

- Ground-state calculation $\rightarrow \phi_i, \epsilon_i$ [V_{xc} LDA]
- $\chi^0(\mathbf{q}, \omega)$
- $\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$

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

$$f_{xc}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \delta(\mathbf{r} - \mathbf{r}') \quad \text{ALDA}$$

Outline

ALDA: Achievements and Shortcomings

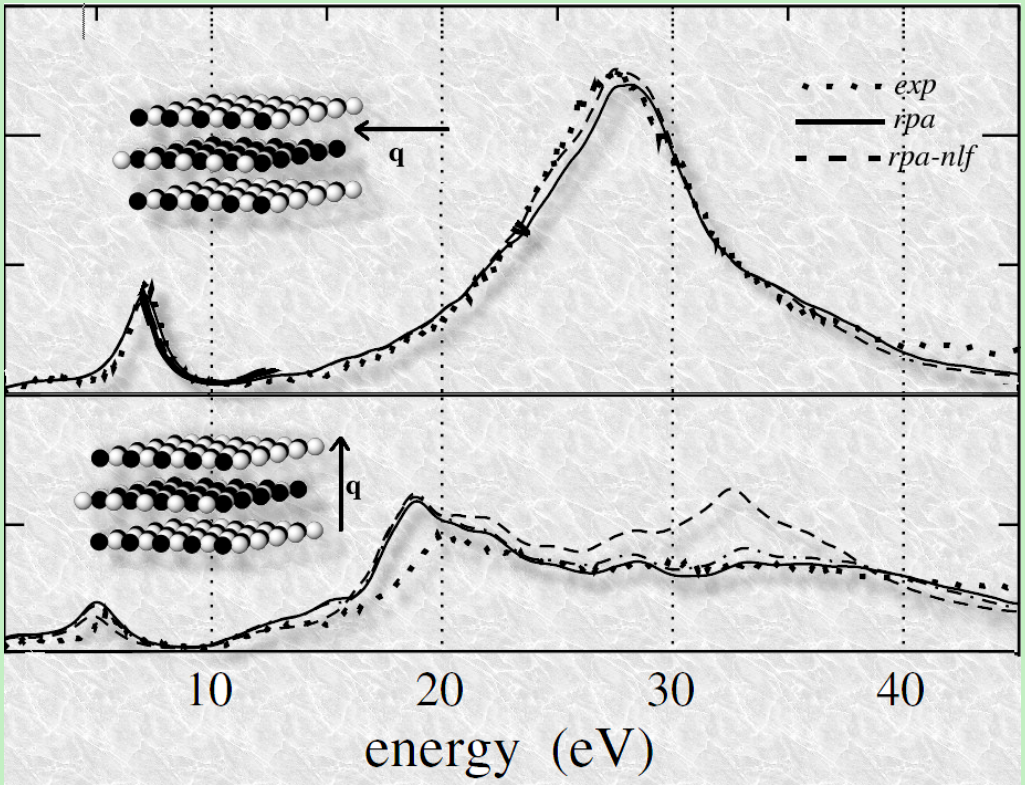
Electron Energy Loss Spectrum of Graphite

RPA vs EXP

$$\chi^{\mathrm{NLF}} = \chi^0 + \chi^0\, v_0\, \chi^{\mathrm{NLF}}$$

$$\chi = \chi^0 + \chi^0\, v\, \chi$$

$$\mathrm{ELS} = -v_0 \mathrm{Im}\left\{\chi_{00}\right\}$$



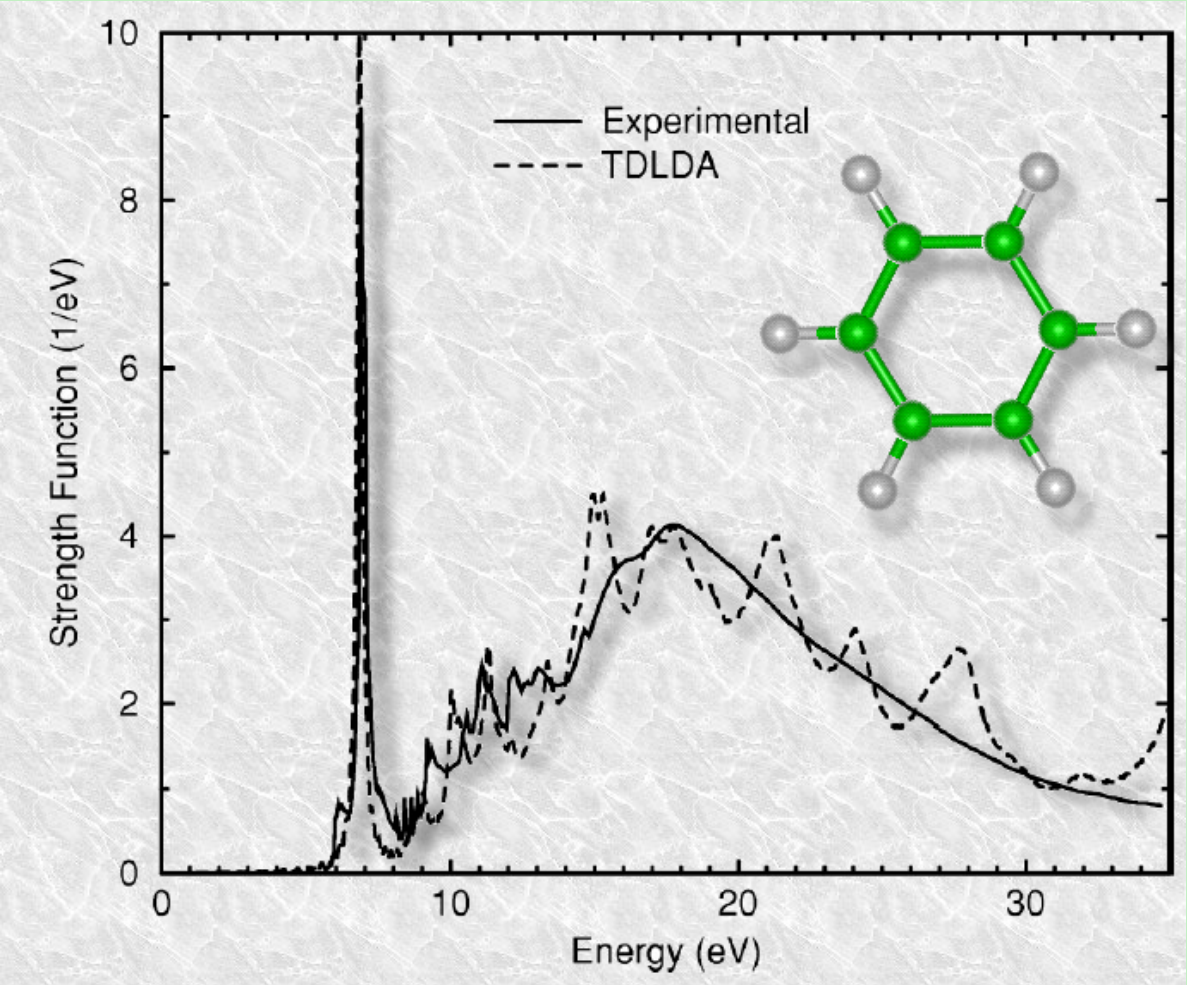
A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ALDA: Achievements and Shortcomings

Photo-absorption cross section of Benzene

ALDA vs EXP

$$\text{Abs} = -\frac{4\pi\omega}{c}\text{Im}\int d\mathbf{r} z n(r,\omega)$$



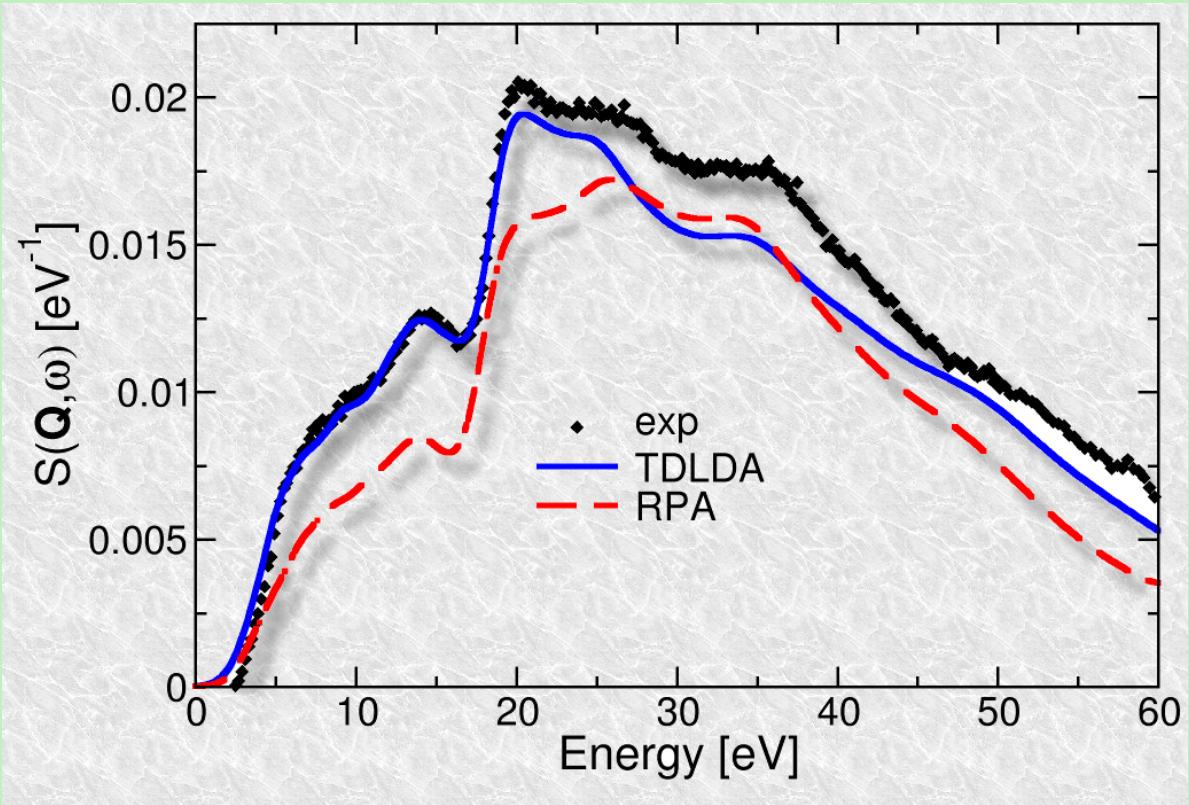
K.Yabana and G.F.Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

ALDA: Achievements and Shortcomings

Inelastic X-ray scattering of Silicon

ALDA vs RPA vs EXP

$$S(\mathbf{q},\omega) = -\frac{\hbar^2 q^2}{4\pi^2 e^2 n} \mathrm{Im}\varepsilon^{-1}_{00}$$



H-C.Weissker *et al.* submitted

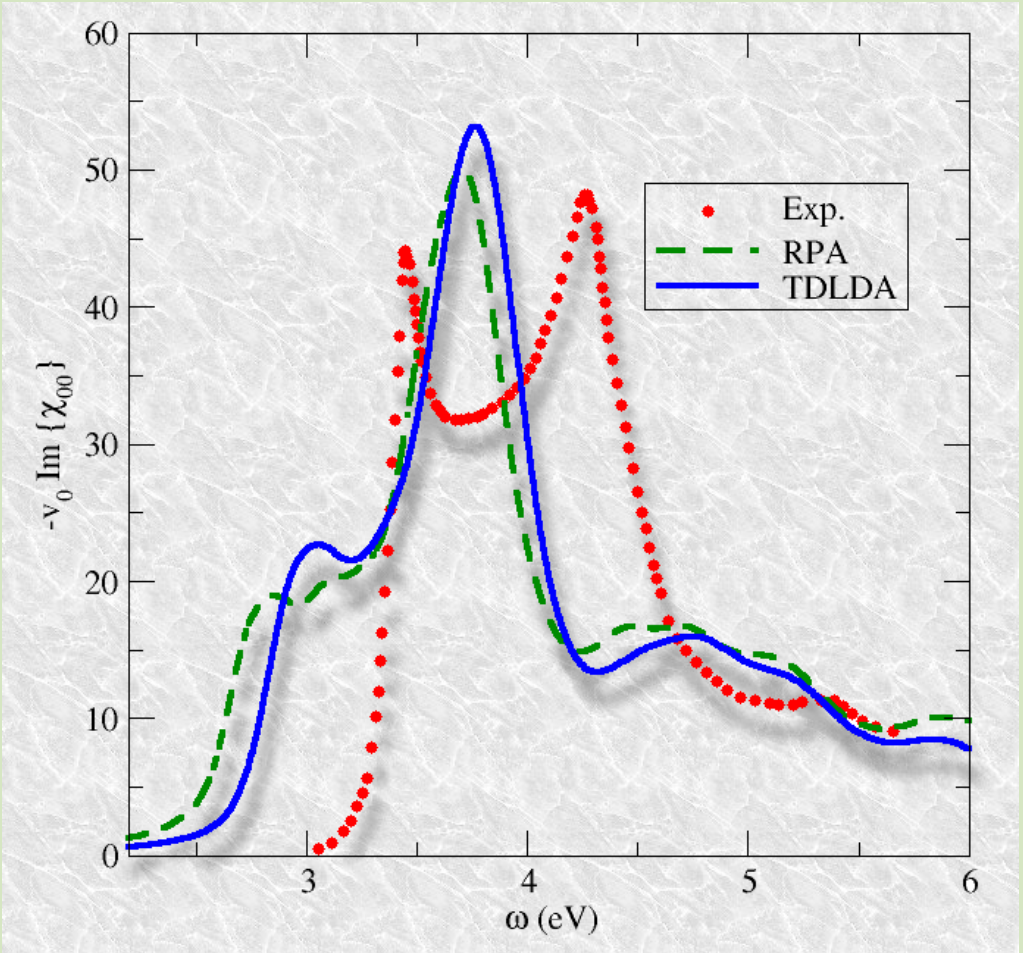
ALDA: Achievements and Shortcomings

Absorption Spectrum of Silicon

ALDA vs RPA vs EXP

$$\bar{\chi} = \chi^0 + \chi^0 \left(\bar{v} + f_{xc}^{\mathrm{ALDA}}\right)\bar{\chi}$$

$$\mathrm{Abs} = -v_0 \mathrm{Im}\left\{\bar{\chi}_{00}\right\}$$



ALDA: Achievements and Shortcomings

Absorption Spectrum of Argon

ALDA vs EXP

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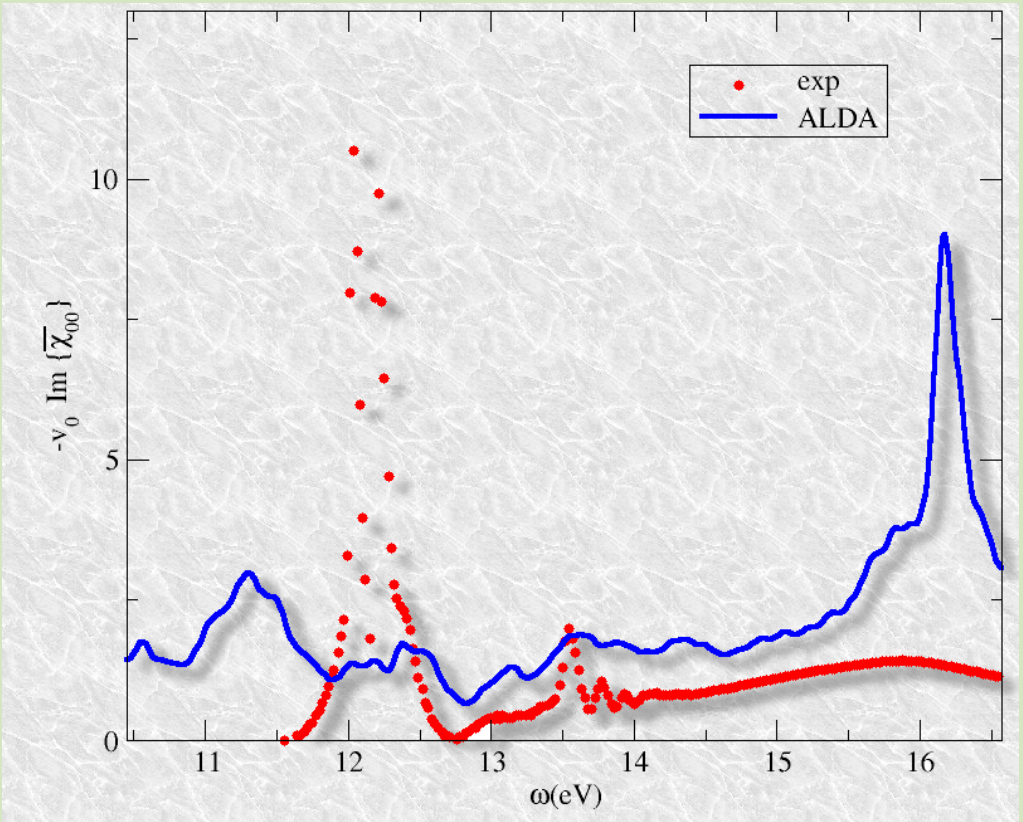

ALDA: Achievements and Shortcomings

Good results

- Photo-absorption of small molecules
- ELS of solids

Bad results

- Absorption of solids

Why?

f_{xc}^{ALDA} is short-range

$$f_{xc}(\mathbf{q} \to 0) \sim \frac{1}{q^2}$$

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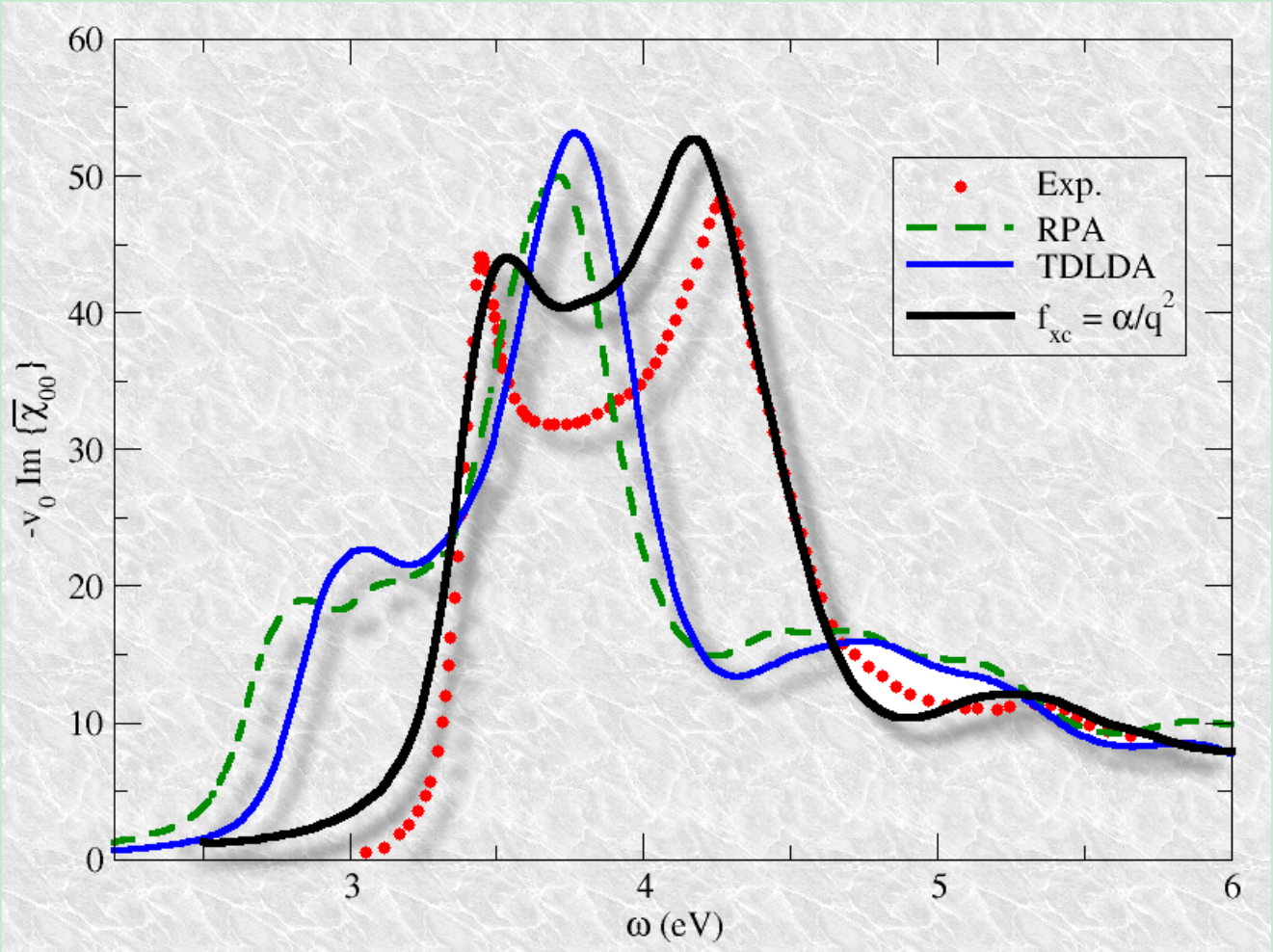
ALDA: Achievements and Shortcomings

Absorption of Silicon $f_{xc} = \frac{\alpha}{q^2}$



L.Reining *et al.* Phys.Rev.Lett. **88**, 66404 (2002)

Outline

Beyond ALDA approximation

The problem of Abs in solids. Towards a better understanding


Reining *et al.* Phys.Rev.Lett. **88**, 66404 (2002)
Long-range kernel


de Boeij *et al.* J.Chem.Phys. **115**, 1995 (2002)
Polarization density functional. Long-range.


Kim and Görling Phys.Rev.Lett. **89**, 96402 (2002)
Exact-exchange


Sottile *et al.* Phys.Rev.B **68**, 205112 (2003)
Long-range and contact exciton.


Botti *et al.* Phys. Rev. B **72**, 125203 (2005)
Dynamic long-range component

Parameters to fit to experiments.

Beyond ALDA approximation

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Beyond ALDA approximation

Abs in solids. Insights from MBPT

Parameter-free Ab initio kernels

Sottile *et al.* Phys.Rev.Lett. **91**, 56402 (2003)
Full many-body kernel. Mapping Theory.

Marini *et al.* Phys.Rev.Lett. **91**, 256402 (2003)
Full many-body kernel. Perturbation Theory.

The Mapping Theory

The idea

$$\text{BSE works} \Rightarrow \begin{cases} \text{we get the ingredients of the BSE} \\ \text{and we put them in TDDFT} \end{cases}$$

The Mapping Theory

The idea

$$L(1234) = L^0_{\mathrm{GW}}(1234) + L^0_{\mathrm{GW}}(1256)\,[v - W]\,L(7834)$$

$$\chi(12) = \chi^0(12) + \chi^0(13)\,[v + f_{xc}]\,\chi(42)$$

$$f_{xc} = \left(\chi^0_{\mathrm{GW}}\right)^{-1} GGWGG \left(\chi^0_{\mathrm{GW}}\right)^{-1}$$

$\times$ still apply GW
$\surd$ solve 2-point eq. for χ (rather than L)

The Mapping Theory

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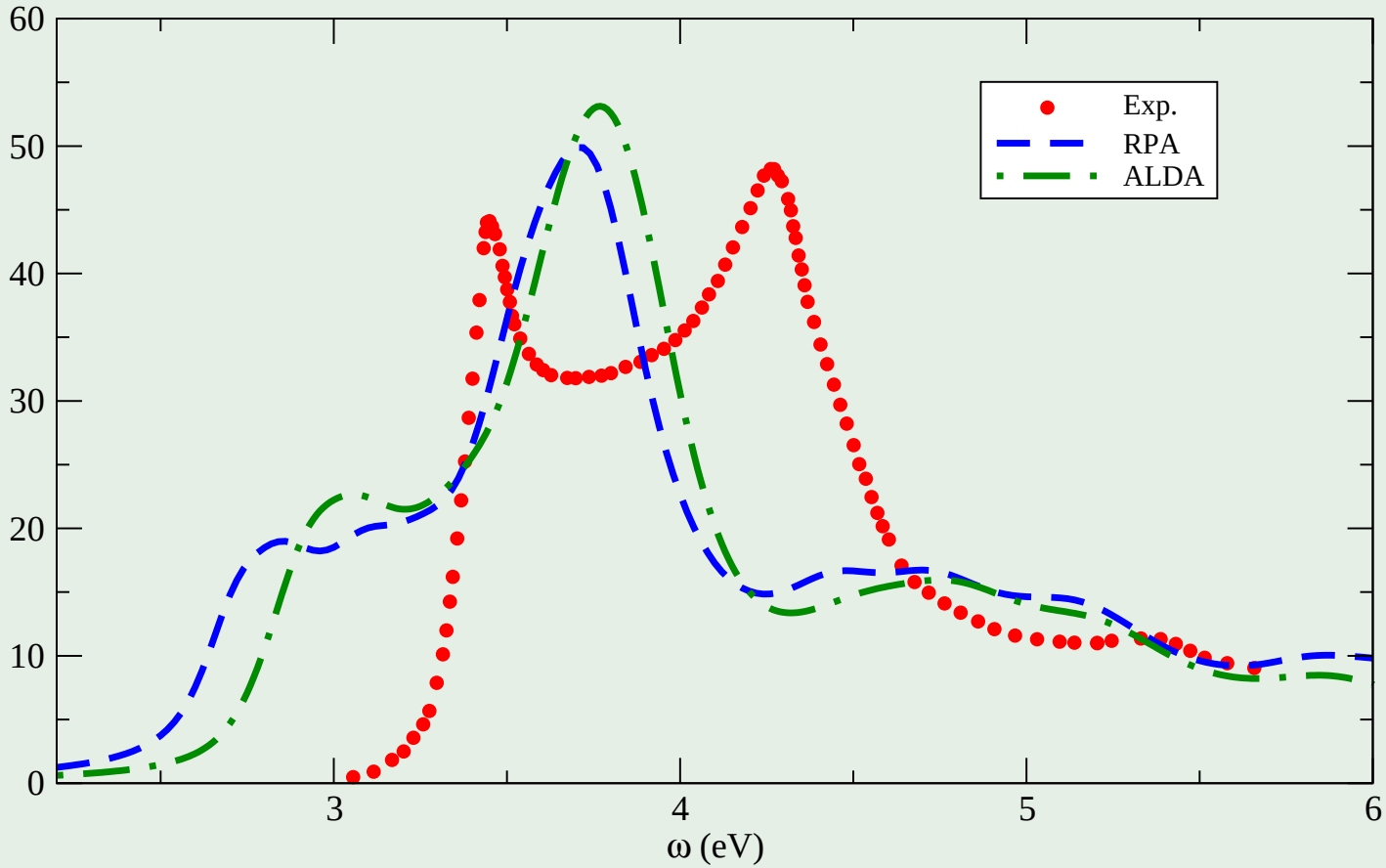
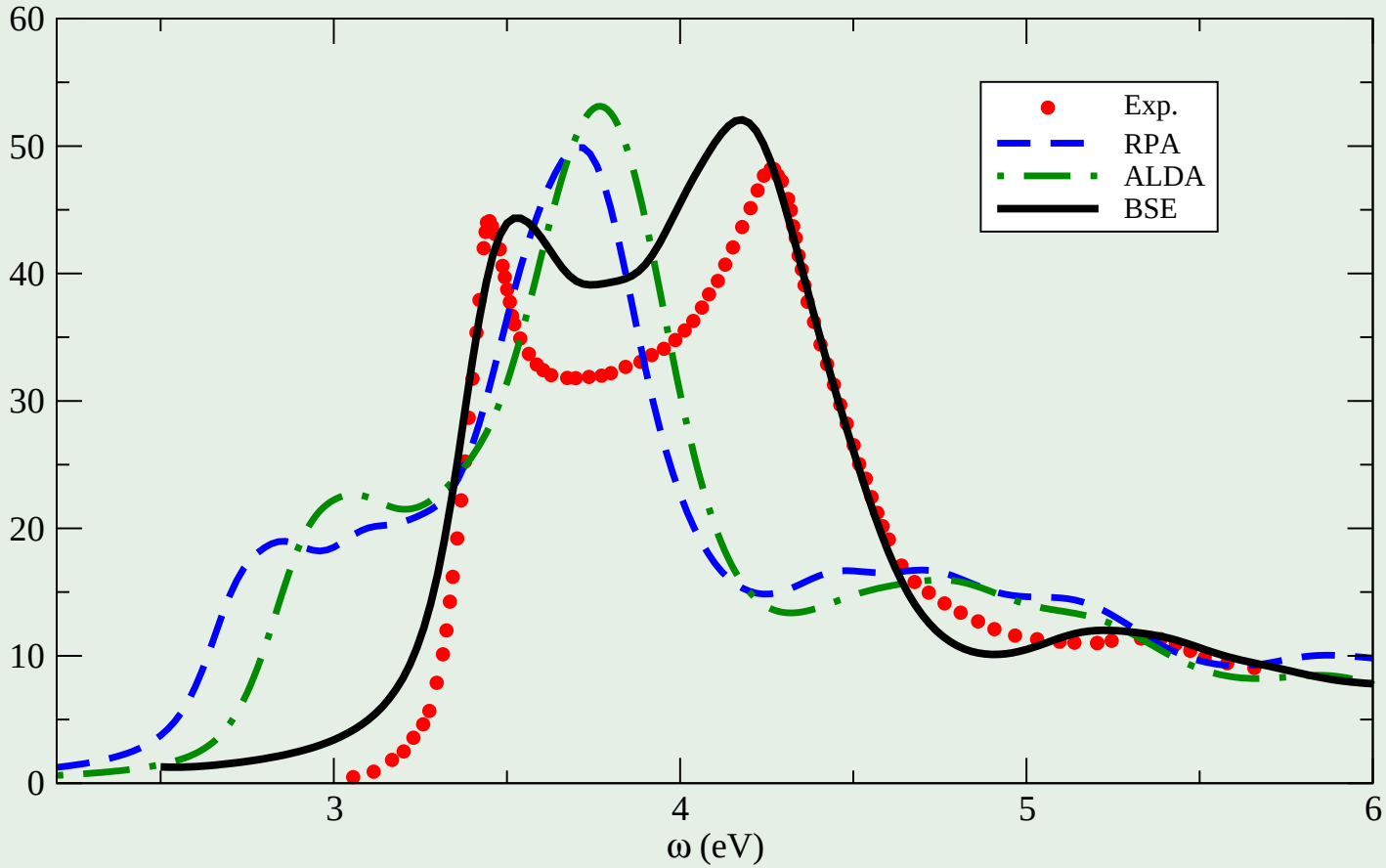
The Mapping Theory: Results

Absorption of Silicon



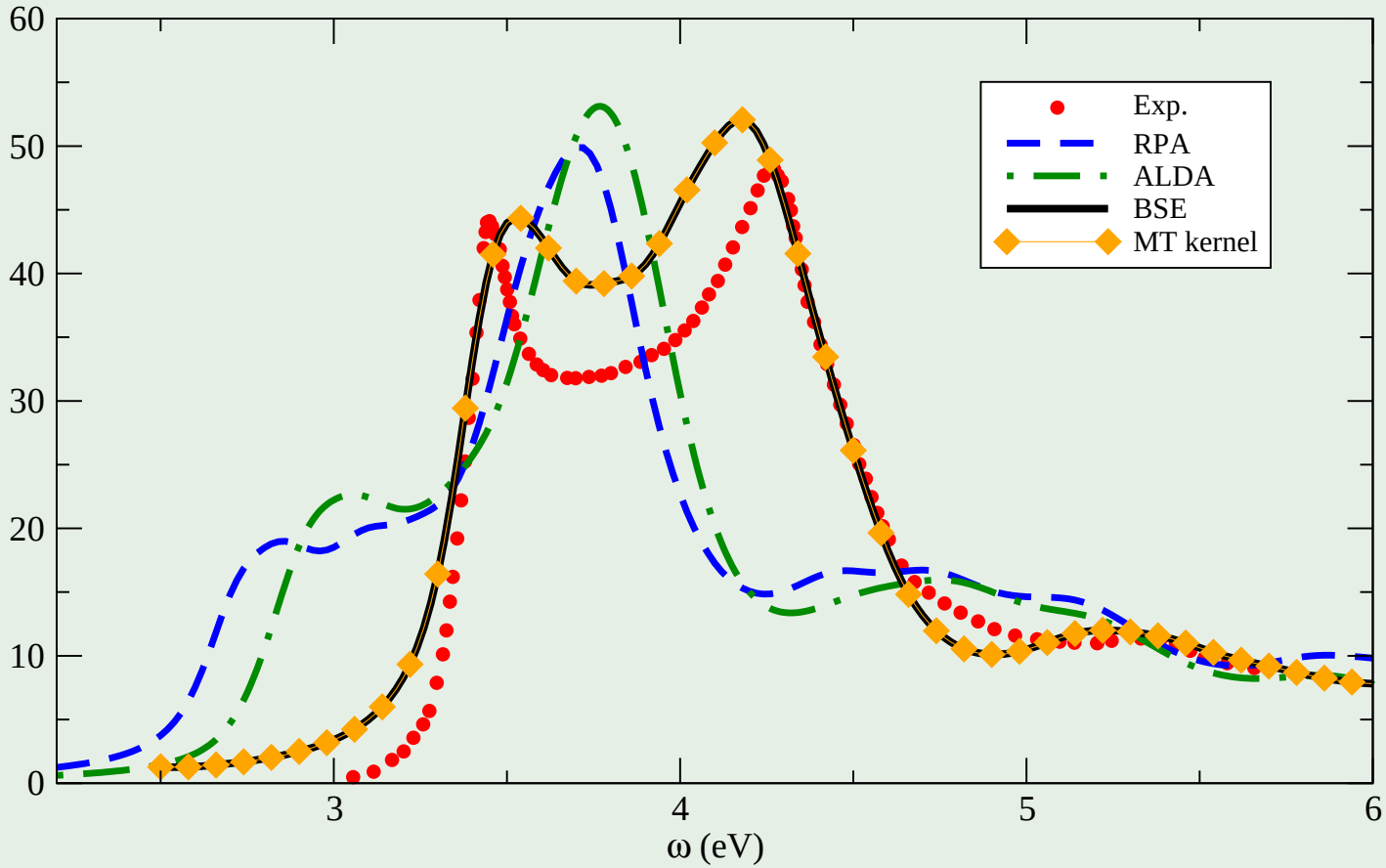
The Mapping Theory: Results

Absorption of Silicon



The Mapping Theory: Results

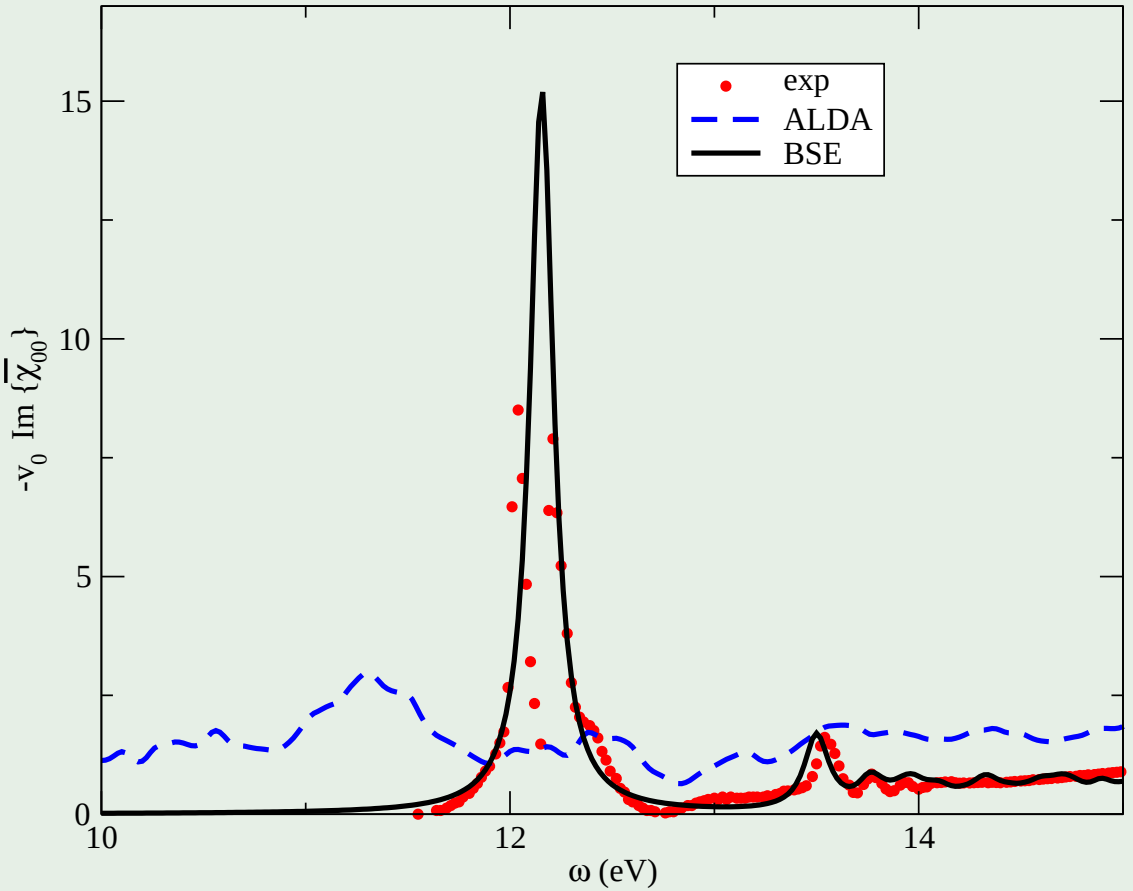
Absorption of Silicon



F.Sottile *et al.* Phys.Rev.Lett **91**, 56402 (2003)

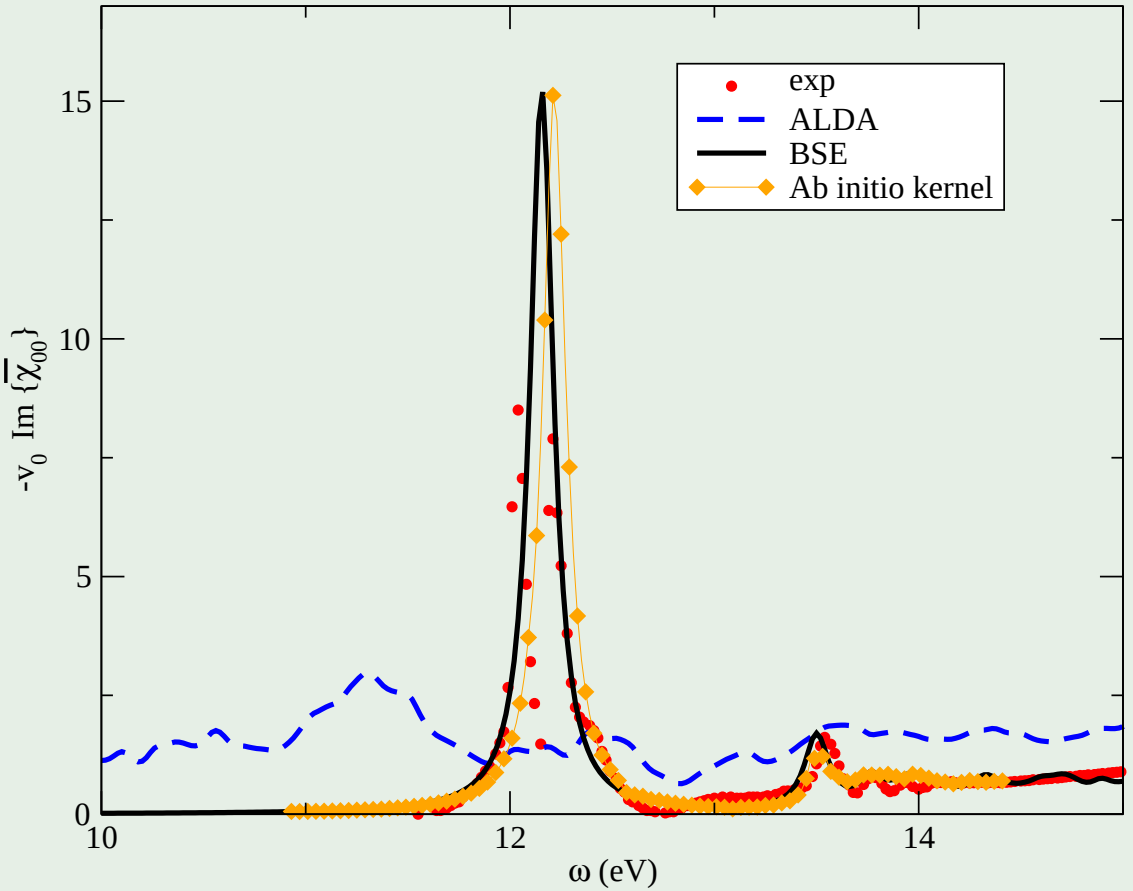
The Mapping Theory: Results

Absorption of Argon



The Mapping Theory: Results

Absorption of Argon



Sottile *et al.* Phys. Rev. B R**76**, 161103 (2007)

The Mapping Theory: Results

Tested also on absorption of SiO_2, DNA bases, Ge-nanowires, RAS of diamond surface, and EELS of LiF.

- Marini *et al.* Phys.Rev.Lett. **91**, 256402 (2003).
- Bruno *et al.* Phys.Rev.B **72** 153310, (2005).
- Palummo *et al.* Phys.Rev.Lett. **94** 087404 (2005).
- Varsano *et al.* J.Phys.Chem.B **110** 7129 (2006).

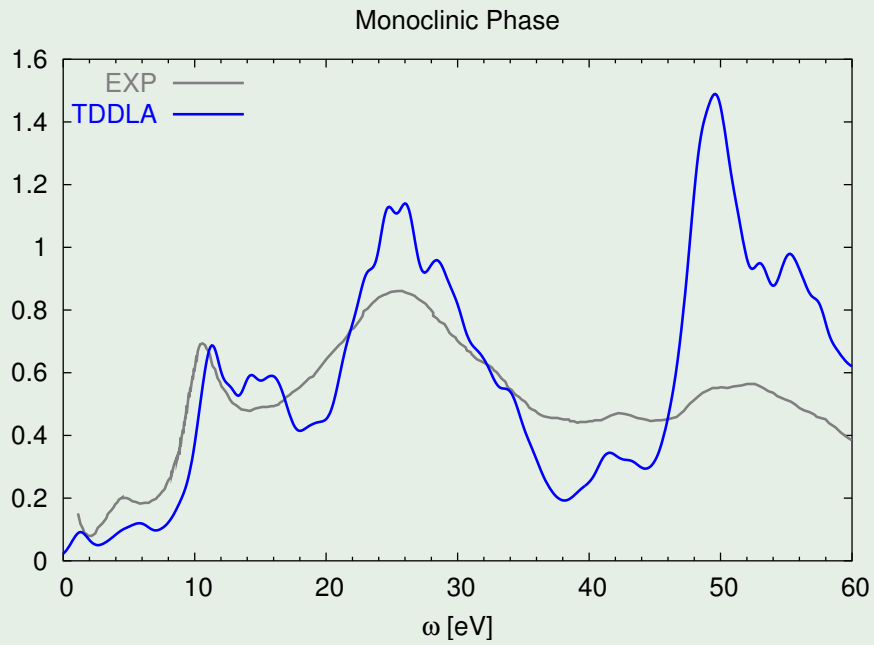
Spectra of simple systems

TDDFT is the method of choice

- √ Absorption spectra of solids and simple molecules
- √ Electron energy loss spectra
- √ Refraction indexes
- √ Inelastic X-ray scattering spectroscopy

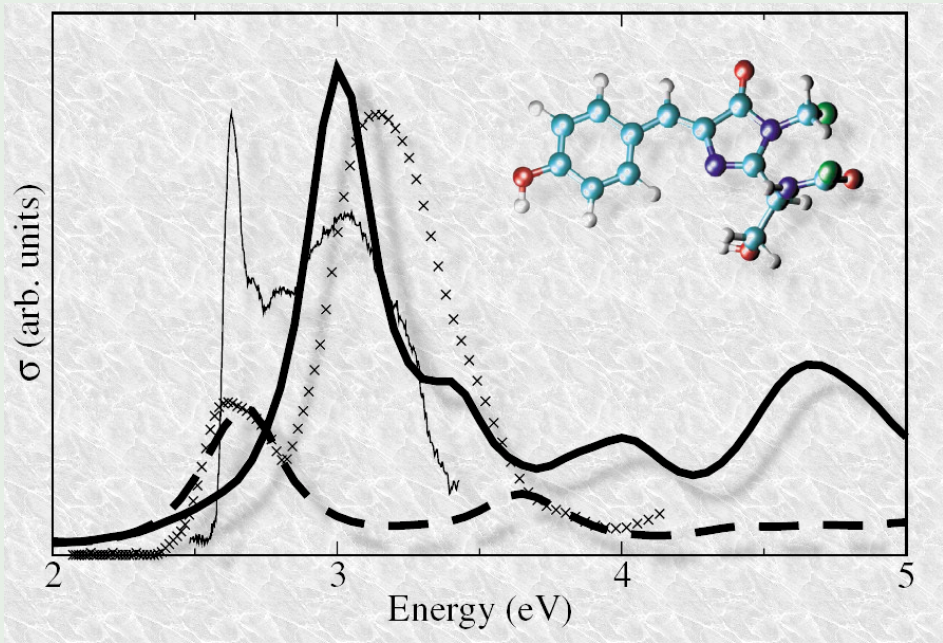
Towards new applications

Strongly correlated systems



EEL spectrum of VO_2

Biological systems



Abs spectrum of Green Fluorescent Protein

M.Gatti, submitted to PRL

M.Marques *et al.* Phys.Rev.Lett **90**, 258101 (2003)

Outline

New Frontiers

TDDFT concept into MBPT

$$\Sigma = GW\Gamma$$

i.e. a promising path to go beyond GW approx through TDDFT

F.Bruneval *et al.* Phys.Rev.Lett **94**, 186402 (2005)

Quantum Transport in TDDFT

$$I(t) = -e \int_{\mathcal{V}} d\mathbf{r} \frac{d}{dt} n(\mathbf{r}, t)$$

total current through a junction

G.Stefanucci *et al.* Europhys.Lett. **67**, 14 (2004)

Let's go back to Ground-State

Total energies calculations via TDDFT

$$E = T_{KS} + V_{ext} + E_H + E_{xc}$$

$$E_{xc} \propto \int d\mathbf{r} d\mathbf{r}' \int_0^1 d\lambda \int_0^\infty du \chi^\lambda(\mathbf{r}, \mathbf{r}', iu)$$

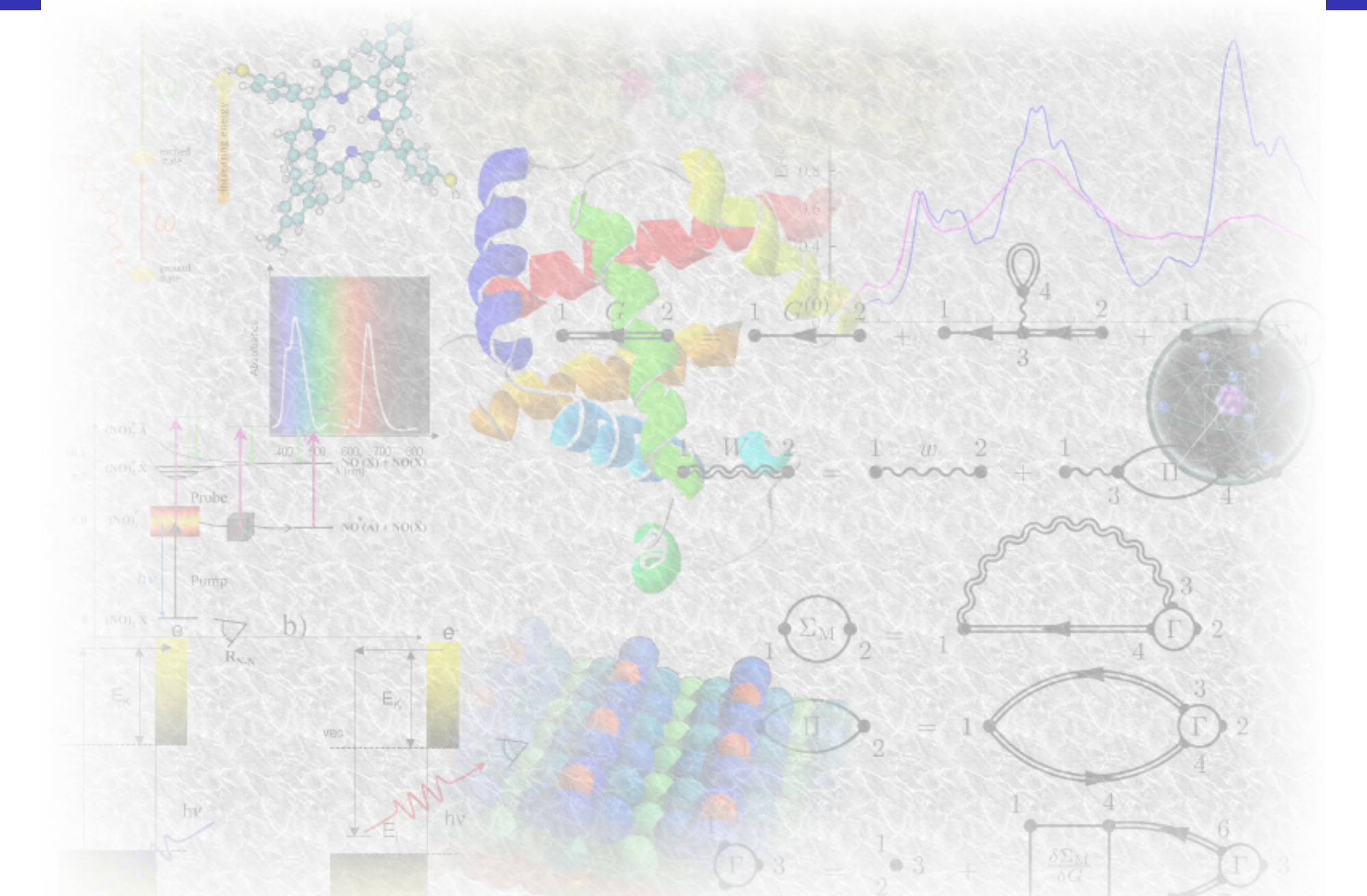
adiabatic connection fluctuation-dissipation theorem

 D.C.Langreth *et al.* Solid State Comm. **17**, 1425 (1975)

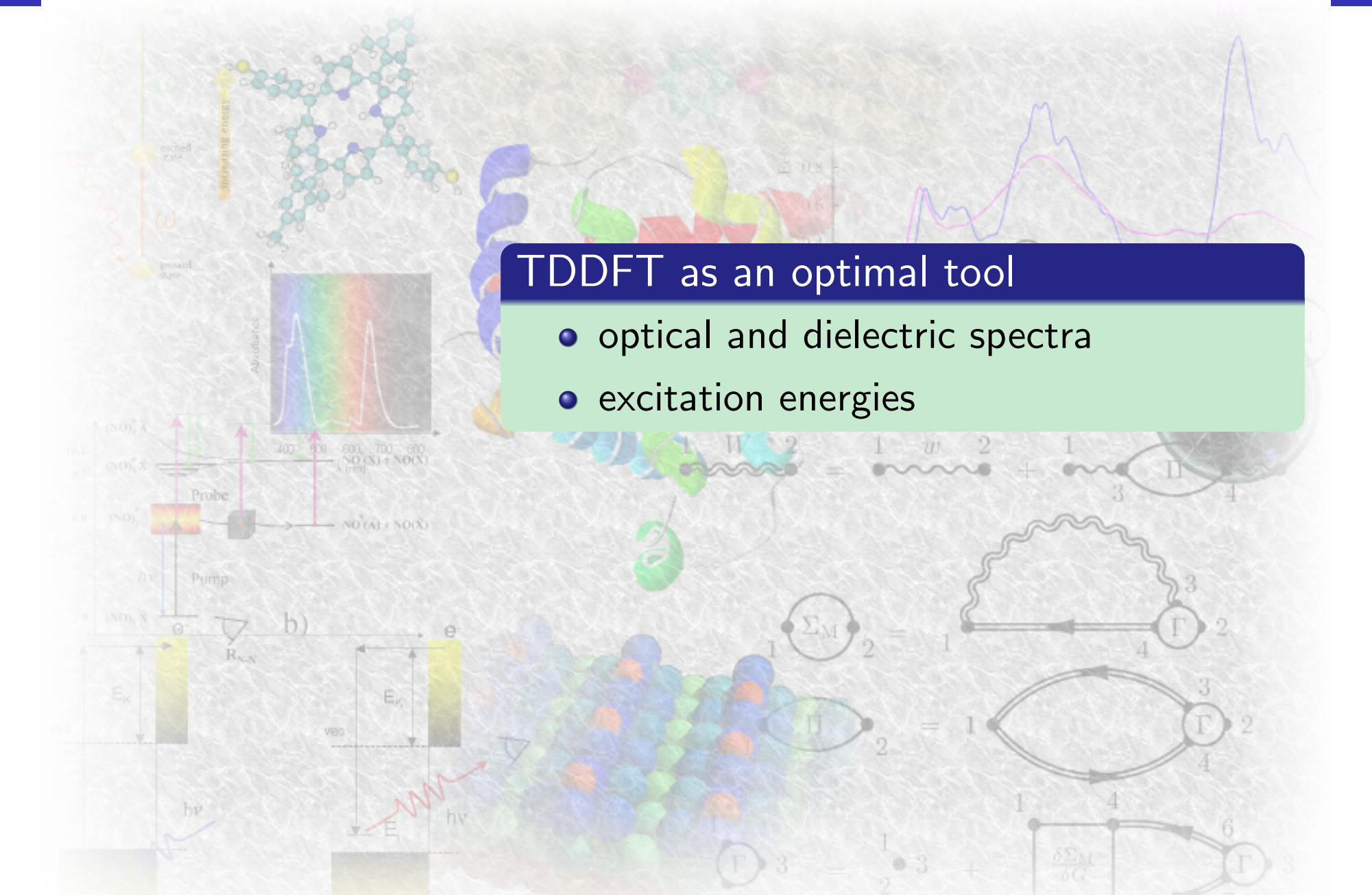
 M.Lein *et al.* **61**, 13431 (2000)

Outline

Perspectives



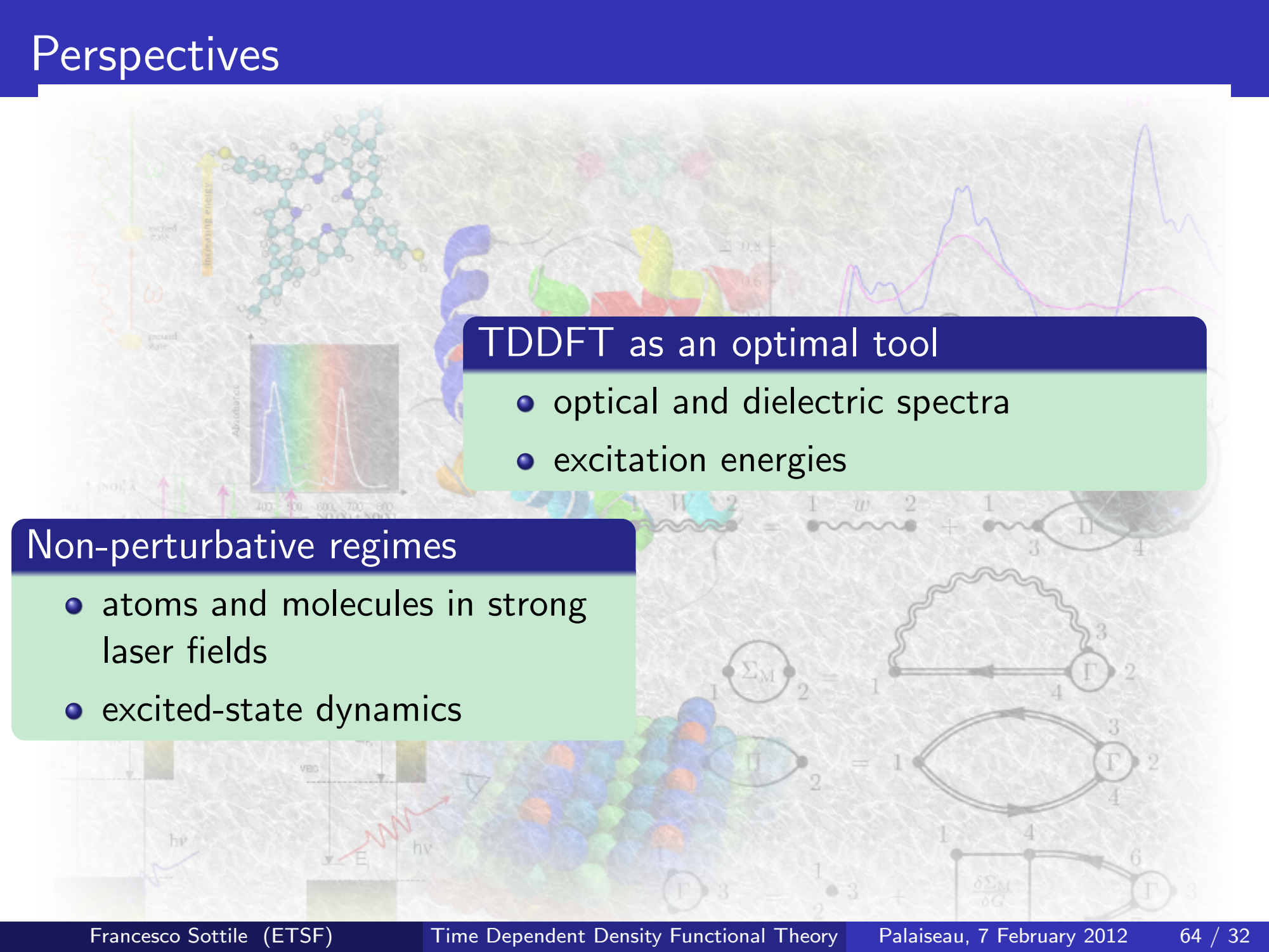
Perspectives



TDDFT as an optimal tool

- optical and dielectric spectra
- excitation energies

Perspectives



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- atoms and molecules in strong laser fields
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Perspectives

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New frontiers application

- ground-state total energy
- quantum transport

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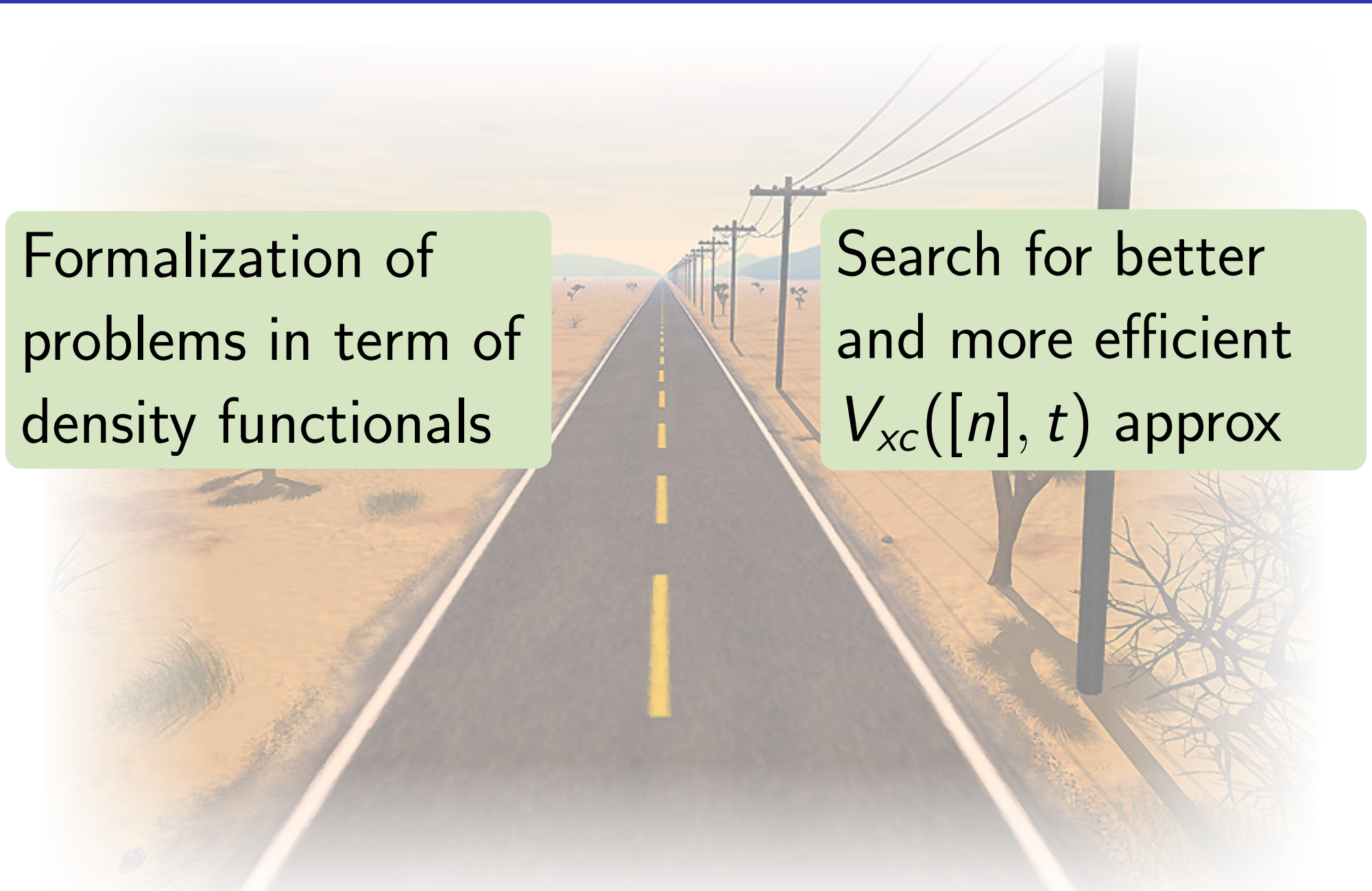
Time-Dependent Density Functional Theory Springer (2006)

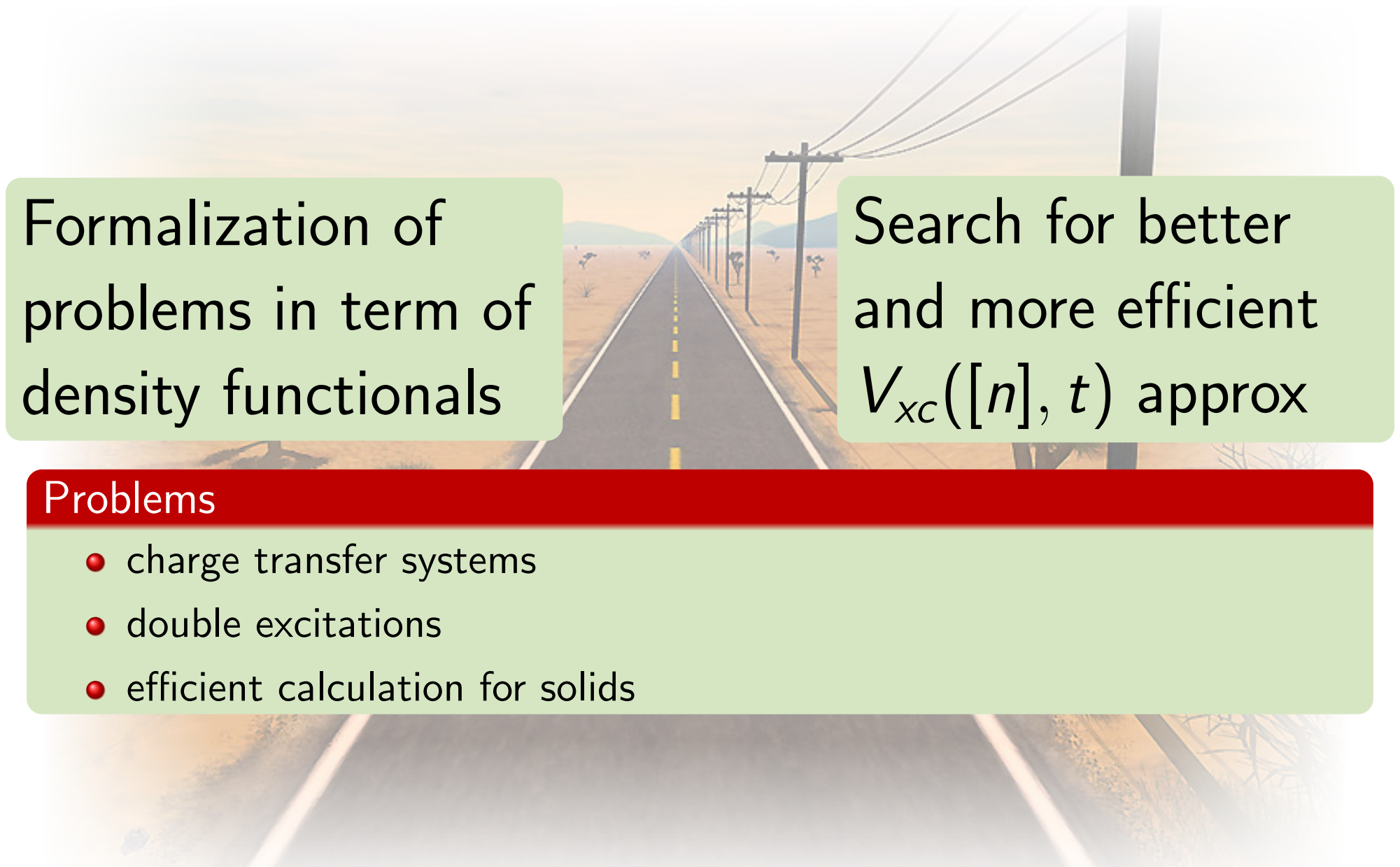
Long road ahead



Formalization of problems in term of density functionals

Search for better and more efficient $V_{xc}([n], t)$ approx

Long road ahead



Formalization of problems in term of density functionals

Search for better and more efficient $V_{xc}([n], t)$ approx

Problems

- charge transfer systems
- double excitations
- efficient calculation for solids

Resources

Codes (more or less) available for TDDFT

- Octopus (Marques,Castro,Rubio) -(real space, real time) - finite systems - GPL
  http://www.tddft.org/programs/octopus/
- DP (Olevano,Reining,Sottile) - (reciprocal space, frequency domain) - solides and finite systems - Academic Free License
  http://theory.polytechnique.fr/codes/dp/dp.html
- Self (Marini) - (reciprocal space, frequency domain)
- Fleszar code
- Rehr (core excitations)
- TDDFT (Bertsch)
- VASP, SIESTA, ADF, TURBOMOLE
- TD-DFPT (Baroni)