Time Dependent Density Functional Theory

A personal view

Francesco Sottile

Laboratoire des Solides Irradiés
Ecole Polytechnique, Palaiseau - France
European Theoretical Spectroscopy Facility (ETSF)

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ETSF
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Outline

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Density Functional ... Why ?

Basic ideas of DFT

1. Any observable of a quantum system can be obtained from the density of the system **alone**.
2. The density of an interacting-particles system can be calculated as the density of an auxiliary system of **non-interacting** particles.

Importance of the density

Example: atom of Carbon (6 electron)

$\Psi(\mathbf{r}_1, .., \mathbf{r}_6)$ 18 coordinates

10 entries/coordinate $\Rightarrow 10^{18}$ entries
8 bytes/entry $\Rightarrow 8 \cdot 10^{18}$ bytes
$5 \cdot 10^9$ bytes/DVD $\Rightarrow 10^{13}$ DVDs

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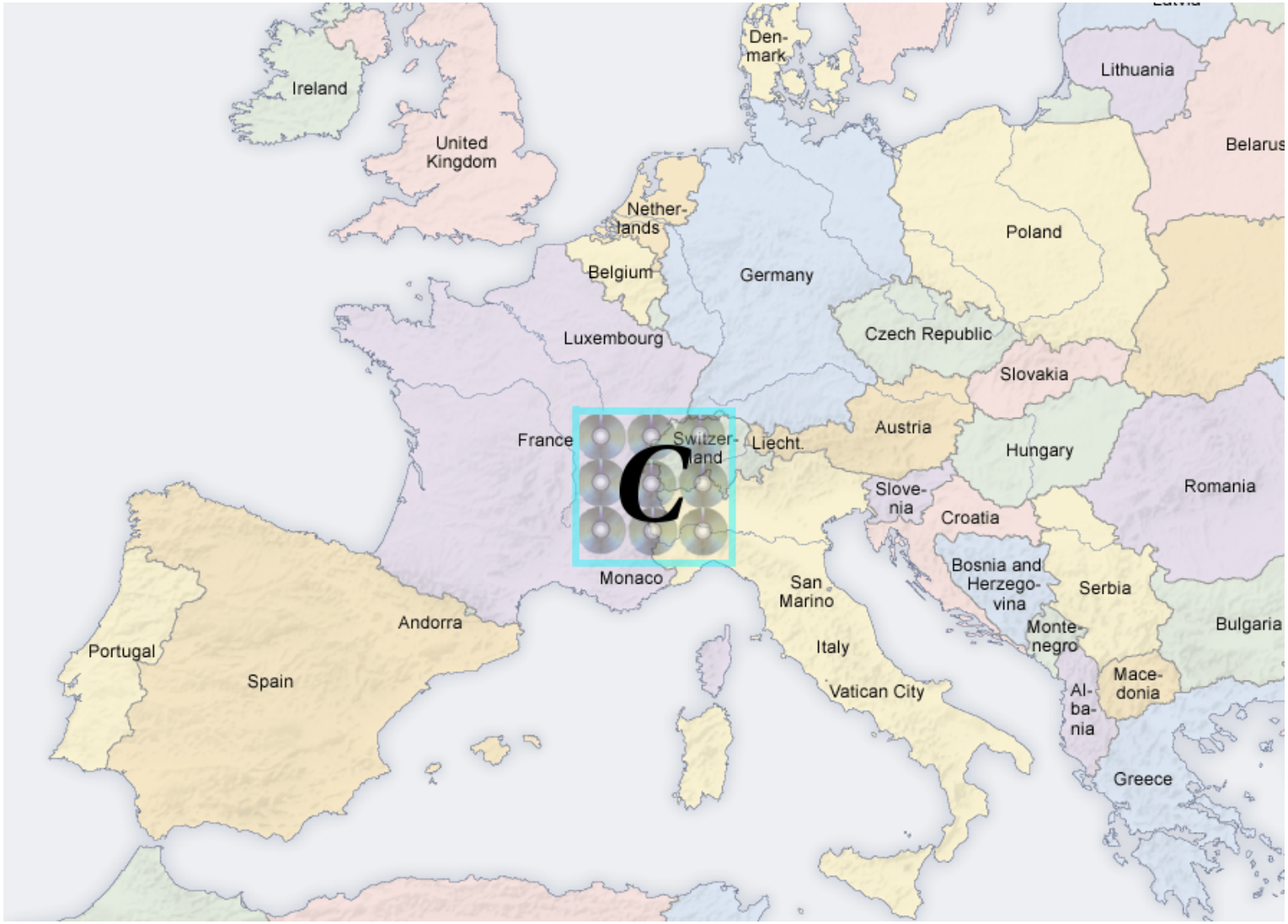

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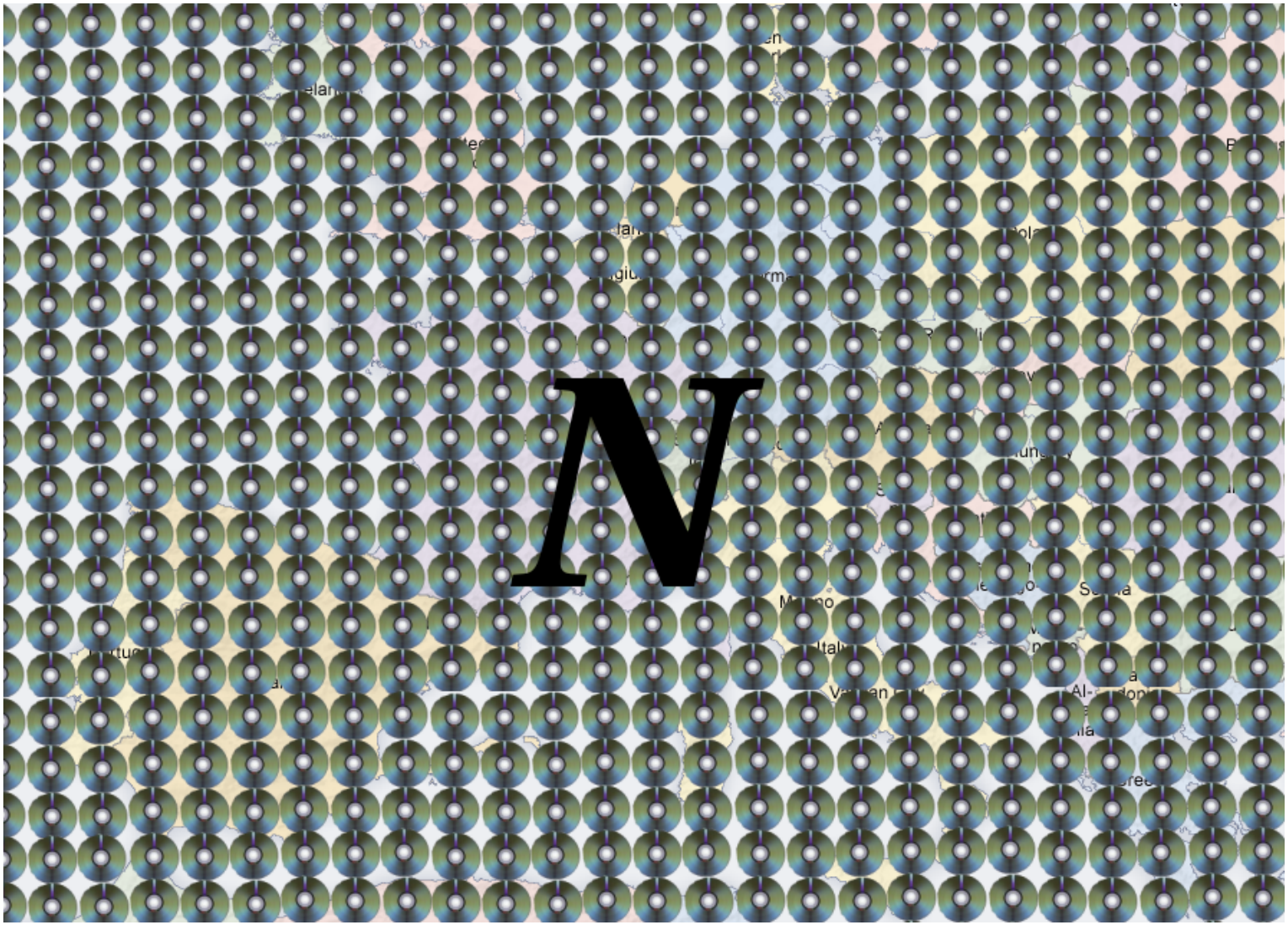

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$$H_i(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r})\psi_i(\mathbf{r})$$

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Density Functional ... Successfull ?

TABLE II: Top-10 cited PR articles. The asterisks denote citation undercount due to citations with missing prepended A/B page numbers – 123 out of 3227 total for item 1 and 120 out of 2640 for item 2.

Impact Rank	Publication			# cites	Av. Age	Impact	Title	Author(s)
1	PR	140	A1133	1965	3227*	26.64	85972	Self-Consistent Equations...	W. Kohn & L. J. Sham
2	PR	136	B864	1964	2460*	28.70	70604	Inhomogeneous Electron Gas	P. Hohenberg & W. Kohn
3	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to...	J. P. Perdew & A. Zunger
4	PRL	45	566	1980	1781	15.42	27463	Ground State of the Electron ...	D. M. Ceperley & B. J. Alder
5	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer
6	PRL	19	1264	1967	1306	15.46	20191	A Model of Leptons	S. Weinberg
7	PRB	12	3060	1975	1259	18.35	23103	Linear Methods in Band Theory	O. K. Andersen
8	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
8	RMP	57	287	1985	1055	9.17	9674	Disordered Electronic Systems	P. A. Lee & T. V. Ramakrishnan
9	RMP	54	437	1982	1045	10.82	11307	Electronic Properties of...	T. Ando, A. B. Fowler, & F. Stern
10	PRB	13	5188	1976	1023	20.75	21227	Special Points for Brillouin-...	H. J. Monkhorst & J. D. Pack

S. Redner http://arxiv.org/abs/physics/0407137

Time Dependent DFT ... Why ?

Large field of research concerned with
many-electron systems in time-dependent fields

Different Phenomena

- absorption spectra
- energy loss spectra
- photo-ionization
- high-harmonic generation
- photo-emission

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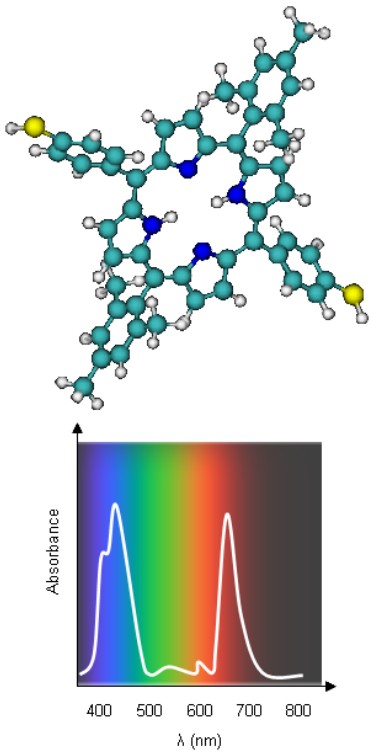

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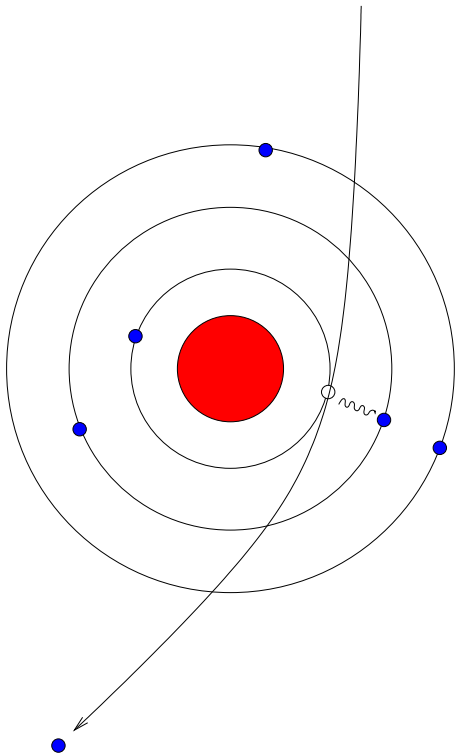

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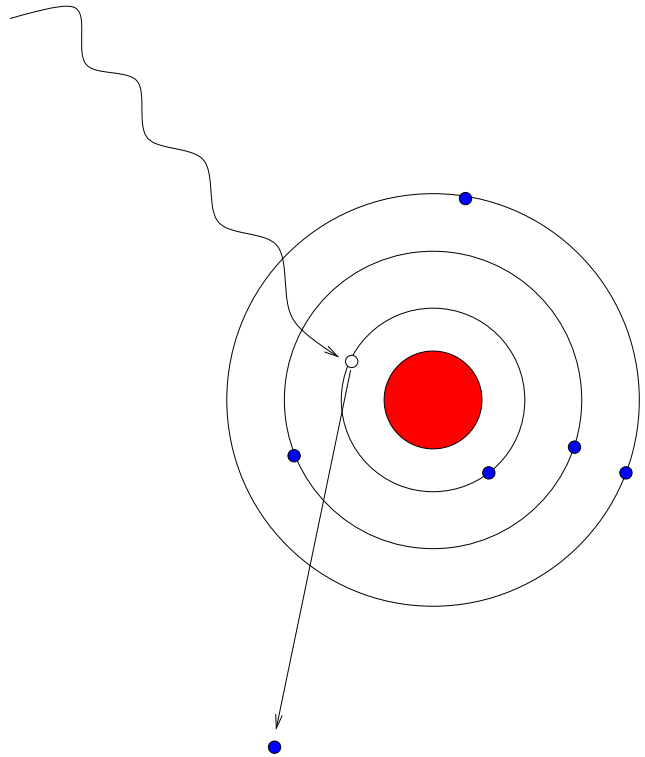

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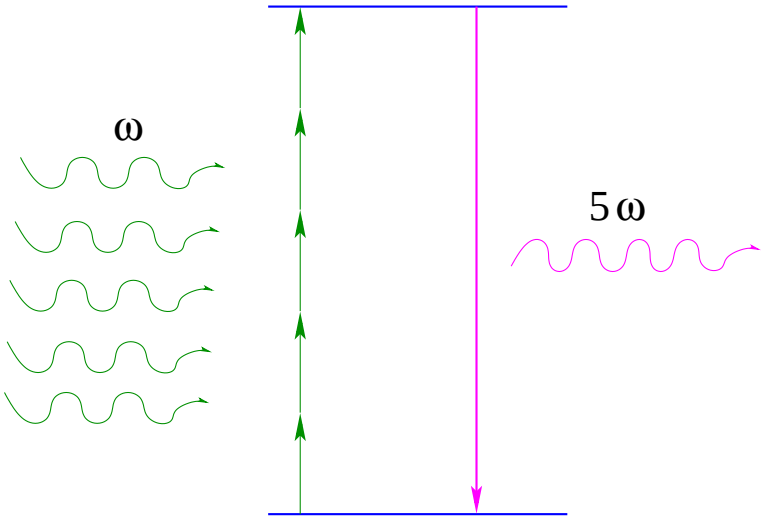

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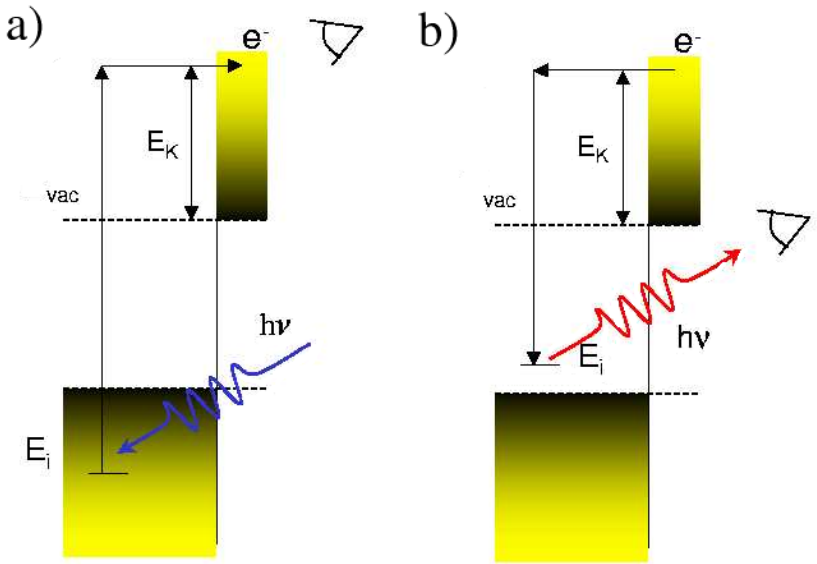

Time Dependent DFT ... Why ?

We need a time dependent theory

$$\Downarrow$$

TDDFT is a promising candidate

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 $n(\mathbf{r})$

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

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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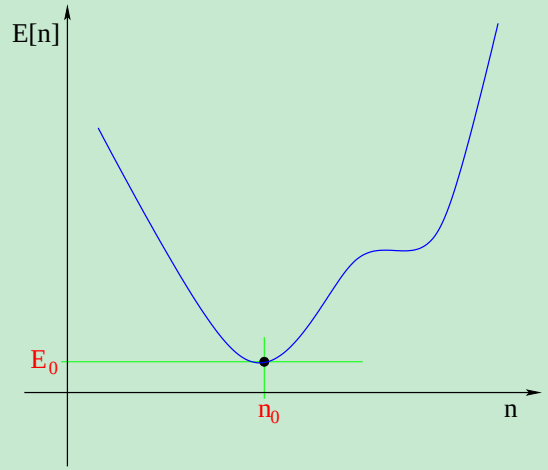
Hohenberg-Kohn theorem 2

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



TDDFT

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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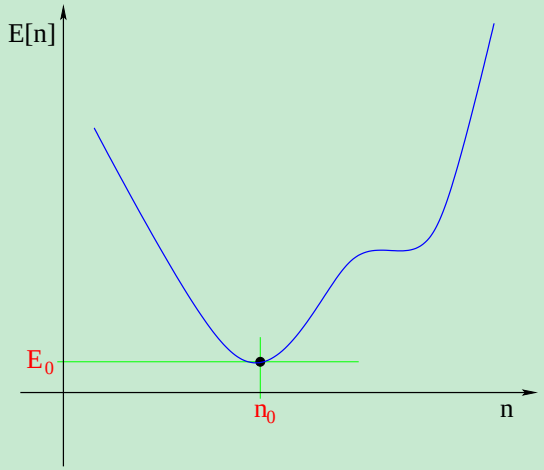

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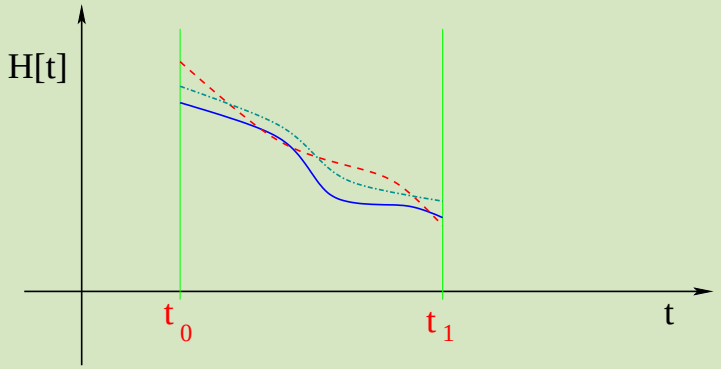

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Kohn-Sham equations

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

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

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

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

TDDFT

Time-dependent Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{tot}(\mathbf{r},t)\right]\phi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t)$$

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V_{xc} functional of the density **at all times** and of the **initial state**.

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Photo-absorption cross section σ

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

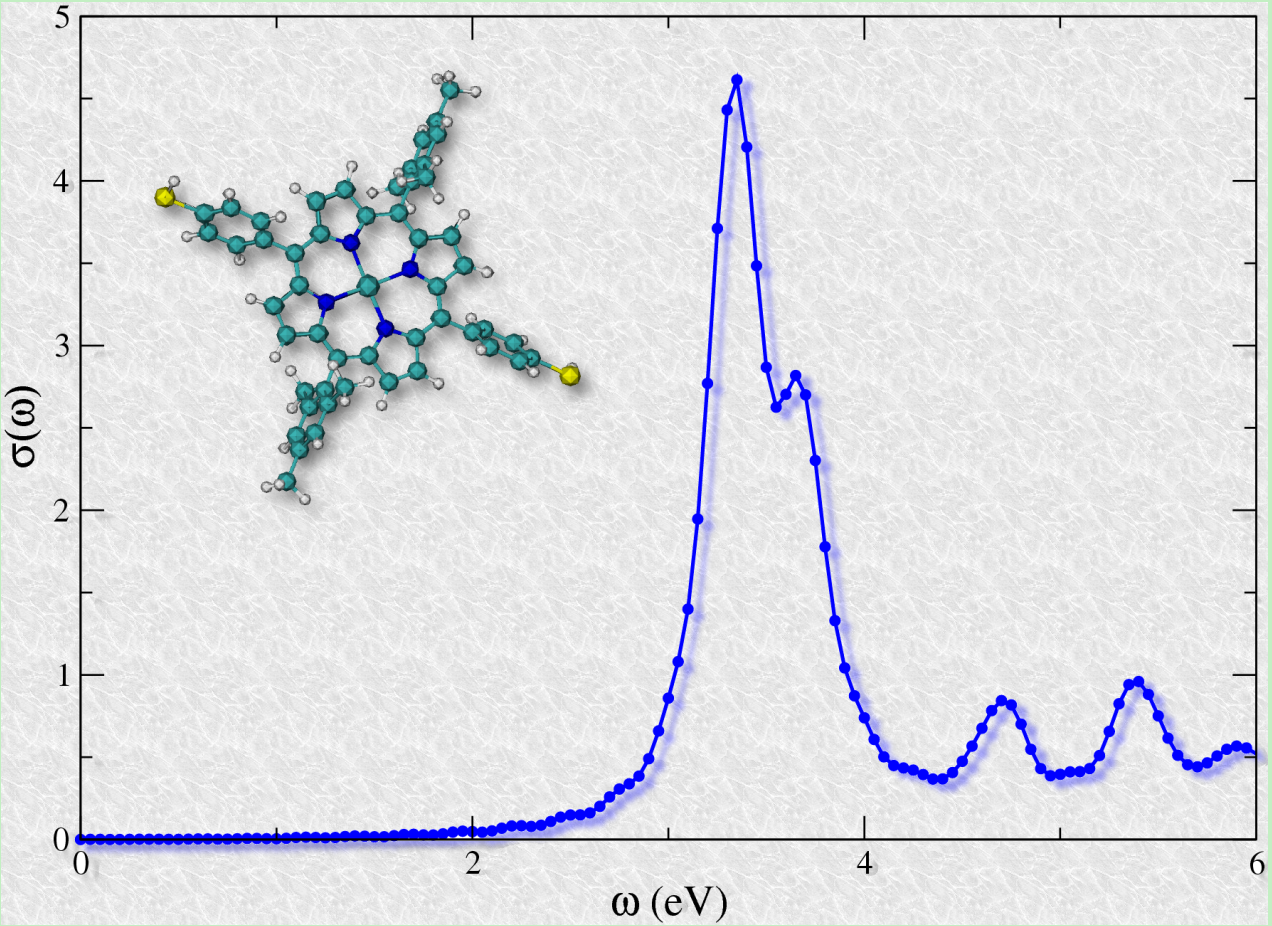
$$\alpha(t) = -\int d\mathbf{r}\, V_{ext}(\mathbf{r}, t) n(\mathbf{r}, t)$$

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

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

The name of the game: TDDFT

Photo-absorption cross section σ: porphyrin



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Other observables

Multipoles

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

Angular momentum

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

Real space - Time evolution approach

Advantages

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

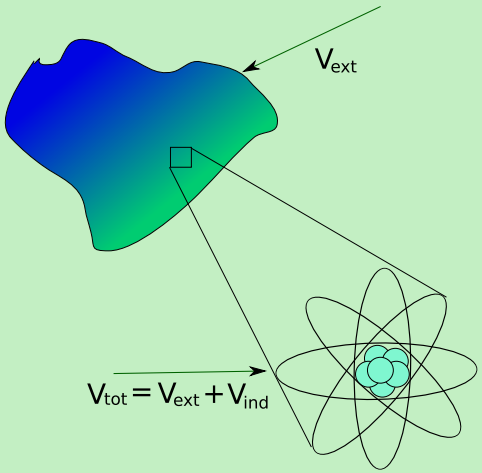
Shortcomings

- 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



$$V_{tot} = \varepsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

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

Dielectric function ε

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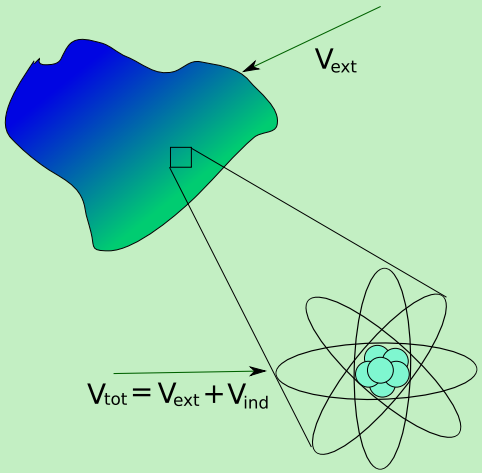

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EELS — R index — ε — Abs — X-ray

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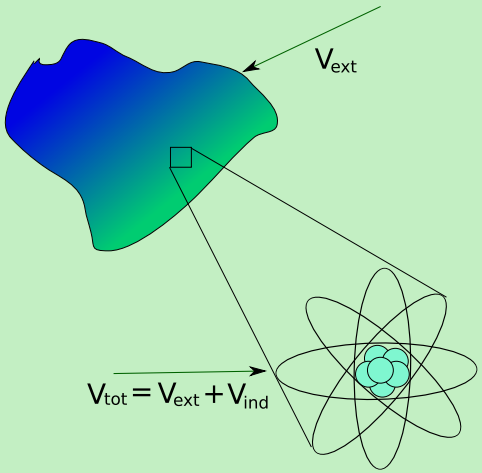

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Linear Response Approach

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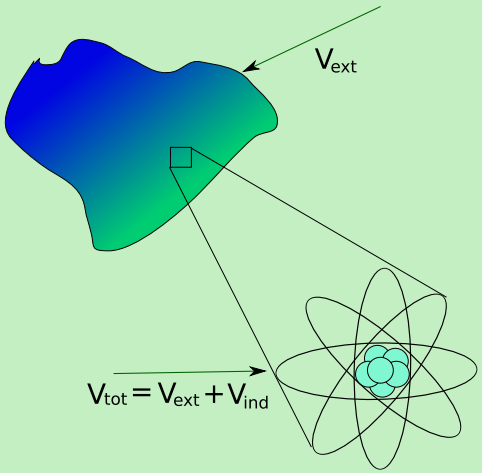

$$V_{tot} = \varepsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

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

Dielectric function ε

EELS R index ε Abs X-ray

Linear Response Approach

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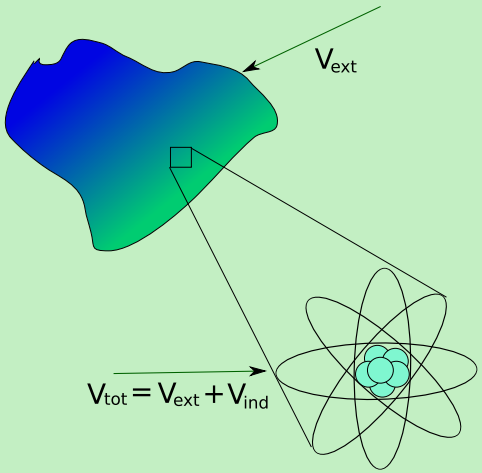

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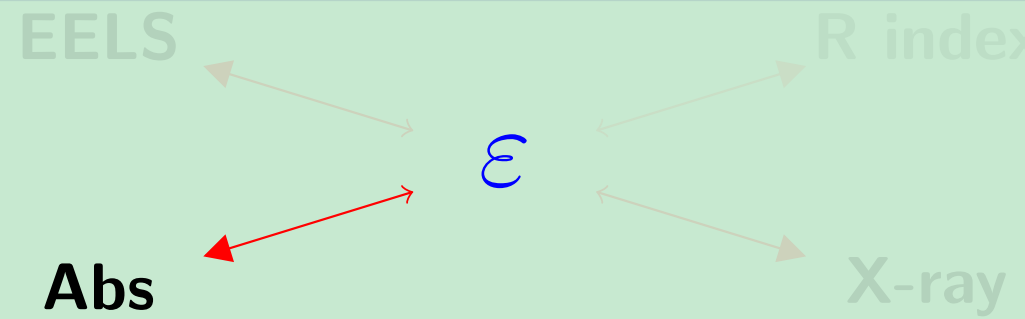

Linear Response Approach

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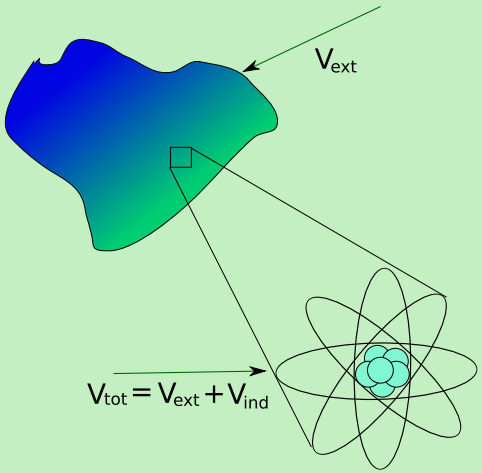

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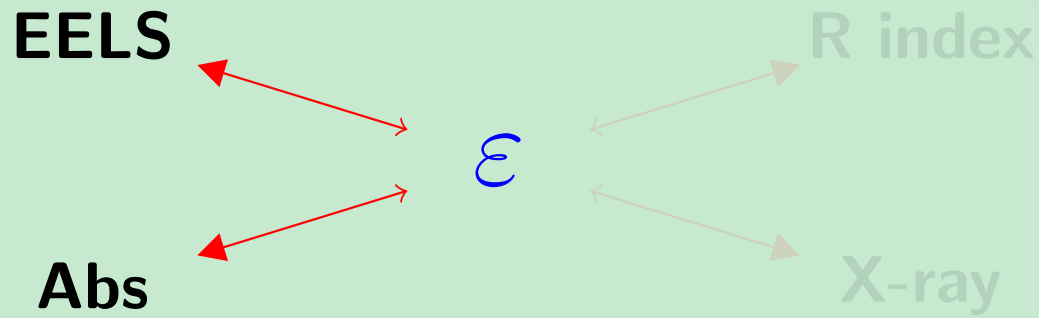

Linear Response Approach

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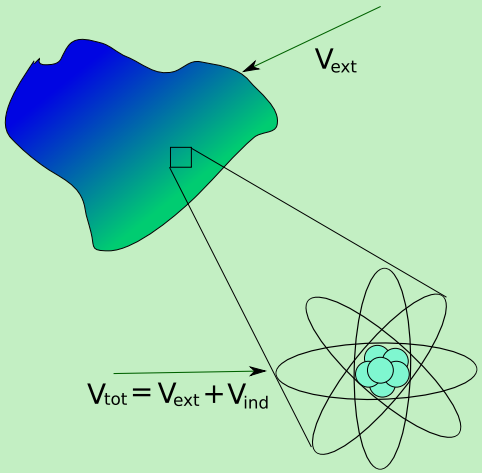

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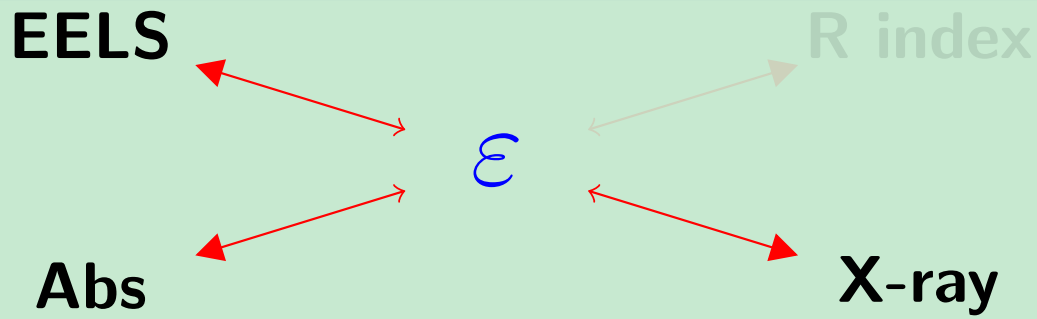

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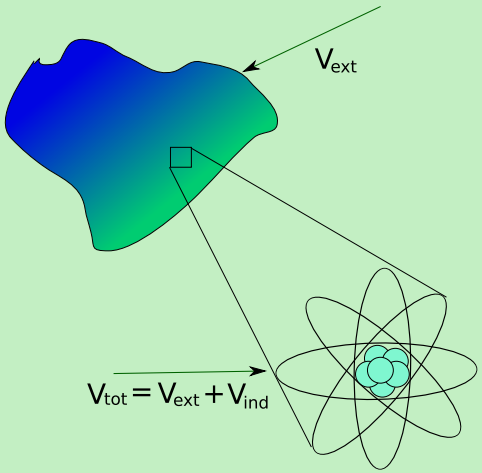

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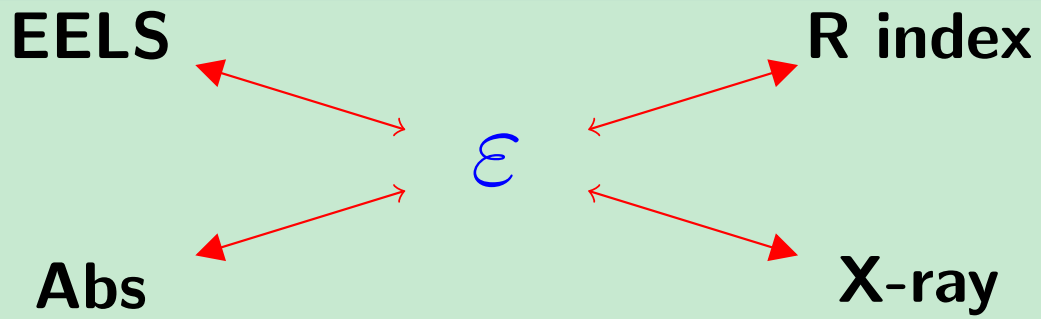

Linear Response Approach

Definition of polarizability

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

χ is the polarizability of the system

Linear Response Approach

Definition of polarizability

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Linear Response Approach

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Linear Response Approach

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χ is the polarizability of the system

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

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

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

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

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

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

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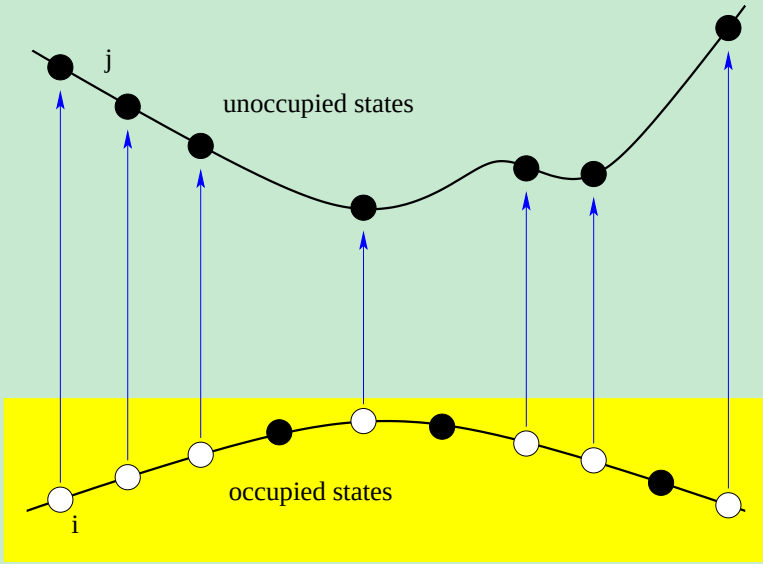

Linear Response Approach

Polarizability

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

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

$\Updownarrow$

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**

Linear Response Approach

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Linear Response Approach

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Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow$ ϕ_i, ϵ_i $[V_{xc}]$
2. $\phi_i, \epsilon_i \longrightarrow \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$
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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Finite systems

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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Solids

Absorption and Energy Loss Spectra

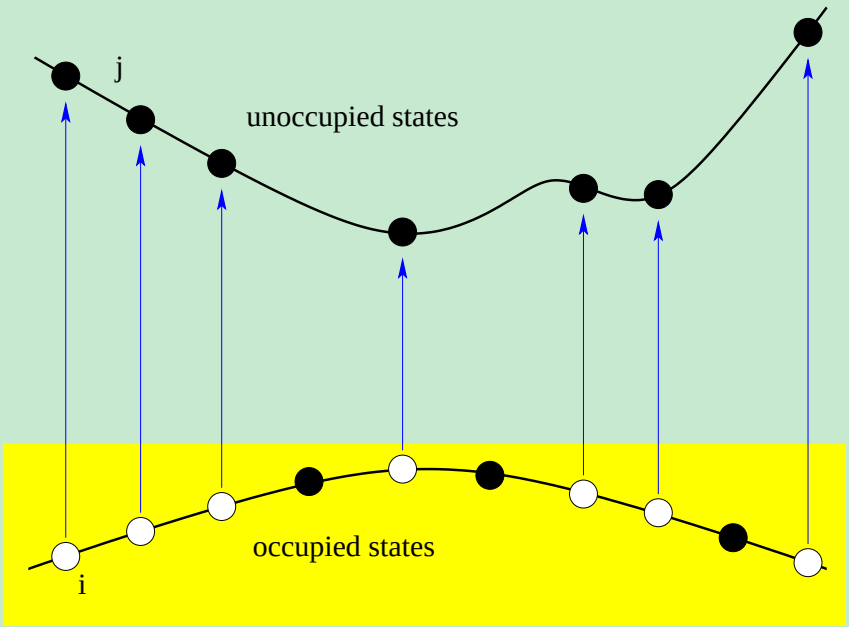
$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) \longrightarrow \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$$

G =reciprocal lattice vector
q =momentum transfer of the perturbation

Solids

Absorption and Energy Loss Spectra

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



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

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

Solids

Absorption and Energy Loss Spectra

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

Solids

Absorption and Energy Loss Spectra

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Solids

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

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Solids

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

Solids

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

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

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

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

Solids

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

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Exercise

$$\mathrm{Im}\left\{\frac{1}{\varepsilon_{00}^{-1}}\right\} = -\mathrm{v}_0\left\{\bar{\chi}_{00}\right\}$$

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

Solids

Energy Loss Spectra $\mathbf{q} \longrightarrow 0$

$$V_{tot}(\mathbf{G}=0) = \varepsilon^{-1}_{00} V_{ext}(\mathbf{G}'=0)$$

$$\mathrm{ELS} = -\mathrm{Im}\left\{\varepsilon^{-1}_{00}\right\} = -v_0 \mathrm{Im}\left\{\chi_{00}\right\}$$

Absorption Spectrum $\mathbf{q} \longrightarrow 0$

$$V_{tot}(\mathbf{G}=0) = \bar{\varepsilon}^{-1}_{00}\left[V_{ext}(\mathbf{G}'=0) + V_H(\mathbf{G}'=0)\right]$$

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

Solids

Energy Loss Spectra $\mathbf{q} \longrightarrow 0$

$$V_{tot}(\mathbf{G}=0) = \varepsilon_{00}^{-1} V_{ext}(\mathbf{G}'=0)$$

$$\mathrm{ELS} = -\mathrm{Im}\left\{\varepsilon_{00}^{-1}\right\} = -v_0 \mathrm{Im}\left\{\chi_{00}\right\}$$

Absorption Spectrum $\mathbf{q} \longrightarrow 0$

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

Solids

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

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

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

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

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

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

microscopic components

Solids

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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$$\text{Abs} = \text{Im} \left\{ \frac{1}{\varepsilon_{00}^{-1}} \right\}$$

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$$\text{Abs}^{\text{NLF}} = \text{Im} \left\{ \varepsilon_{00} \right\}$$

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 $\longrightarrow \phi_i, \epsilon_i$ [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

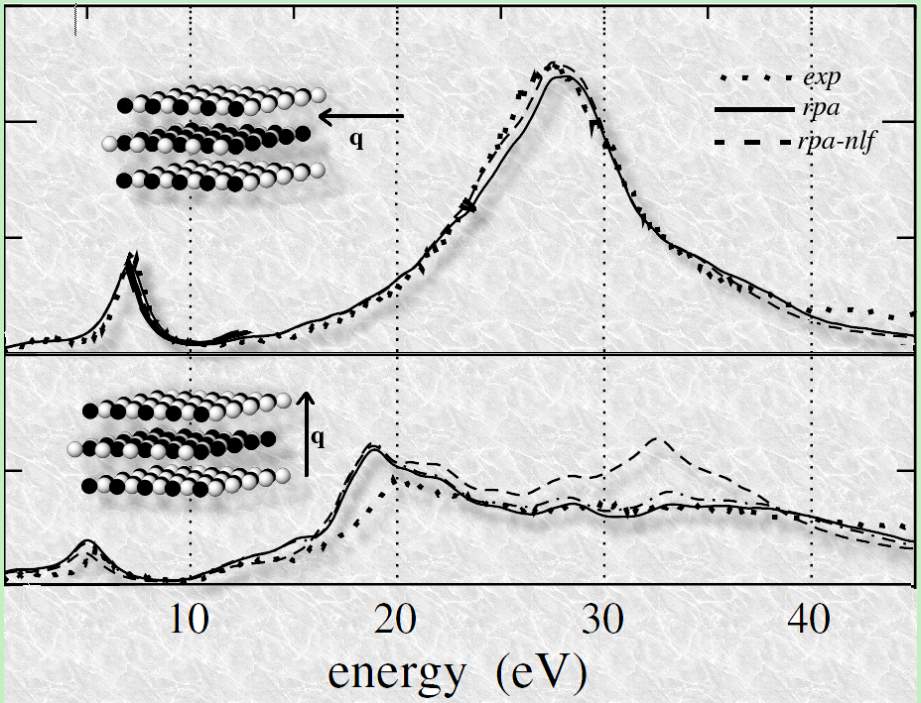
Electron Energy Loss Spectrum of Graphite

RPA vs EXP

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

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

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



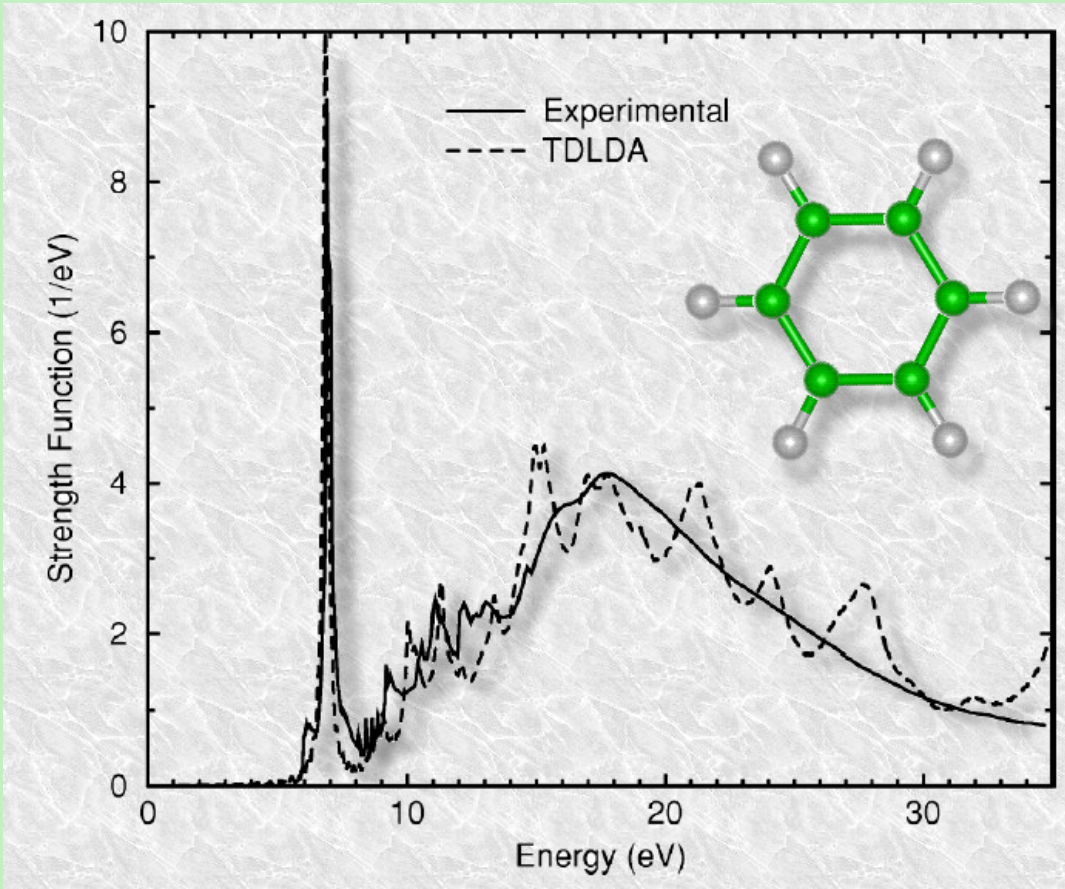
A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ALDA: Achievements and Shortcomings

Photo-absorption cross section of Benzene

ALDA vs EXP

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



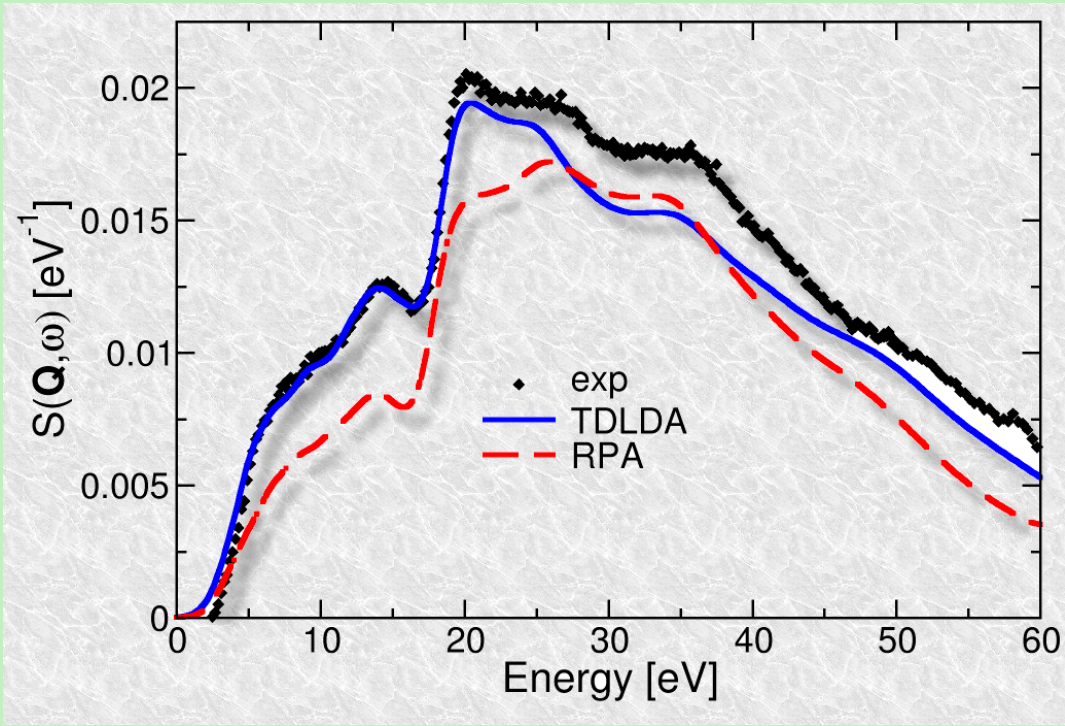
K.Yabana and G.F.Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

ALDA: Achievements and Shortcomings

Inelastic X-ray scattering of Silicon

ALDA vs RPA vs EXP

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



H-C.Weissker *et al.* submitted

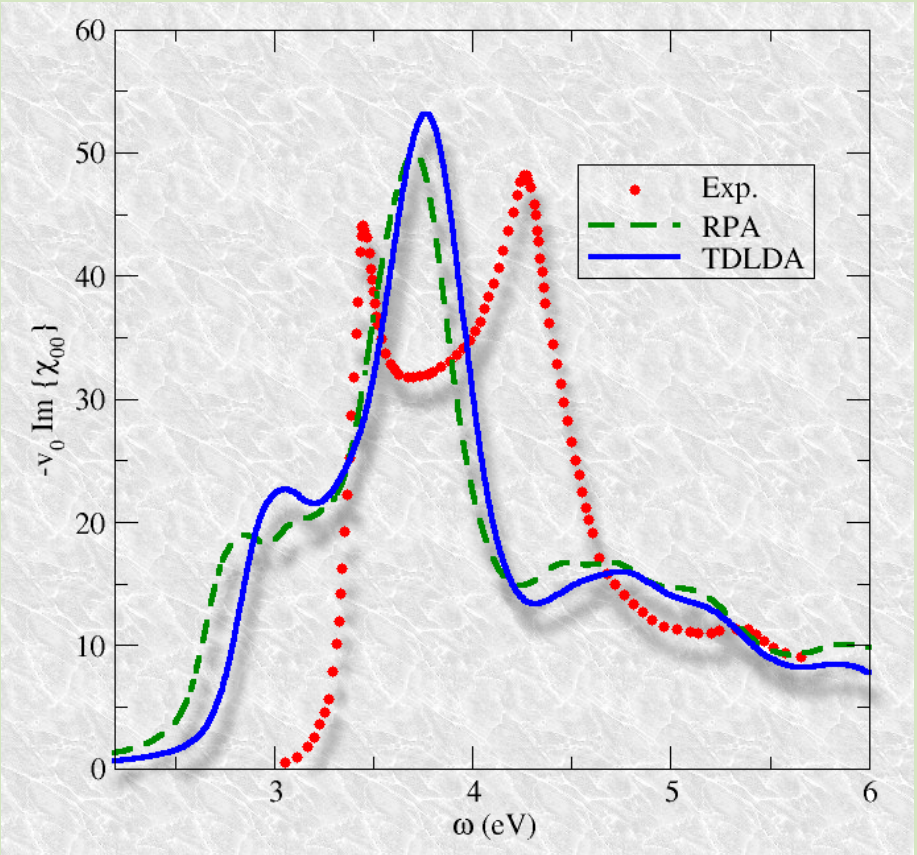
ALDA: Achievements and Shortcomings

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

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

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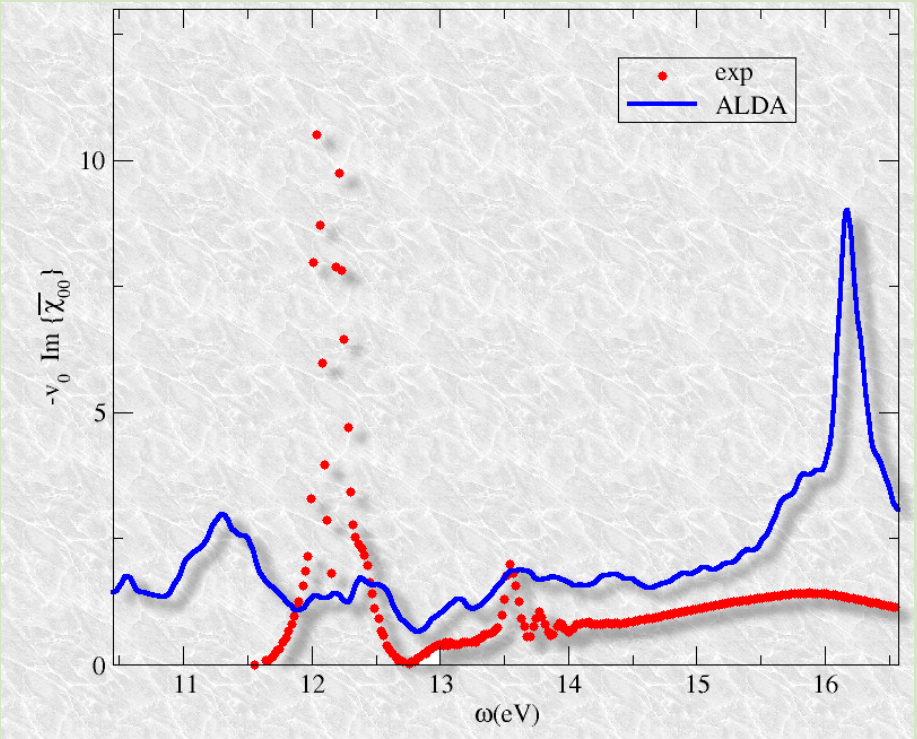

ALDA: Achievements and Shortcomings

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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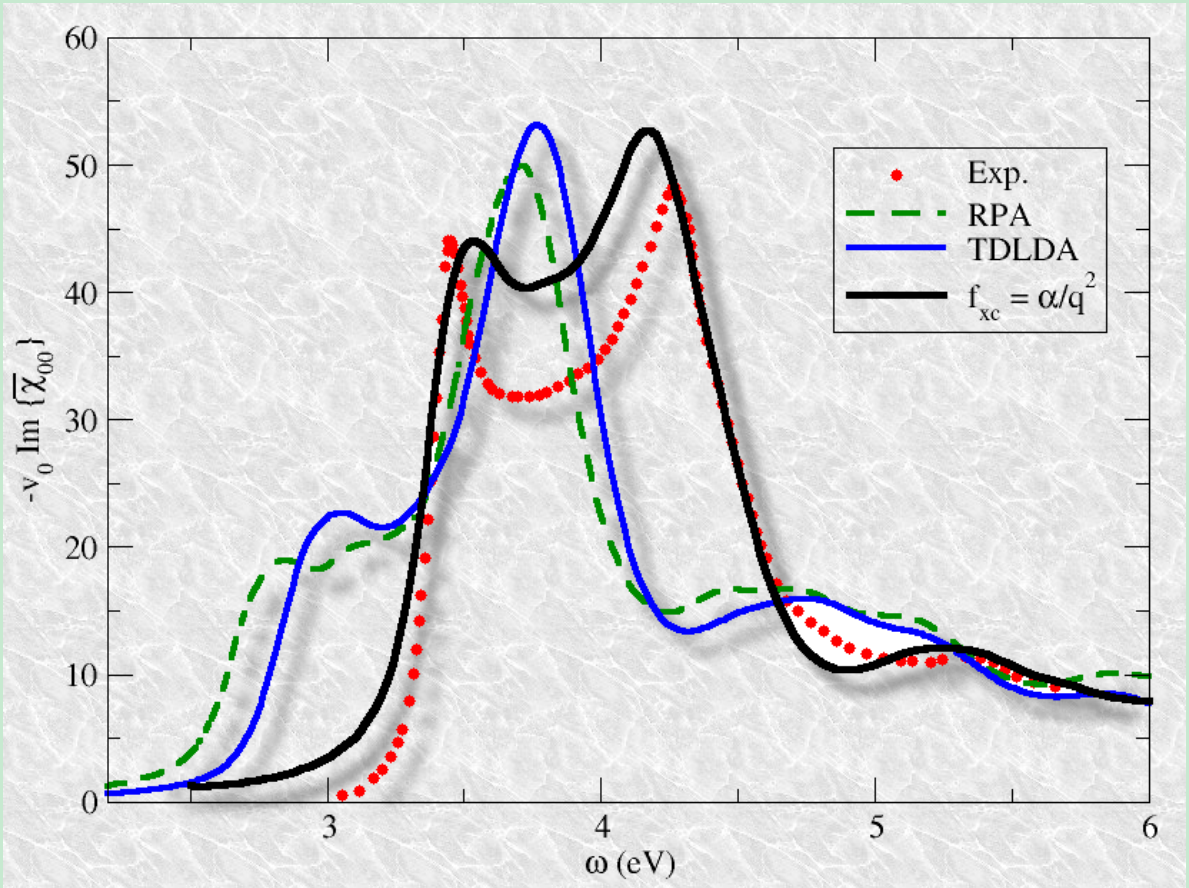
ALDA: Achievements and Shortcomings

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.

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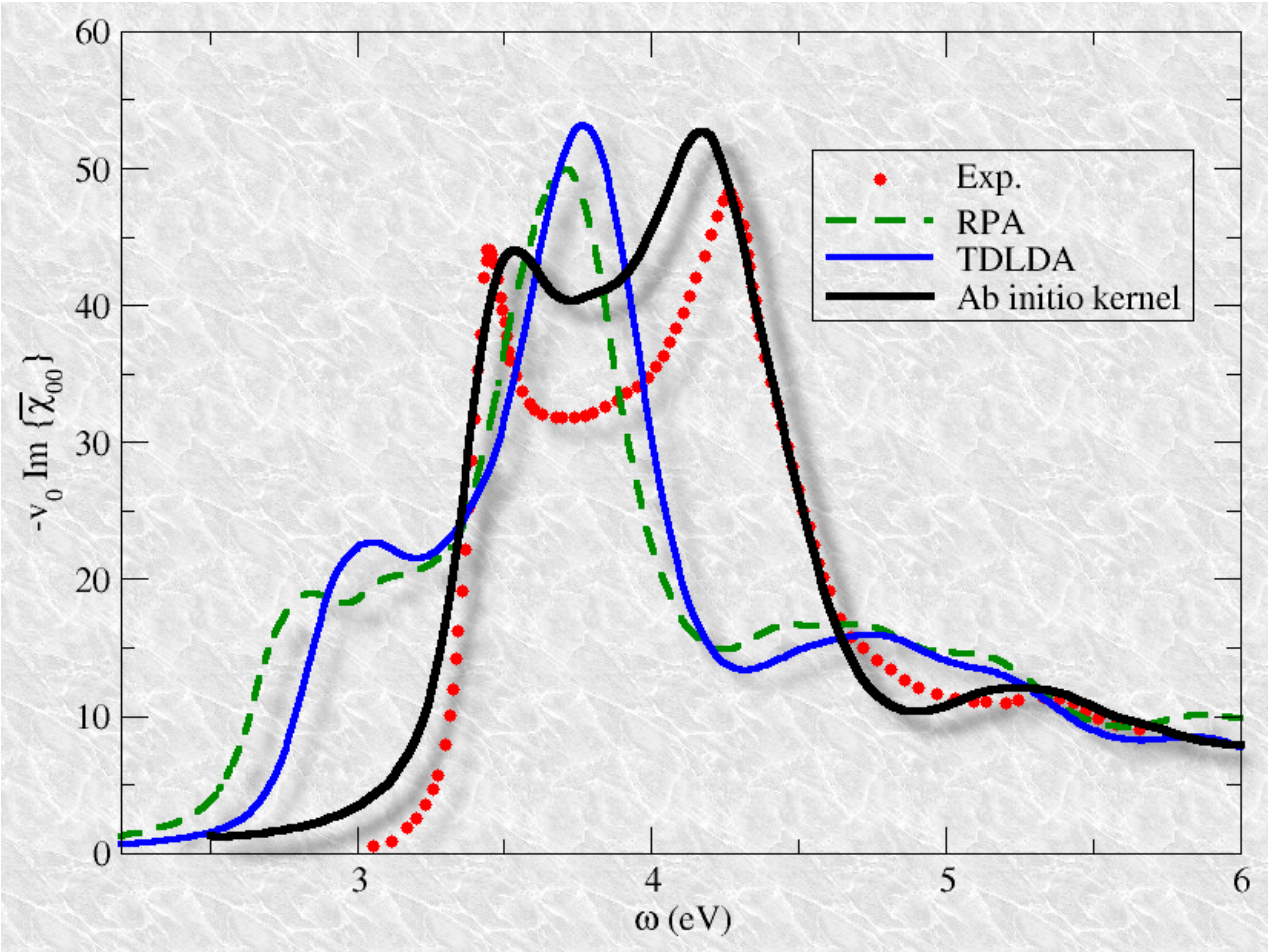
Abs in solids. Insights from MBPT

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.

Beyond ALDA approximation



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

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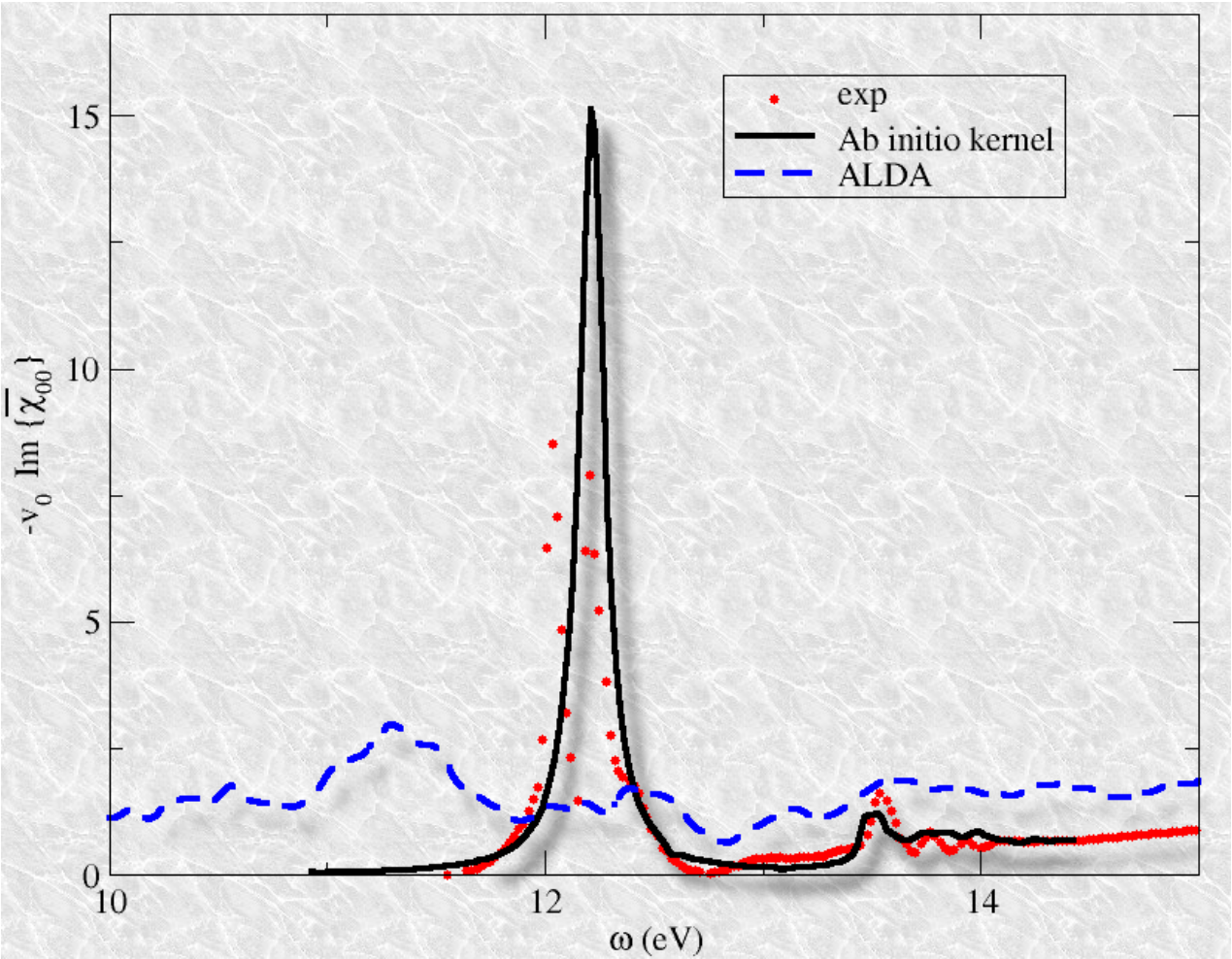


Sottile *et al.* submitted.

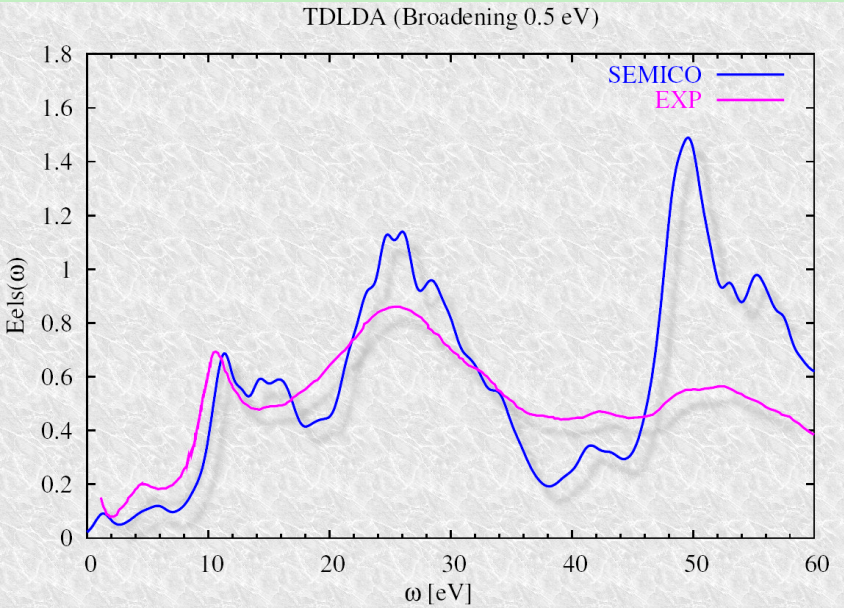
Spectra of simple systems

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

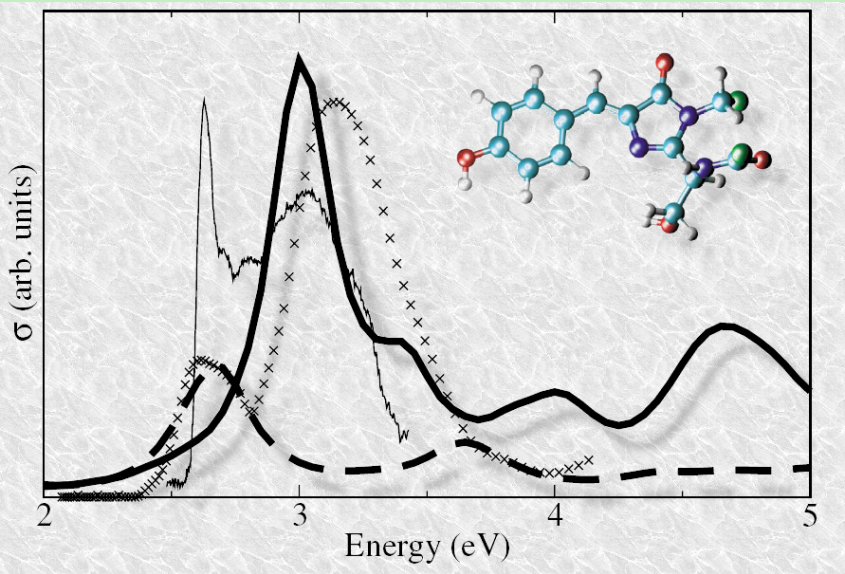
Strongly correlated systems



EEL spectrum of VO_2

M.Gatti, preliminary results

Biological systems



Abs spectrum of Green Fluorescent Protein

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)

New Frontiers

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)

New Frontiers

Let's go back to Ground-State

Total energies calculations via TDDFT

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

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

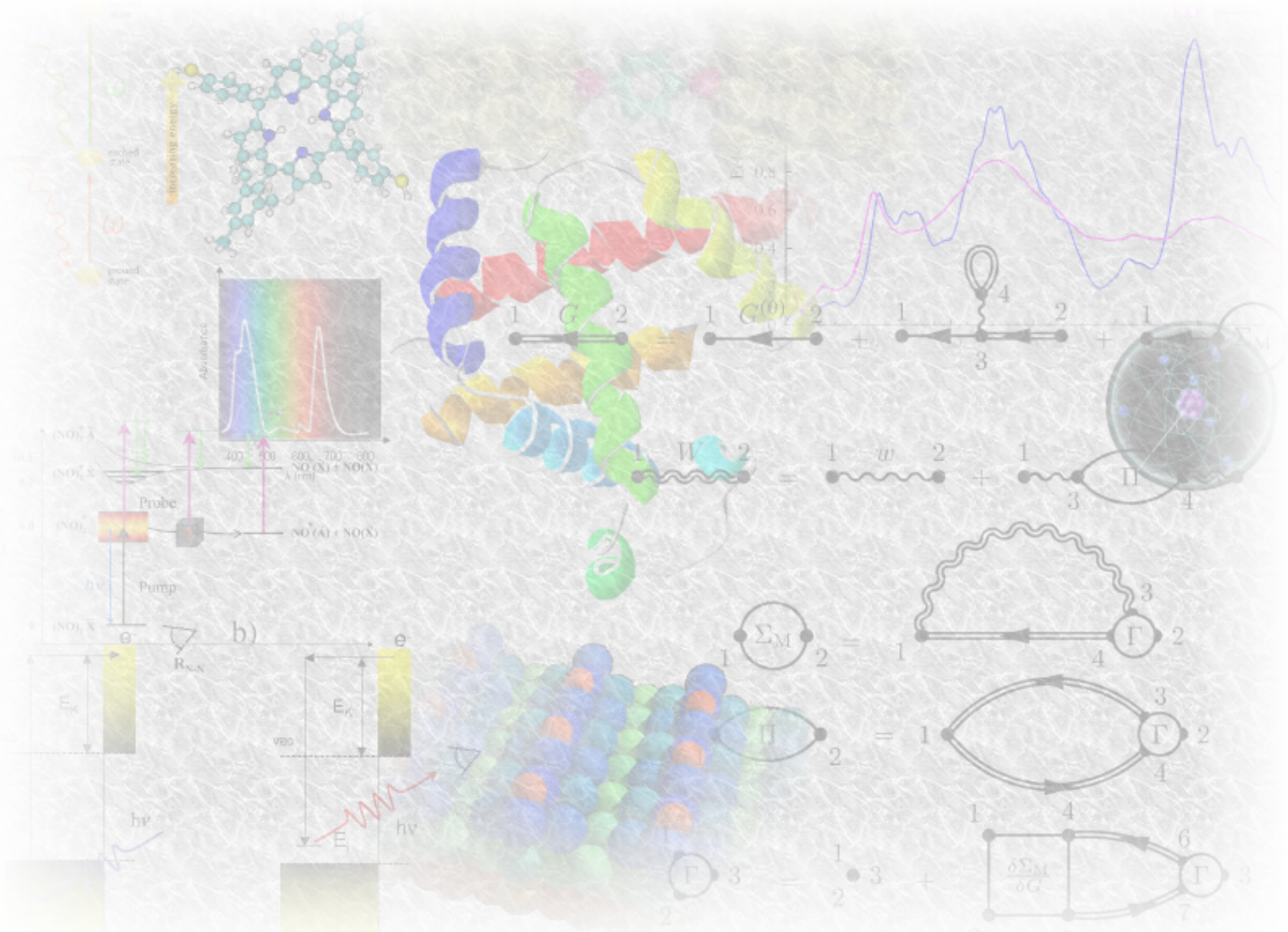
adiabatic connection fluctuation-dissipation theorem

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

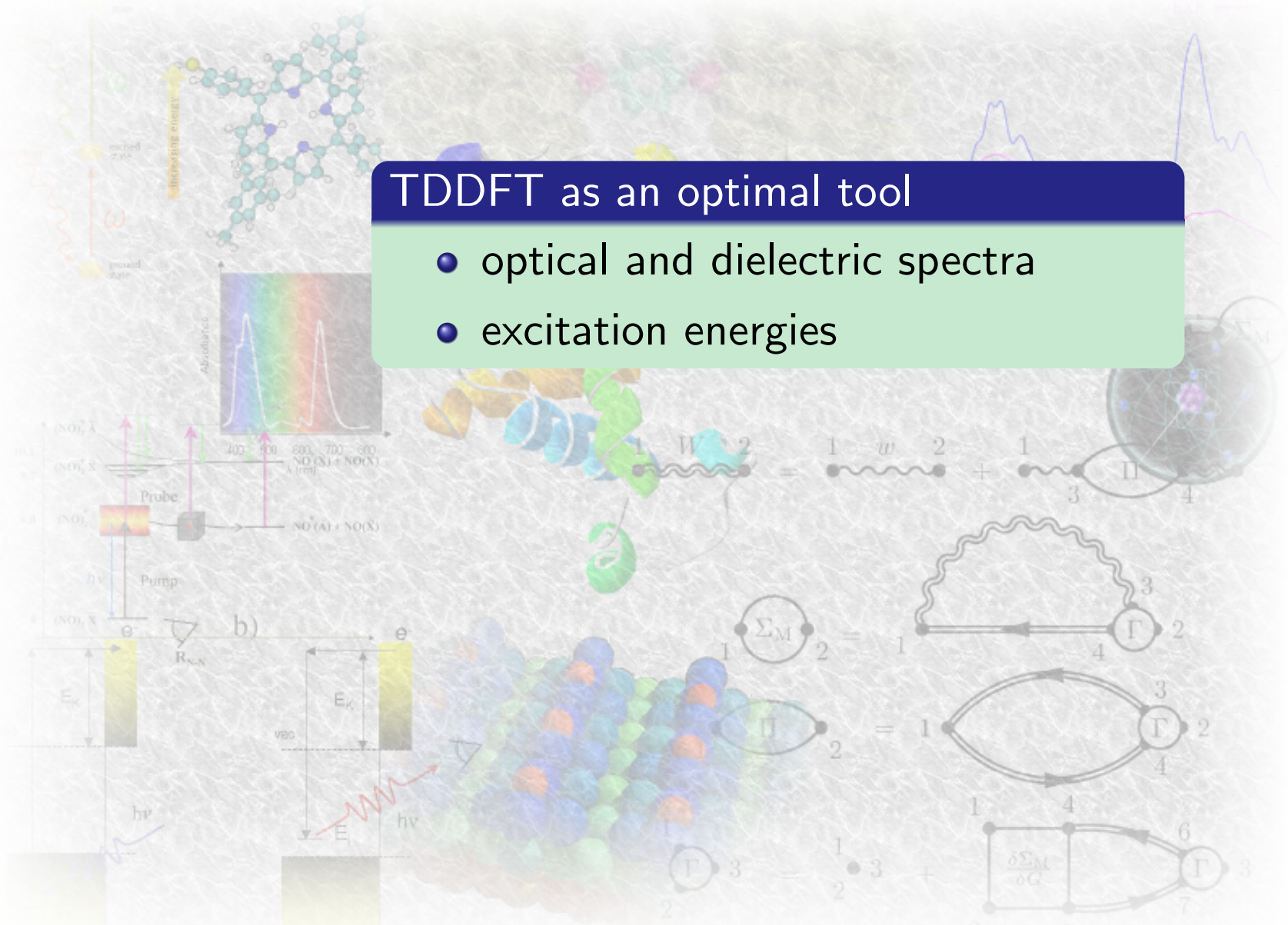
M.Lein *et al.* **61**, 13431 (2000)

Outline

Perspectives



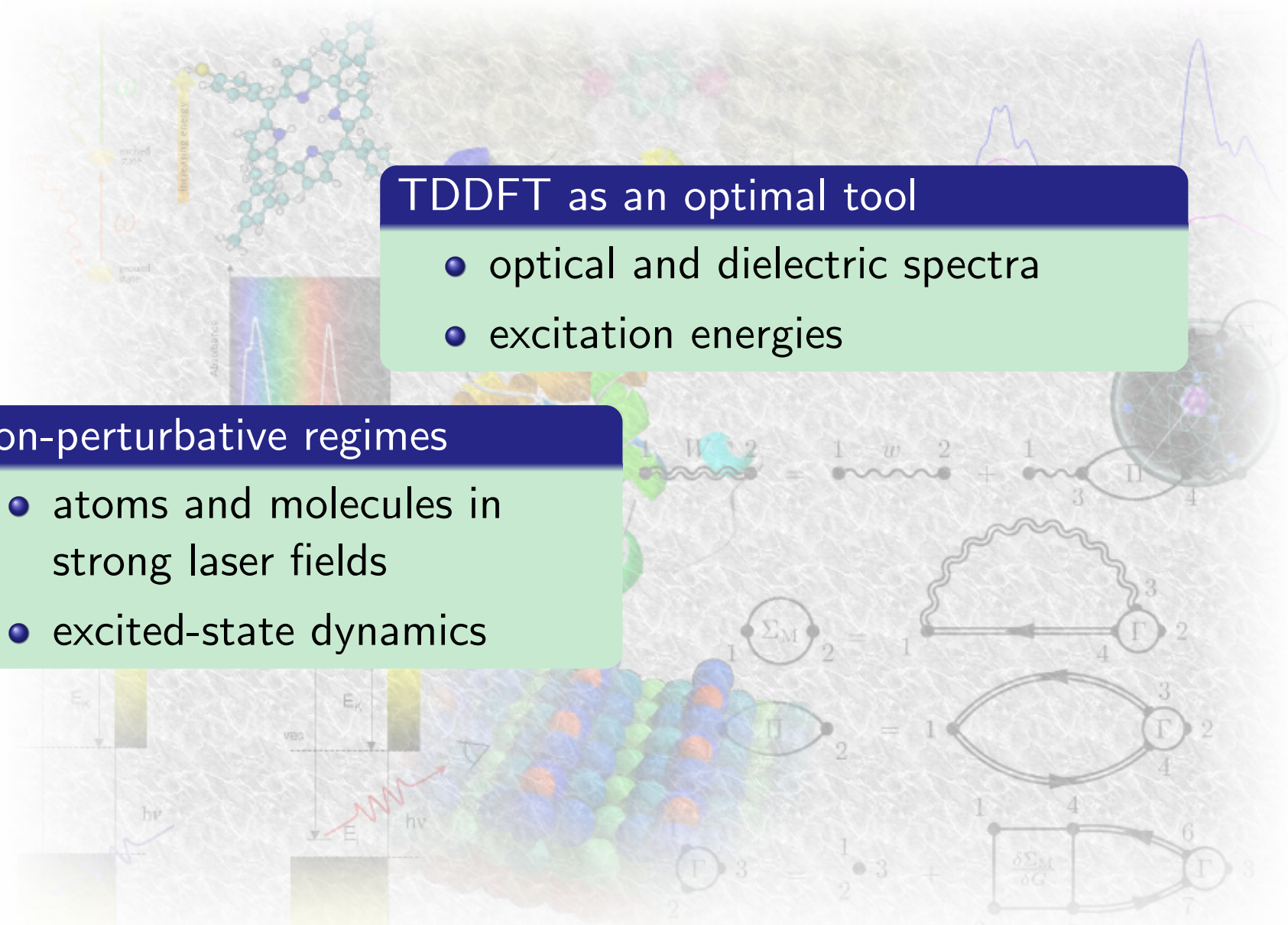
Perspectives



TDDFT as an optimal tool

- optical and dielectric spectra
- excitation energies

Perspectives



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- atoms and molecules in strong laser fields
- excited-state dynamics

Perspectives

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New frontiers application

- ground-state total energy
- quantum transport

Perspectives

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New frontiers application

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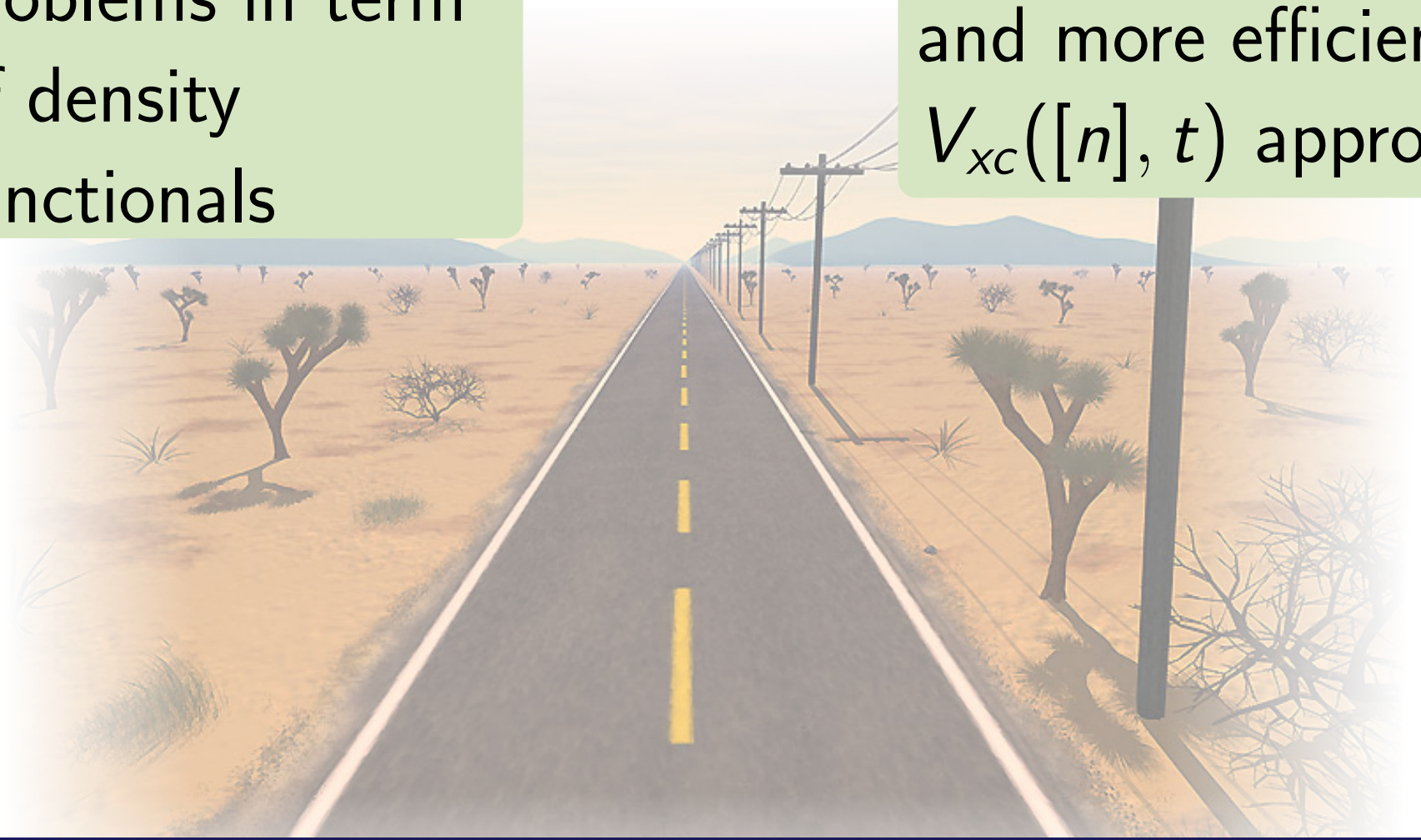
Time-Dependent Density Functional Theory Springer (2006)

Long road ahead

Formalization of problems in term of density functionals

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



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 - soon GPL
  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)

School on Electronic Excitations and Spectroscopies : Theory and Codes

Cecam, Lyon Dec. 11 2006 to Dec. 15 2006

http://www.cecam.fr/index.php?content=activities/tutorial&action=details&wid=123