Time Dependent Density Functional Theory

An introduction

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Outline

1. Introduction: why TD-DFT ?
2. (Just) A bit of Formalism - The Boring Part
   - TDDFT: the Foundation
   - Linear Response Formalism
3. TDDFT in practice:
   - The ALDA: Achievements and Shortcomings
   - The Quest for the Holy Functional
   - New Frontiers
4. Perspectives and Resources

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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 Nitrogen (7 electron)

$\Psi(\mathbf{r}_1, .., \mathbf{r}_7)$ 21 coordinates

10 entries/coordinate $\Rightarrow 10^{21}$ entries
8 bytes/entry $\Rightarrow 8 \cdot 10^{21}$ bytes
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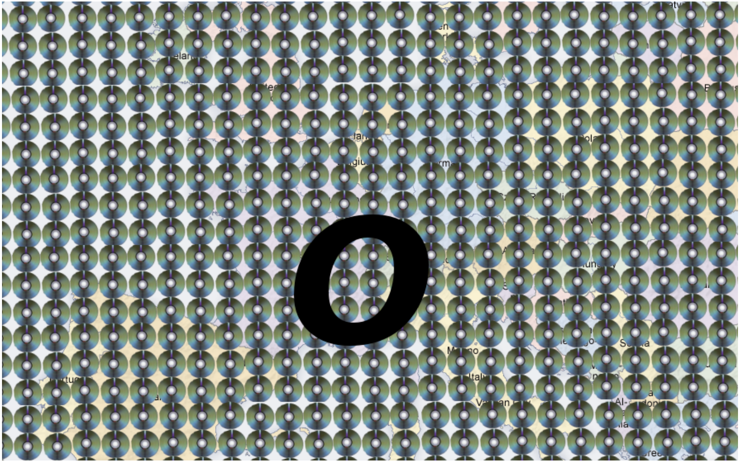

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$$H_i(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r})\psi_i(\mathbf{r})$$

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Density Functional ... Successful ?

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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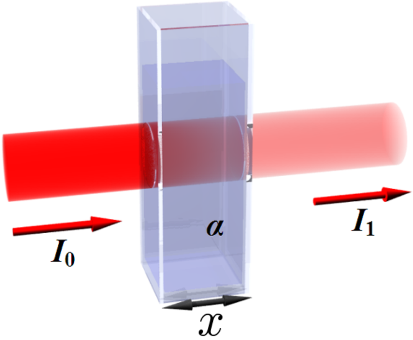

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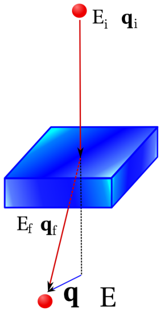

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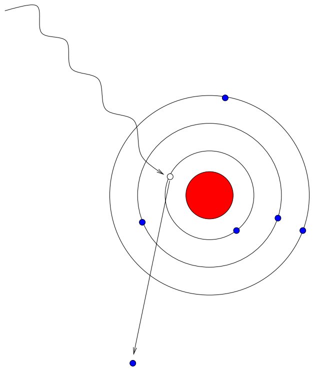

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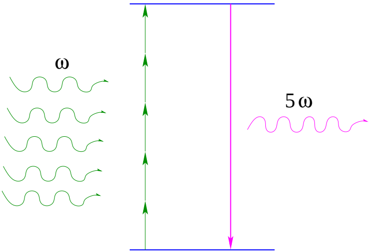

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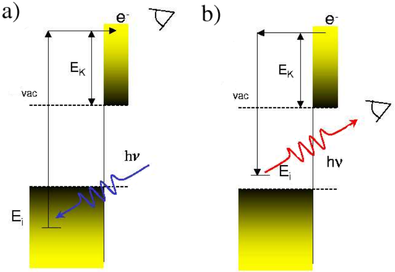

Time Dependent DFT ... Why ?

We need a time dependent theory

$$\Downarrow$$

TDDFT is a promising candidate

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The name of the game: TDDFT

DFT	TDDFT

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 $n(\mathbf{r})$

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

P. Hohenberg and W. Kohn Phys.Rev. **136**, B864 (1964)

(Fermi, Slater)

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.

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

Time-dependent problem

First-order differential equation

Initial-value problem

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

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- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \quad \Longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
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What about infinite systems?

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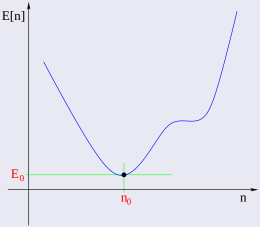
DFT	TDDFT

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.



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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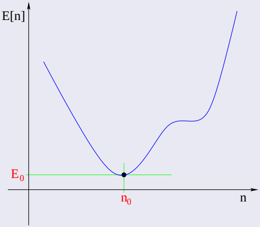

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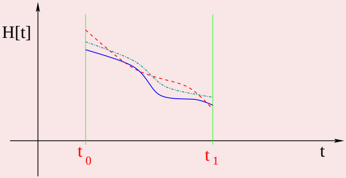

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Kohn-Sham equations

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

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

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

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

TDDFT

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Demonstrations, further readings, etc.

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$$\left\langle \varphi(t) | \hat{O}(t) | \varphi(t) \right\rangle = O[n, \varphi^0](t)$$

Kohn-Sham equations

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

Kohn-Sham equations

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

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

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

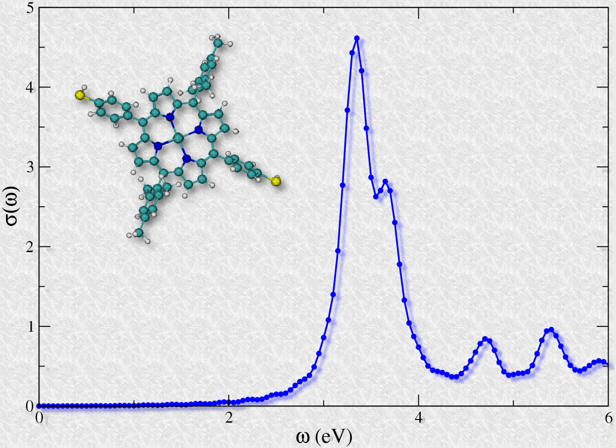
$$\alpha(t) = -\int d\mathbf{r} V_{ext}(\mathbf{r}, t) n(\mathbf{r}, t)$$

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

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

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

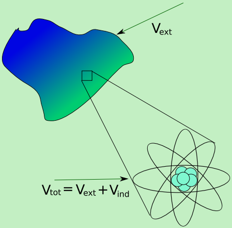
- Difficulties in approximating the $V_{xc}[n](\mathbf{r}, t)$ functional of the history of the density
- Real space not necessarily suitable for solids
- Does not explicitly take into account a "small" perturbation. Interesting quantities (excitation energies) are contained in the linear response function!

Outline

1. Introduction: why TD-DFT ?
2. (Just) A bit of Formalism - The Boring Part
   - TDDFT: the Foundation
   - Linear Response Formalism
3. TDDFT in practice:
   - The ALDA: Achievements and Shortcomings
   - The Quest for the Holy Functional
   - New Frontiers
4. Perspectives and Resources

Linear Response Approach

System submitted to an external perturbation



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

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

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

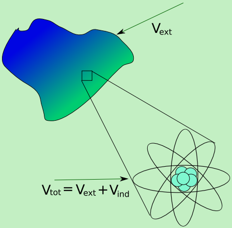
Dielectric function ε

EELS ↔ ε ↔ **R index**

Abs ↔ ε ↔ **X-ray**

Linear Response Approach

System submitted to an external perturbation



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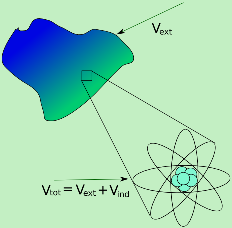

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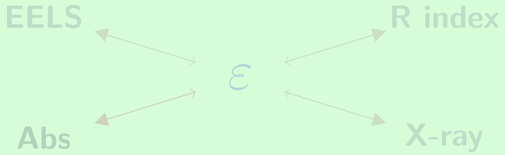

Linear Response Approach

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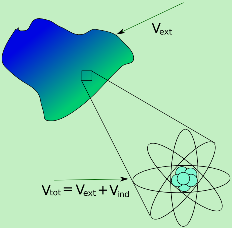

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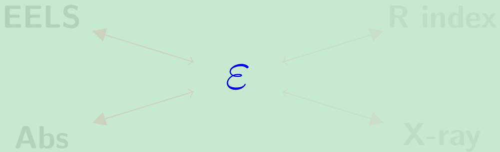

Linear Response Approach

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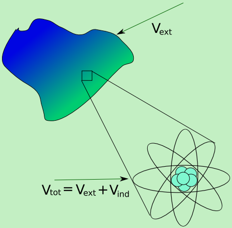

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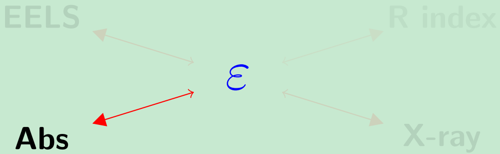

Linear Response Approach

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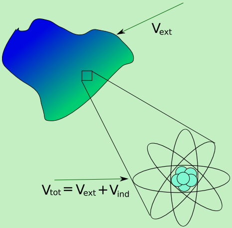

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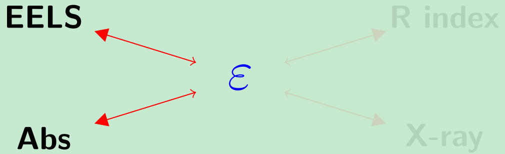

Linear Response Approach

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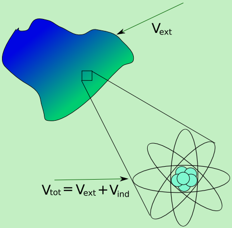

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Linear Response Approach

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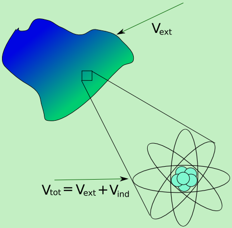

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Dielectric function ε

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Abs ↔ ε ↔ **X-ray**

Linear Response Approach

Definition of polarizability

$$\text{not polarizable} \;\Rightarrow\; V_{tot} = V_{ext} \;\Rightarrow\; \varepsilon^{-1} = 1$$

$$\text{polarizable} \;\Rightarrow\; V_{tot} \neq V_{ext} \;\Rightarrow\; \varepsilon^{-1} \neq 1$$

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

χ is the polarizability of the system

Linear Response Approach

Definition of polarizability

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

χ is the polarizability of the system

Linear Response Approach

Definition of polarizability

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Linear Response Approach

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

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

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

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

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

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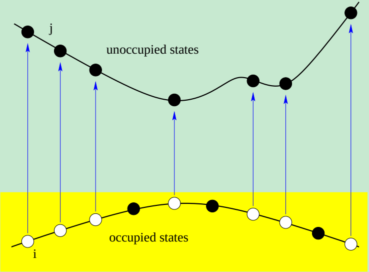

Linear Response Approach

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 $\mathbf{f_{xc}}$ = **exchange-correlation kernel**

Linear Response Approach

Polarizability

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$$\chi = \left[1 - \chi^0 \left(v + f_{xc}\right)\right]^{-1} \chi^0$$

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Linear Response Approach

Polarizability

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

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Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow \quad \phi_i, \epsilon_i \qquad [V_{xc}]$
2. $\phi_i, \epsilon_i \quad \longrightarrow \quad \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$
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. $\chi = \chi^0 + \chi^0 \left(v + f_{xc}\right) \chi$

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

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

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

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

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

Finite systems

Photo-absorption cross spectrum

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Periodic Systems

A better representation: Fourier space

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

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

Periodic Systems

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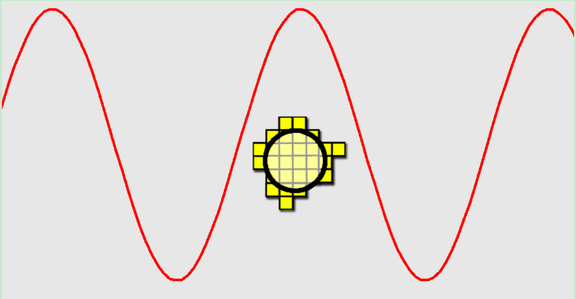
Periodic Systems

Macroscopic average



average over distance d:

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

Periodic Systems

Macroscopic average

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

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

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

$$= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{0},\omega)$$

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

macroscopic inverse dielectric function $\varepsilon^{-1}_{00}(\mathbf{q},\omega)$

Periodic Systems

Macroscopic average

$$
\begin{aligned}
\langle f(\mathbf{r},\omega)\rangle_{\mathbf{R}} &= \frac{1}{\Omega_R}\int d\mathbf{r} f(\mathbf{r},\omega) \\
&= \frac{1}{\Omega_R}\int d\mathbf{r}\left[\int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} f(\mathbf{q}+\mathbf{G},\omega) e^{i\mathbf{G}\cdot\mathbf{r}}\right] \\
&= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{G},\omega) \frac{1}{\Omega_R} \sum_{\mathbf{G}} \int d\mathbf{r} e^{i\mathbf{G}\cdot\mathbf{r}} \\
&= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{0},\omega)
\end{aligned}
$$

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

macroscopic inverse dielectric function $\varepsilon^{-1}_{00}(\mathbf{q},\omega)$

Periodic Systems

Macroscopic average

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

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

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

$$= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{0},\omega)$$

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

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Periodic Systems

Macroscopic average

$$\begin{aligned}\langle f(\mathbf{r},\omega)\rangle_{\mathbf{R}} &= \frac{1}{\Omega_R}\int d\mathbf{r} f(\mathbf{r},\omega)\\ &= \frac{1}{\Omega_R}\int d\mathbf{r}\left[\int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}}\sum_{\mathbf{G}} f(\mathbf{q}+\mathbf{G},\omega)e^{i\mathbf{G}\cdot\mathbf{r}}\right]\\ &= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{G},\omega)\frac{1}{\Omega_R}\sum_{\mathbf{G}}\int d\mathbf{r} e^{i\mathbf{G}\cdot\mathbf{r}}\\ &= \int d\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}} f(\mathbf{q}+\mathbf{0},\omega)\end{aligned}$$

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

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Periodic Systems

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

macroscopic inverse dielectric function $\quad \varepsilon_{00}^{-1}(\mathbf{q},\omega)$

Absorption coefficient

General solution of Maxwell's equation

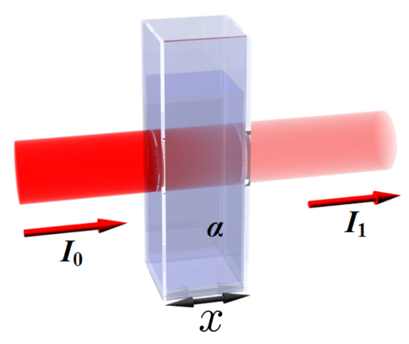
$$\begin{aligned} \text{in vacuum} \quad & \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(x/c - t)} \\ \text{in a medium} \quad & \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(Nx/c - t)} \end{aligned}$$

Absorption coefficient

General solution of Maxwell's equation

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

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



Absorption coefficient

General solution of Maxwell's equation

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

complex (macroscopic) refractive index N

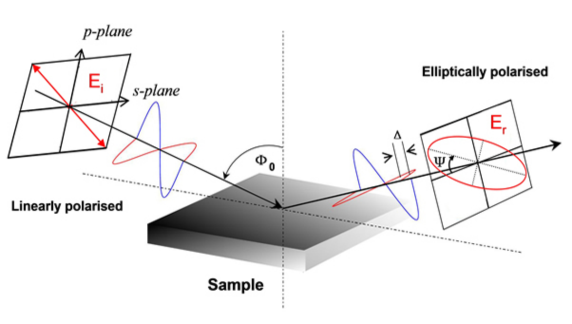
$$N = \sqrt{\varepsilon_M} = \nu + i\kappa \quad ; \quad \mathbf{D} = \varepsilon_M \mathbf{E}$$

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

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

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!

Dielectric Function in Crystals

Let's calculate ε_M

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

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$

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Dielectric Function in Crystals

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WRONG!

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Let's calculate ε_M

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$

$$\mathbf{D}(\mathbf{q},\omega) = \varepsilon_{\mathbf{0}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$

$$\neq \varepsilon_{\mathbf{00}}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega)$$

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

Dielectric Function in Crystals

Let's calculate ε_M

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega)$$
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$$\neq \varepsilon_{\mathbf{0}\mathbf{0}}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega)$$

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

Dielectric Function in Crystals

Let's calculate ε_M

$$\begin{aligned} \mathbf{D}(\mathbf{q}+\mathbf{G},\omega) &= \varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega) \\ \mathbf{D}(\mathbf{q},\omega) &= \varepsilon_{\mathbf{0G}'}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega) \\ &\neq \varepsilon_{\mathbf{00}}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega) \end{aligned}$$

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

Dielectric Function in Crystals

Let's calculate ε_M

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

$$\mathbf{E}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q}+\mathbf{G}',\omega)$$

$$\mathbf{E}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon^{-1}_{\mathbf{G}\mathbf{0}}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q},\omega)$$

$$\mathbf{E}(\mathbf{q},\omega) = \varepsilon^{-1}_{\mathbf{0}\mathbf{0}}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q},\omega)$$

$$\varepsilon_M = \frac{1}{\varepsilon^{-1}_{00}}$$

Dielectric Function in Crystals

Let's calculate ε_M

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$$\varepsilon_M = \frac{1}{\varepsilon^{-1}_{00}}$$

Dielectric Function in Crystals

The Energy Loss Spectra

Imaginary part of the macroscopic inverse dielectric function

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

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

Dielectric Function in Crystals

The Energy Loss Spectra

Imaginary part of the macroscopic <u>inverse</u> dielectric function

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

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

Dielectric Function in Crystals

Absoprtion Spectra

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

Energy Loss Spectra

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

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

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

without local fields.

Solids

Reciprocal space

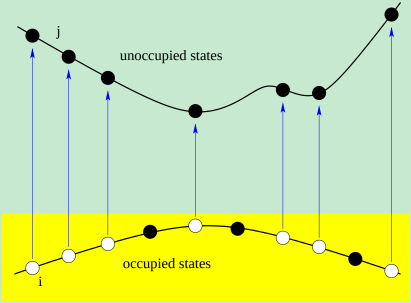
$$\chi^0(\mathbf{r},\mathbf{r}',\omega) \longrightarrow \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

$\mathbf{G}$ =reciprocal lattice vector
$\mathbf{q}$ =momentum transfer of the perturbation

Solids

Reciprocal space

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



Solids

Reciprocal space

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

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

Solids

Reciprocal space

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

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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)

Solids

Reciprocal space

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Solids

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

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Solids

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

Solids

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

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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 $\mathbf{q} \to 0$

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Exercise

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

Solids

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

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

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

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

Solids

Microscopic components $\bar{v}$

$\bar{v}$ = local field effects

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

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

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Microscopic components $\bar{v}$

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

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

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

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

Exercise

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

Outline

1. Introduction: why TD-DFT ?
2. (Just) A bit of Formalism - The Boring Part
   - TDDFT: the Foundation
   - Linear Response Formalism
3. TDDFT in practice:
   - The ALDA: Achievements and Shortcomings
   - The Quest for the Holy Functional
   - New Frontiers
4. Perspectives and Resources

TDDFT in practice

Practical schema and approximations

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

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

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

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ALDA: Achievements and Shortcomings

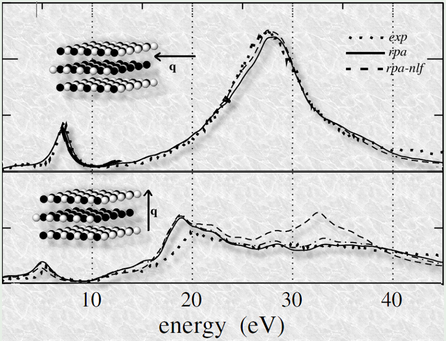
Electron Energy Loss Spectrum of Graphite

RPA vs EXP

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

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

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



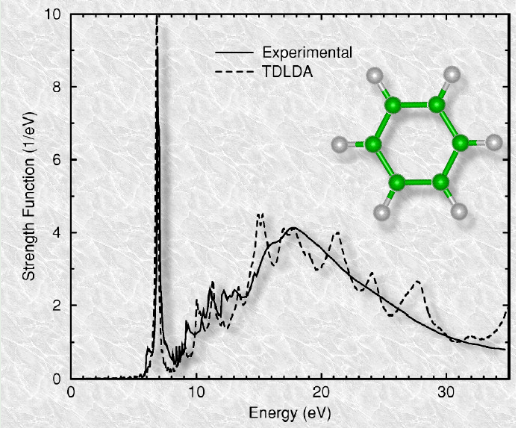
A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ALDA: Achievements and Shortcomings

Photo-absorption cross section of Benzene

ALDA vs EXP

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



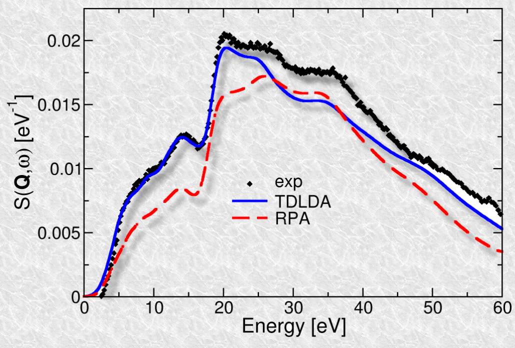
K.Yabana and G.F.Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

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

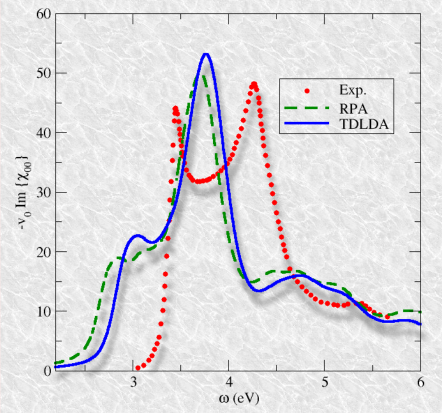
ALDA: Achievements and Shortcomings

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

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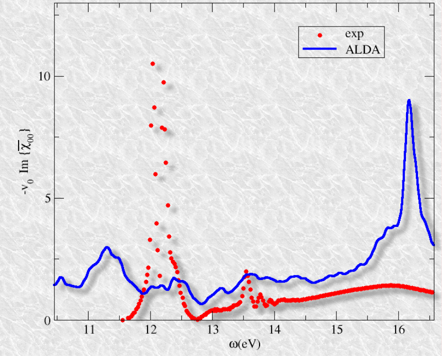

ALDA: Achievements and Shortcomings

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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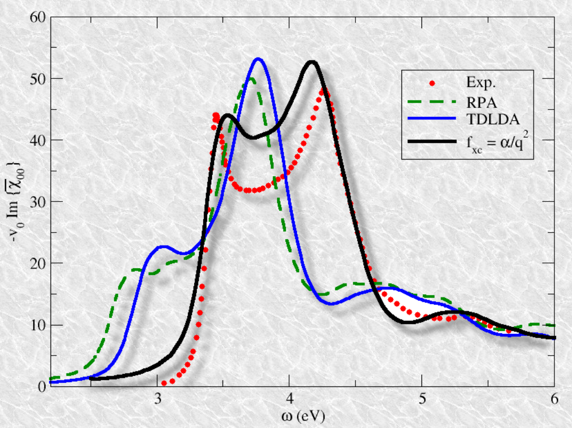
ALDA: Achievements and Shortcomings

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



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

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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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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

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

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

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

× still apply GW
√ solve 2-point eq. for χ (rather than L)

The Mapping Theory

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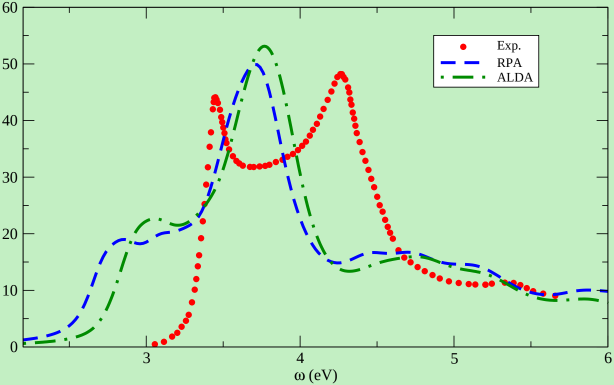
The Mapping Theory: Results

Absorption of Silicon



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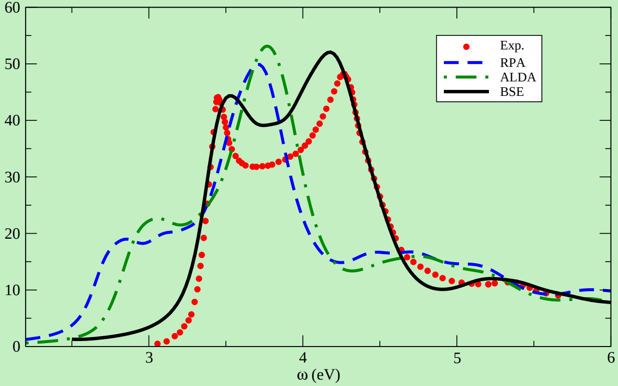

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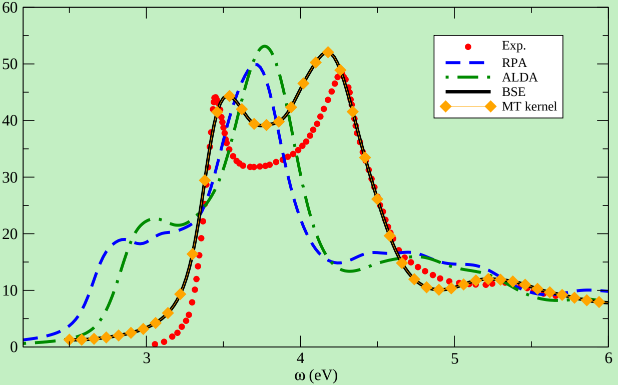
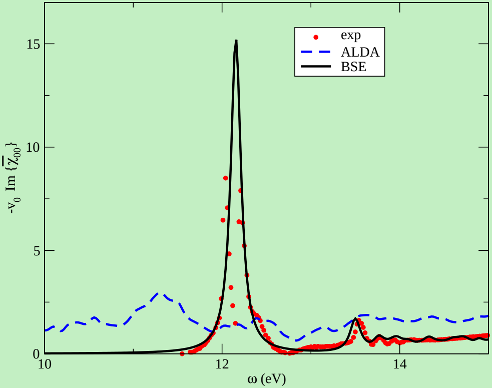


F.Sottile *et al.* Phys.Rev.Lett **91**, 56402 (2003)

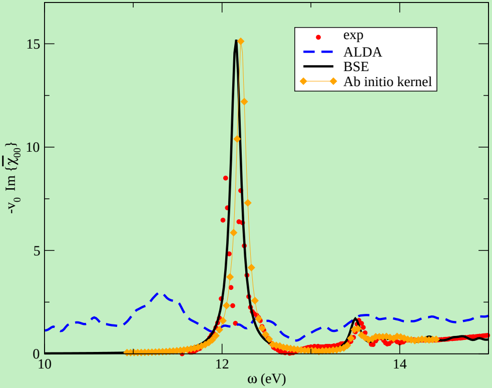
The Mapping Theory: Results

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).

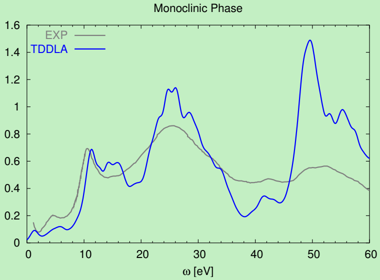
Spectra of simple systems

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

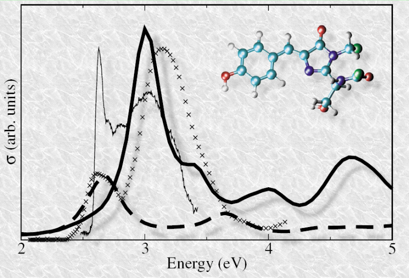
Strongly correlated systems



EEL spectrum of VO_2

M.Gatti, submitted to PRL

Biological systems



Abs spectrum of Green Fluorescent Protein

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

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New Frontiers

TDDFT concept into MBPT

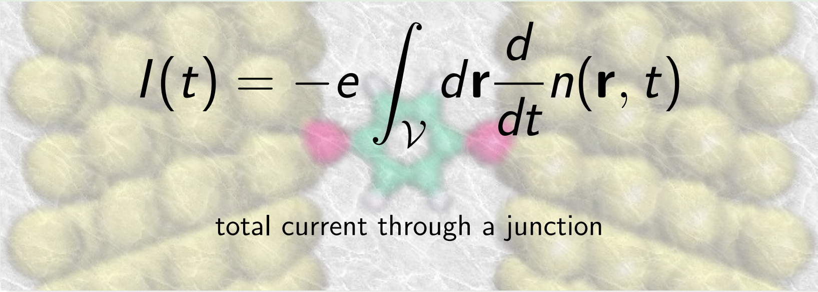
$$\Sigma = GW\Gamma$$

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)

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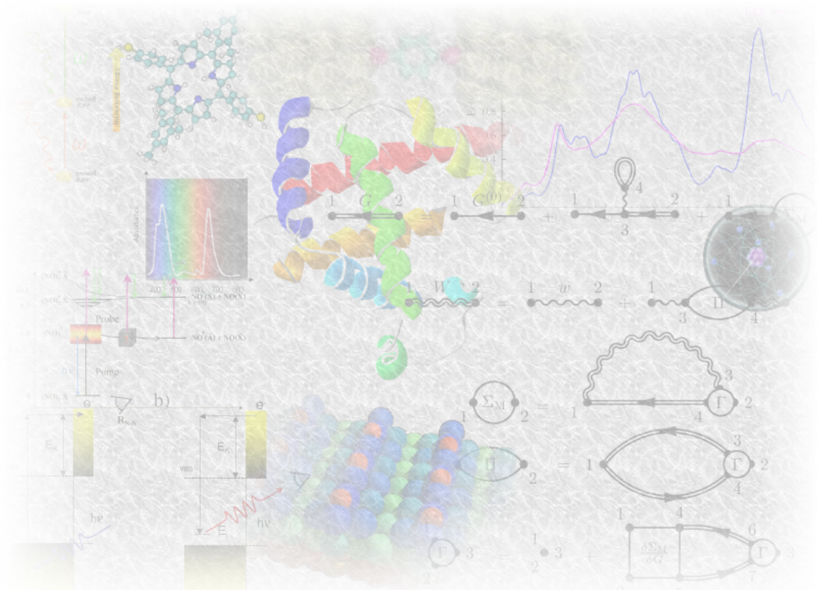
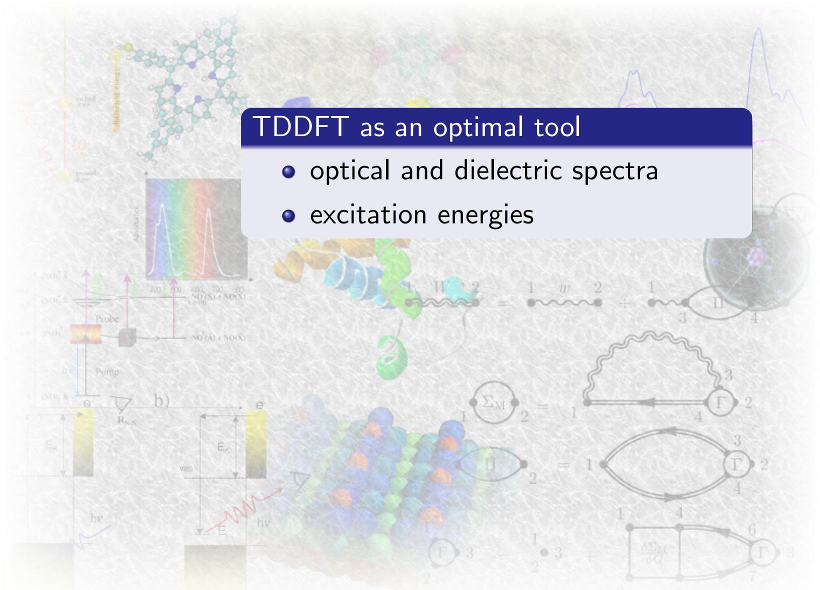
Perspectives



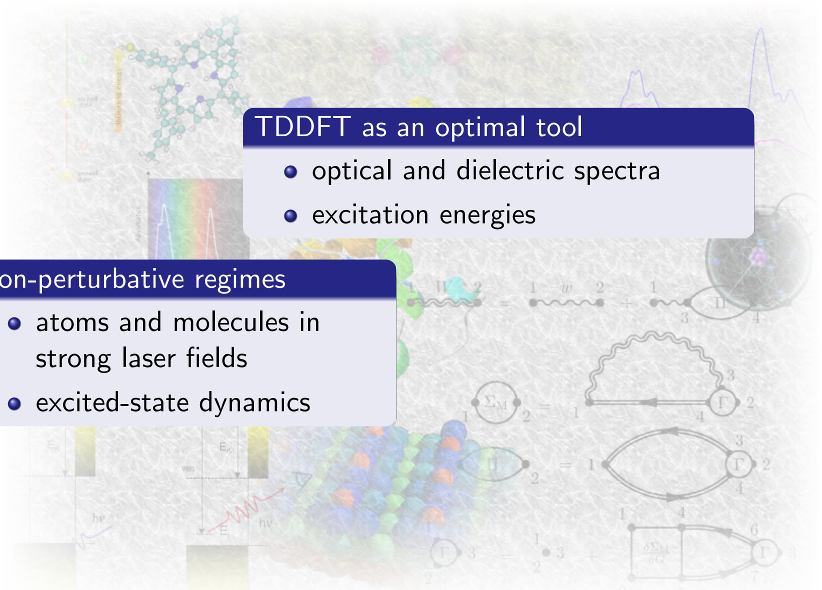
Perspectives



TDDFT as an optimal tool

- optical and dielectric spectra
- excitation energies

Perspectives



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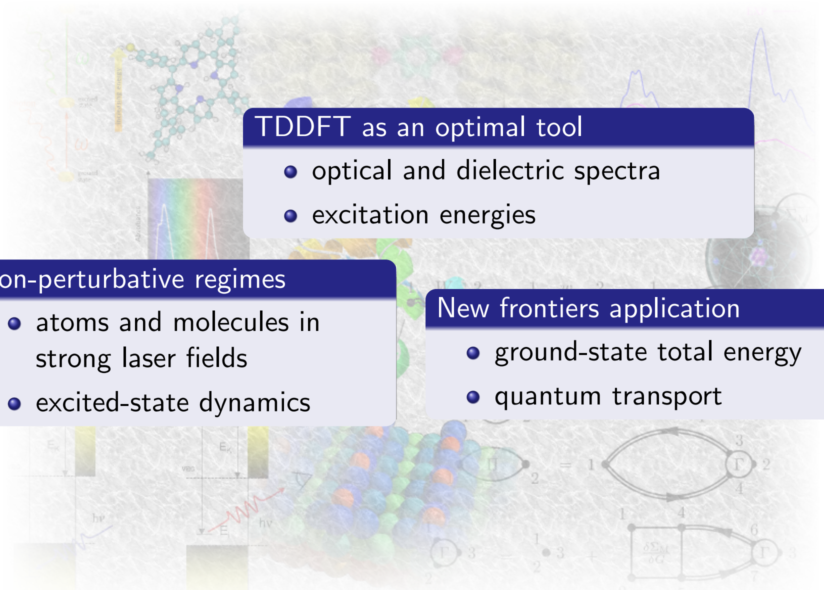
Non-perturbative regimes

- 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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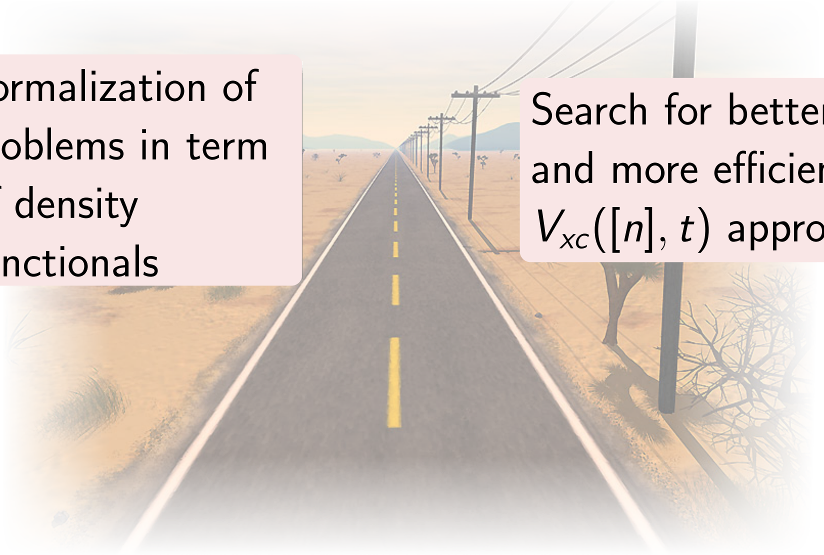
- quantum transport

Time-Dependent Density Functional Theory Springer (2006)

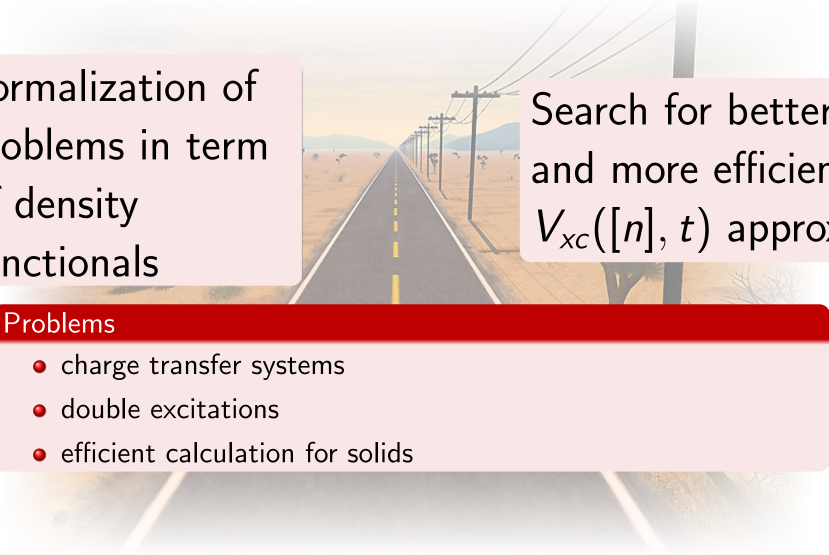
Long road ahead



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)