Time Dependent Density Functional Theory

An Introduction

Francesco Sottile

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

Belfast, 29 Jun 2007

Outline

Outline

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.

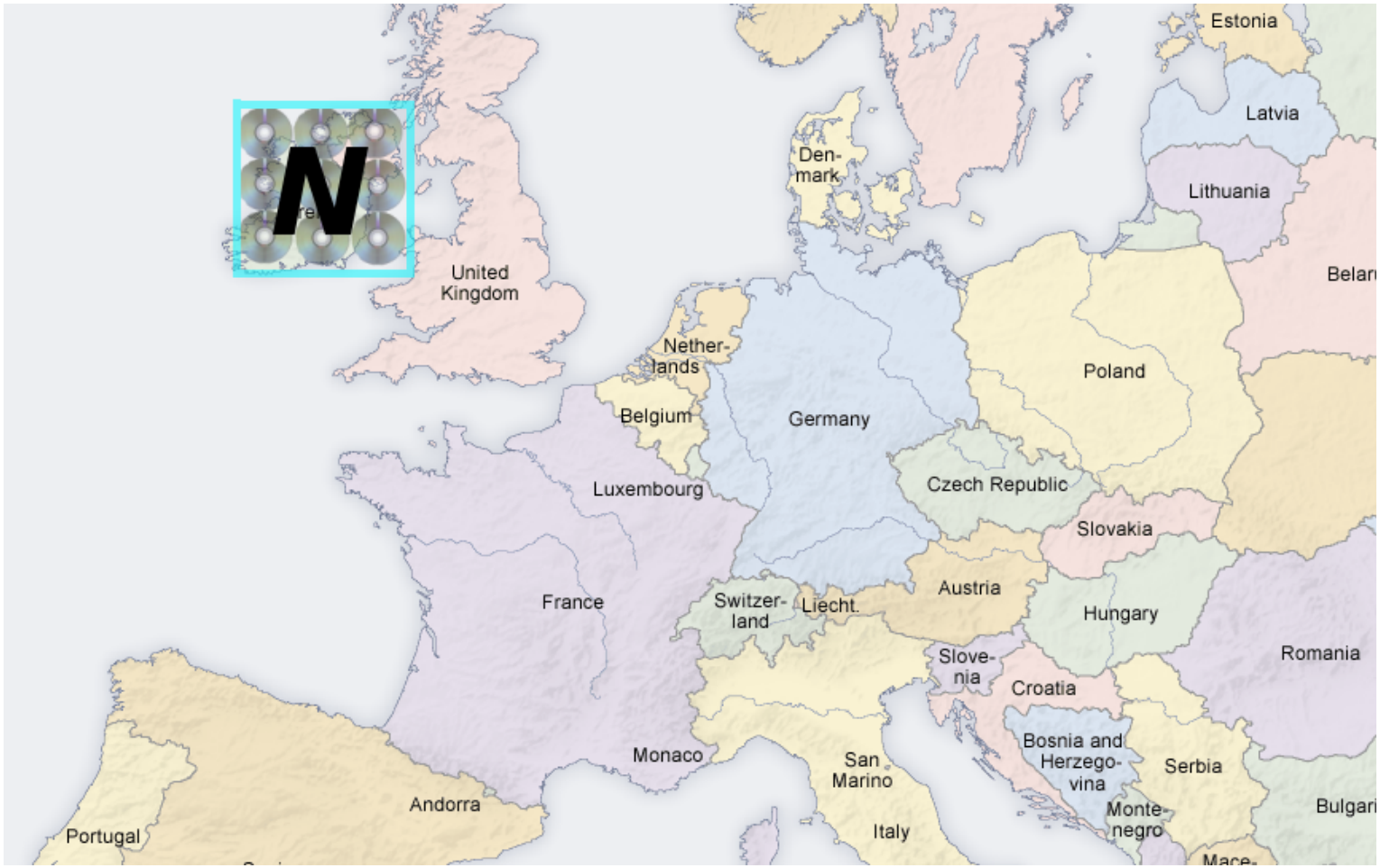
Importance of the density

Example: atom of Nitrogen (7 electron)

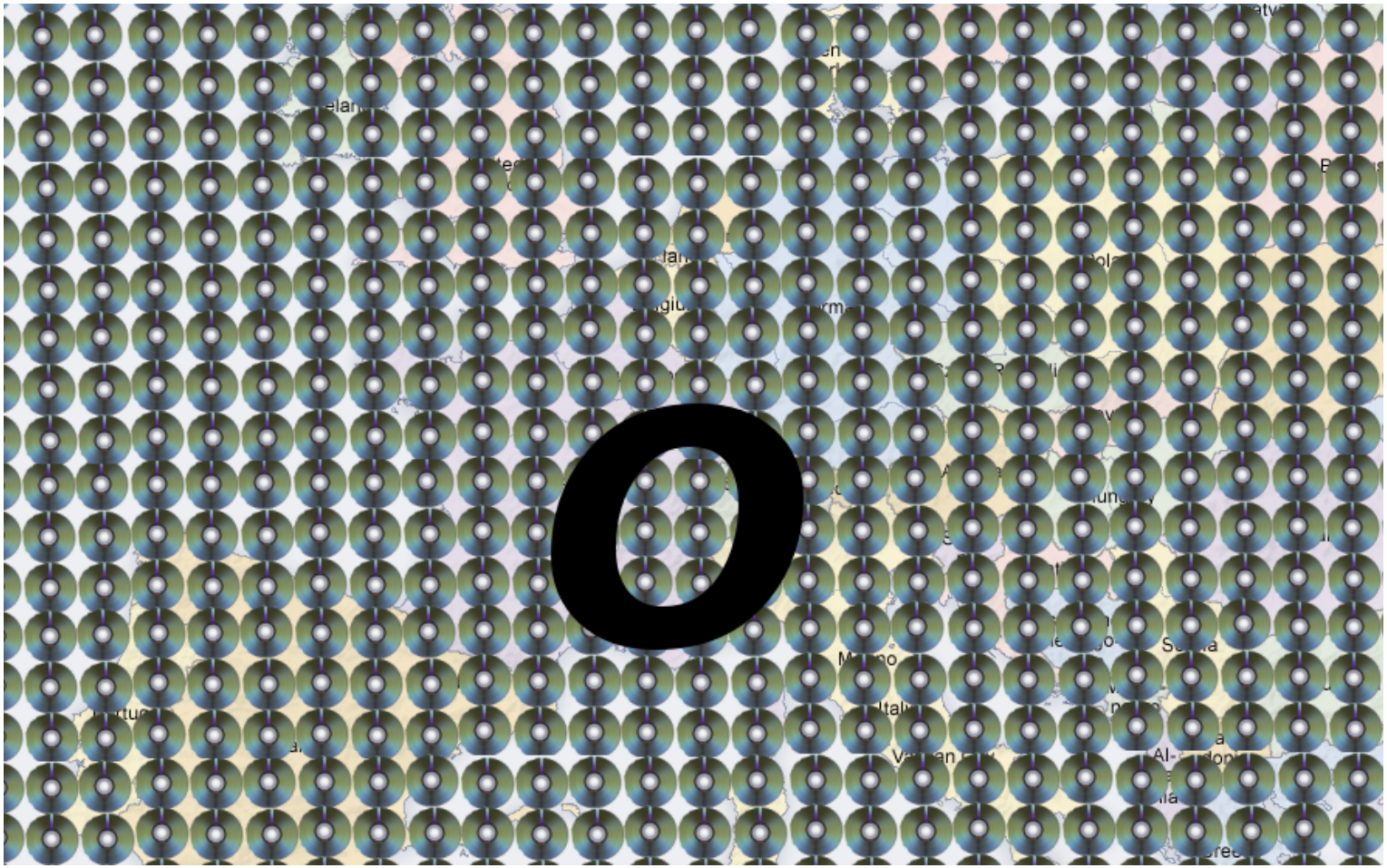
$$\Psi(\mathbf{r}_1, .., \mathbf{r}_7) \quad 21 \text{ coordinates}$$

$$10 \text{ entries/coordinate} \Rightarrow 10^{21} \text{ entries}$$
$$8 \text{ bytes/entry} \Rightarrow 8 \cdot 10^{21} \text{ bytes}$$
$$4.7 \times 10^9 \text{ bytes/DVD} \Rightarrow 2 \times 10^{12} \text{ DVDs}$$

Density Functional ... Why ?



Density Functional ... Why ?



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)

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

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

Importance of non-interacting

The Kohn-Sham one-particle equations

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

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)

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

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

Importance of non-interacting

The Kohn-Sham one-particle equations

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

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

Time Dependent DFT ... Why ?

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

Different Phenomena

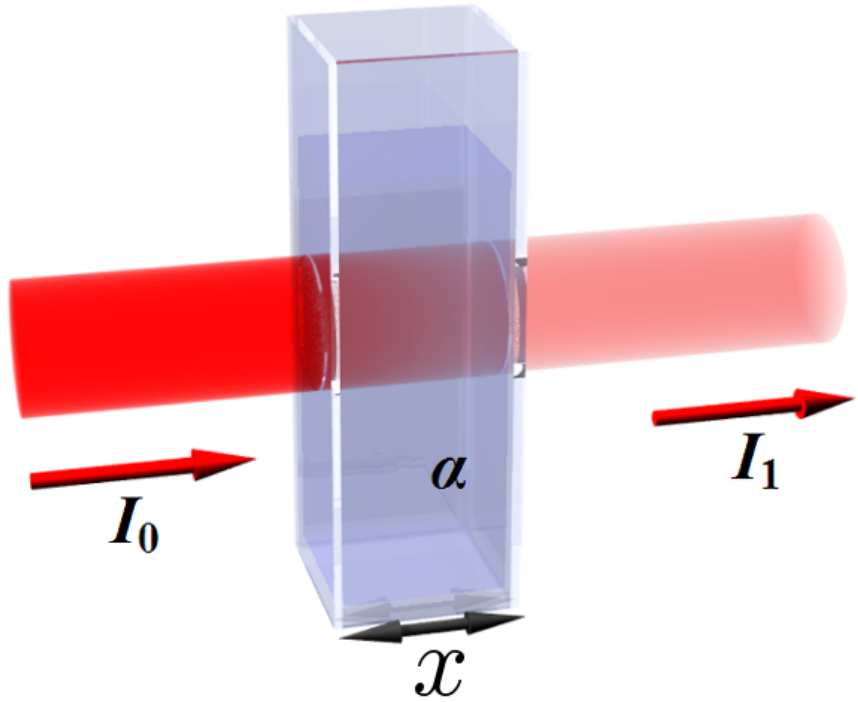
- absorption spectra
- energy loss spectra
- photo-ionization
- high-harmonic generation
- photo-emission

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

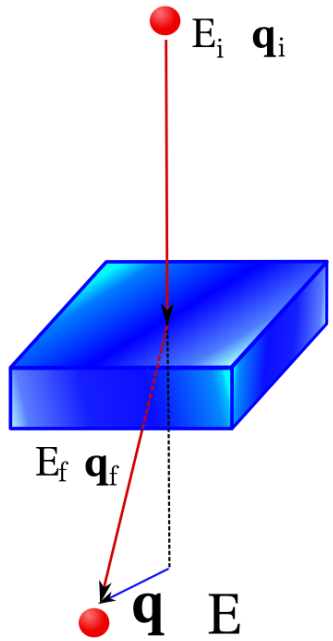


Time Dependent DFT ... Why ?

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

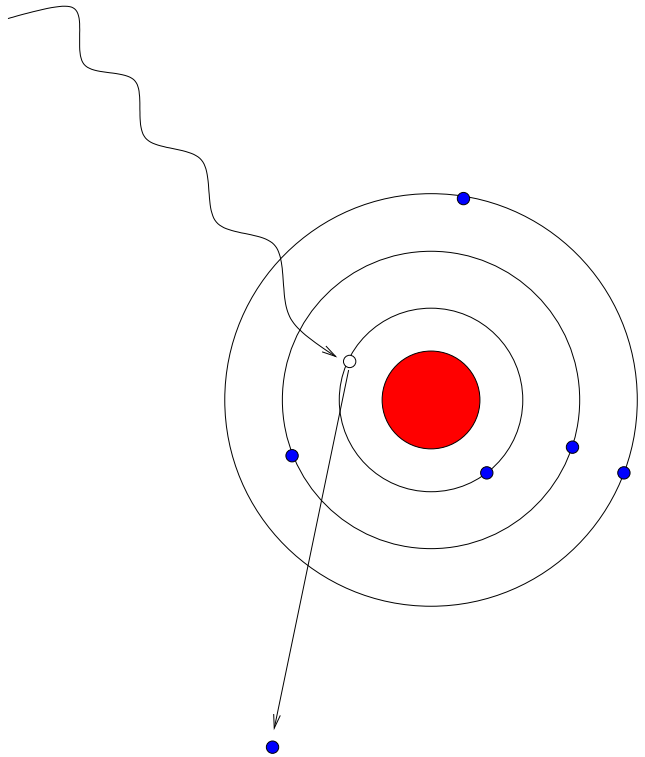


Time Dependent DFT ... Why ?

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

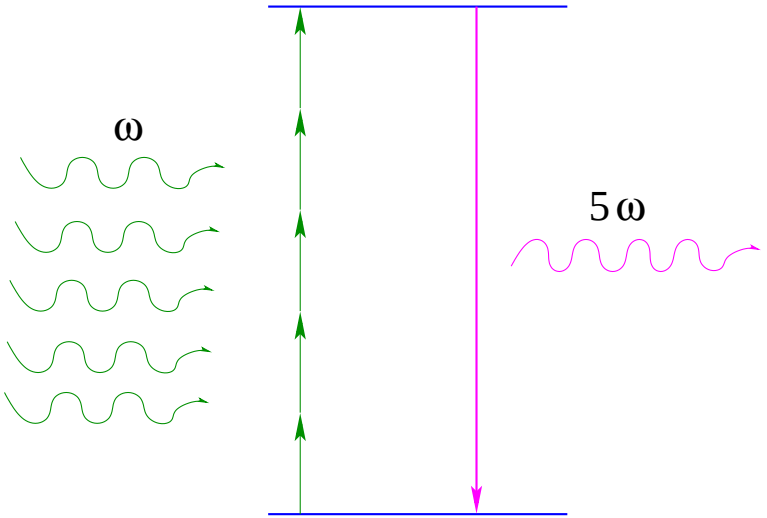


Time Dependent DFT ... Why ?

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

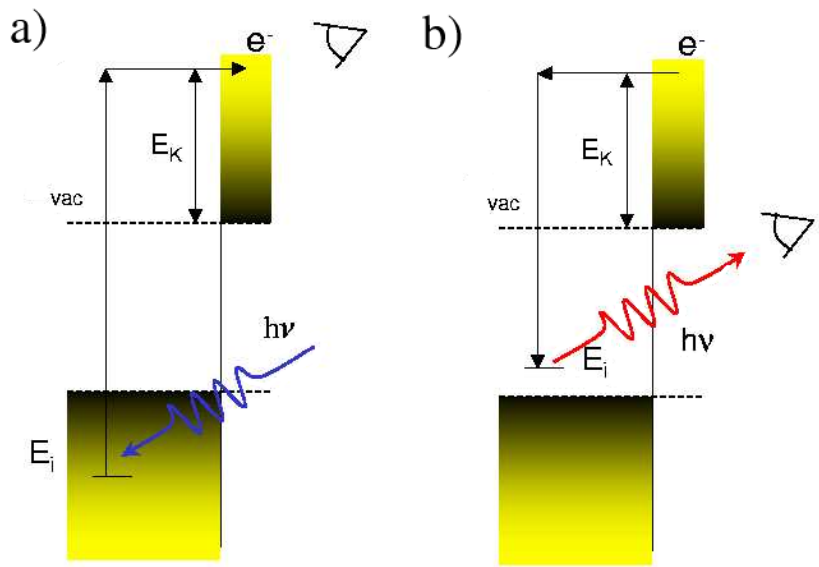


Time Dependent DFT ... Why ?

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



Time Dependent DFT ... Why ?

We need a time dependent theory

$$\Downarrow$$

TDDFT is a promising candidate

Outline

Outline

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 $n(\mathbf{r})$

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

P. Hohenberg and W. Kohn
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** $\varphi^0 = \varphi(t = 0)$

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

E. Runge and E.K.U. Gross
Phys.Rev.Lett. **52**, 997 (1984)

(Ando,Zangwill and Soven)

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 $n(\mathbf{r})$

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

P. Hohenberg and W. Kohn
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** $\varphi^0 = \varphi(t = 0)$

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

E. Runge and E.K.U. Gross
Phys.Rev.Lett. **52**, 997 (1984)
(Ando,Zangwill and Soven)

The name of the game: TDDFT

DFT

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

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

The name of the game: TDDFT

DFT

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

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

The name of the game: 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** $\varphi^0 = \varphi(t = 0)$

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

E. Runge and E.K.U. Gross

Phys.Rev.Lett. **52**, 997 (1984)

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

The name of the game: TDDFT

Runge-Gross theorem

- $V_{ext}(\mathbf{r},t) \neq V'_{ext}(\mathbf{r},t) \iff \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$
- $\nabla \cdot [n \nabla V_{ext}] \neq \nabla \cdot [n \nabla V'_{ext}] \iff n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$n(\mathbf{r},t) \longrightarrow V_{ext}(\mathbf{r},t) + c(t) \longrightarrow \varphi e^{ic(t)}$$

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

What about infinite systems?

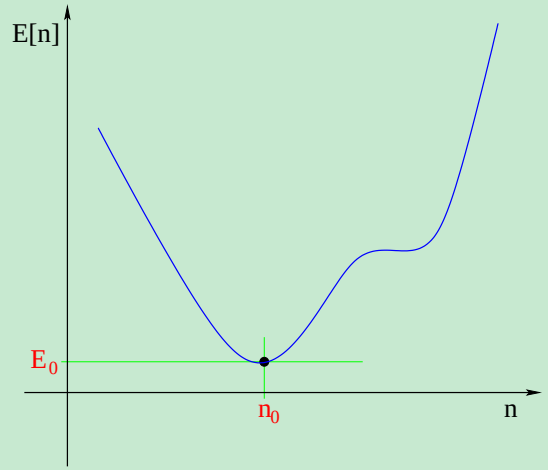
The name of the game: TDDFT

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

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

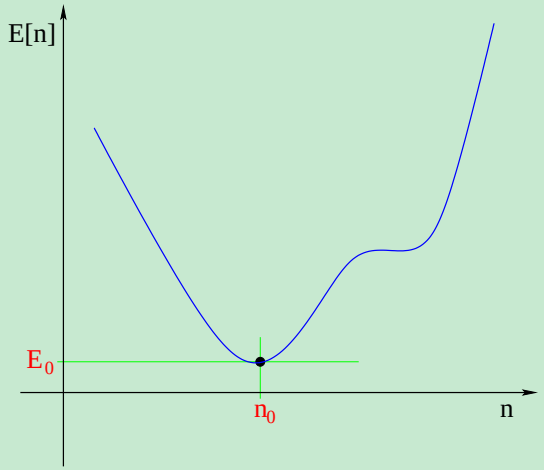
The name of the game: TDDFT

DFT

TDDFT

Hohenberg-Kohn theorem 2

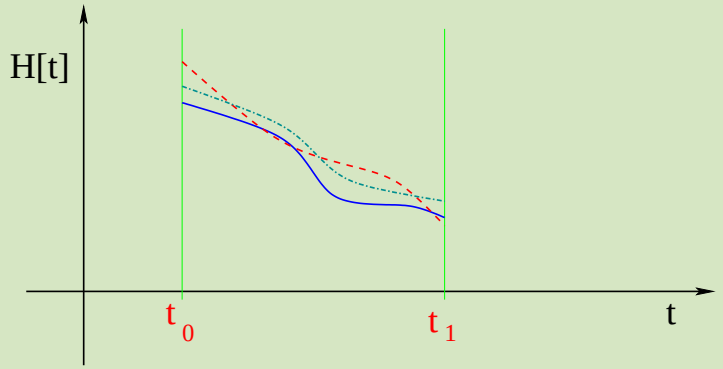
The total energy functional has a minimum, the ground-state energy E_0, corresponding to the ground-state density n_0.



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

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



The name of the game: TDDFT

DFT

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

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

$$V_{tot}(\mathbf{r},t) = V_{ext}(\mathbf{r},t) + \int v(\mathbf{r},\mathbf{r}')n(\mathbf{r}',t)d\mathbf{r}' + V_{xc}([n]\mathbf{r},t)$$

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

Unknown exchange-correlation time-dependent potential.
V_{xc} functional of the density **at all times** and of the **initial state**.

The name of the game: TDDFT

DFT

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

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

$$V_{tot}(\mathbf{r},t) = V_{ext}(\mathbf{r},t) + \int v(\mathbf{r},\mathbf{r}')n(\mathbf{r}',t)d\mathbf{r}' + V_{xc}([n]\mathbf{r},t)$$

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

Unknown exchange-correlation time-dependent potential.
V_{xc} functional of the density **at all times** and of the **initial state**.

The name of the game: TDDFT

Demonstrations, further readings, etc.

R. van Leeuwen
Int.J.Mod.Phys. **B15**, 1969 (2001)

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

$$\frac{\delta V_{xc}([n], \mathbf{r}, t)}{\delta n(\mathbf{r}', t')} = \frac{\delta^2 A_{xc}[n]}{\delta n(\mathbf{r}, t)\delta n(\mathbf{r}', t')}$$

Causality-Symmetry dilemma

The name of the game: TDDFT

Demonstrations, further readings, etc.

R. van Leeuwen
Int.J.Mod.Phys. **B15**, 1969 (2001)

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

$$\frac{\delta V_{xc}\left([n],\mathbf{r},t\right)}{\delta n(\mathbf{r}',t')}=\frac{\delta^2 A_{xc}[n]}{\delta n(\mathbf{r},t)\delta n(\mathbf{r}',t')}$$

Causality-Symmetry dilemma

The name of the game: TDDFT

Demonstrations, further readings, etc.

R. van Leeuwen
Int.J.Mod.Phys. **B15**, 1969 (2001)

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

$$\frac{\delta V_{xc}\left([n],\mathbf{r},t\right)}{\delta n(\mathbf{r}',t')}=\frac{\delta^2 A_{xc}[n]}{\delta n(\mathbf{r},t)\delta n(\mathbf{r}',t')}$$

Causality-Symmetry dilemma

The name of the game: TDDFT

Demonstrations, further readings, etc.

R. van Leeuwen
Int.J.Mod.Phys. **B15**, 1969 (2001)

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

$$\frac{\delta V_{xc}\left([n],\mathbf{r},t\right)}{\delta n(\mathbf{r}',t')}=\frac{\delta^2 A_{xc}[n]}{\delta n(\mathbf{r},t)\delta n(\mathbf{r}',t')}$$

Causality-Symmetry dilemma

The name of the game: TDDFT

DFT

Hohenberg-Kohn theorem

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

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

Kohn-Sham equations

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

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 $n(\mathbf{r})$ and of **the initial state** $\varphi^0 = \varphi(t=0)$

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

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)

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)

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)

First Approach: Time Evolution of KS equations

Photo-absorption cross section σ

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

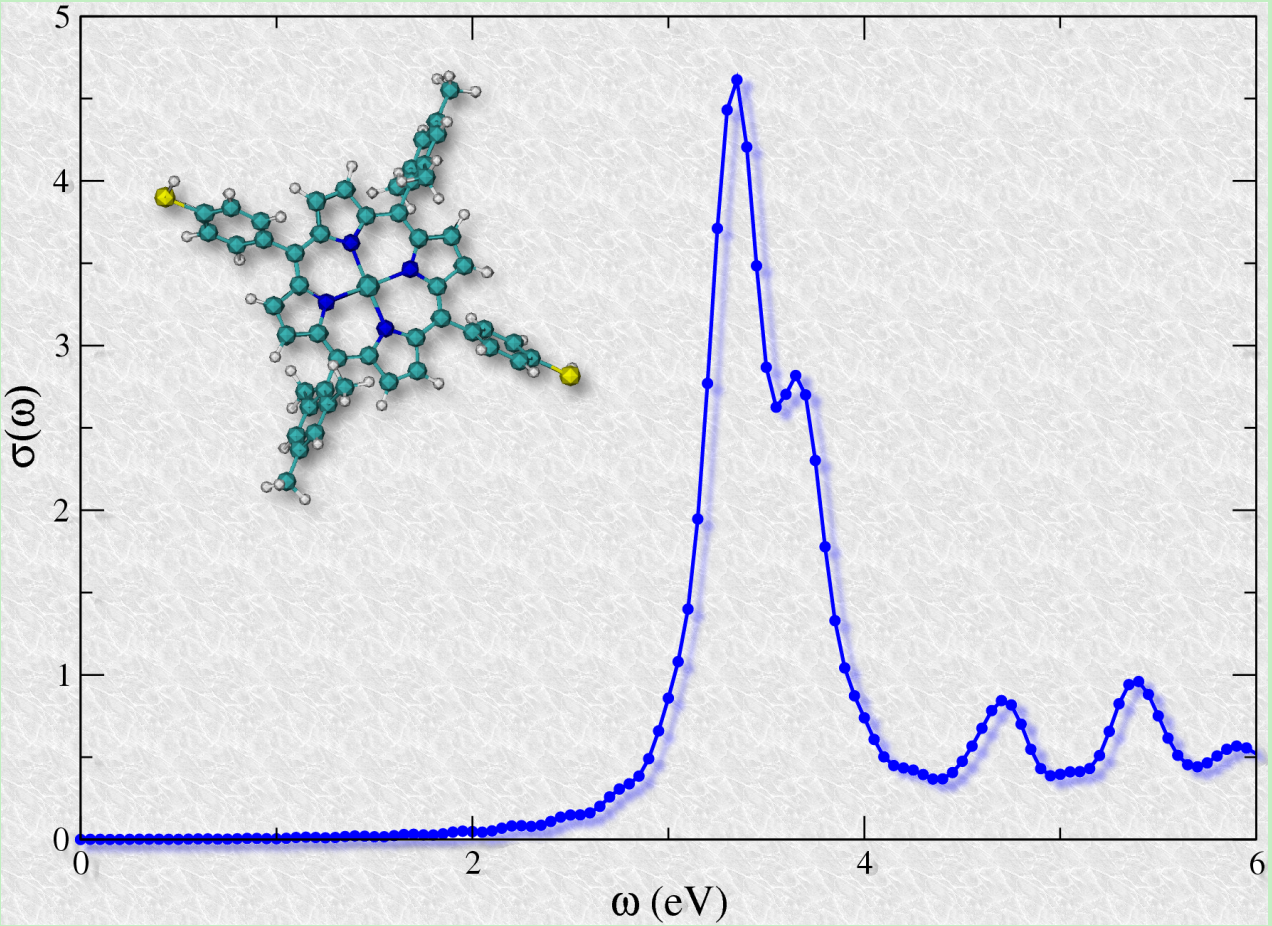
$$\alpha(t) = -\int d\mathbf{r}\, V_{ext}(\mathbf{r}, t) n(\mathbf{r}, t)$$

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

Polarizability

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

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

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)

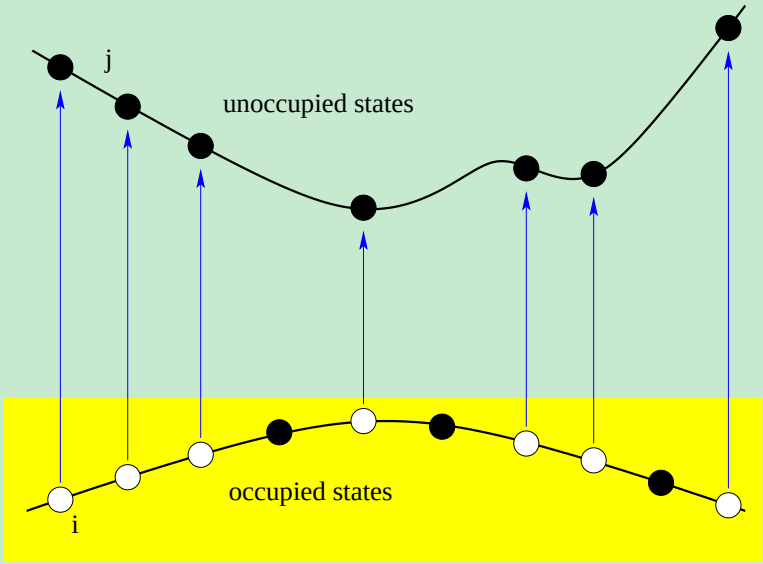
Linear Response Approach

Polarizability

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

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

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



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

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

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

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

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

with f_{xc} = exchange-correlation kernel

Linear Response Approach

Polarizability

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

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

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

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

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

with f_{xc} = exchange-correlation kernel

Linear Response Approach

Polarizability

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

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

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

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

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

with f_{xc} = exchange-correlation kernel

Linear Response Approach

Polarizability

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

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

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

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

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

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

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

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

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

- $f_{xc} = \begin{cases} \frac{\delta V_{xc}}{\delta n} \\ \text{“any” other function} \end{cases}$

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

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

Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow \quad \phi_i, \epsilon_i \quad [V_{xc}]$
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. $\chi = \chi^0 + \chi^0 (v + f_{xc})\, \chi$

A comment

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

Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow \quad \phi_i, \epsilon_i \quad [V_{xc}]$
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. $\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$

A comment

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

Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow \quad \phi_i, \epsilon_i \quad [V_{xc}]$
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. $\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$

A comment

- $f_{xc} = \begin{cases} \frac{\delta V_{xc}}{\delta n} \\ \text{“any” other function} \end{cases}$

Finite systems

Photo-absorption cross spectrum in Linear Response

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

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

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

Finite systems

Photo-absorption cross spectrum in Linear Response

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

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

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

Finite systems

Photo-absorption cross spectrum in Linear Response

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

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

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

Solids

Reciprocal space

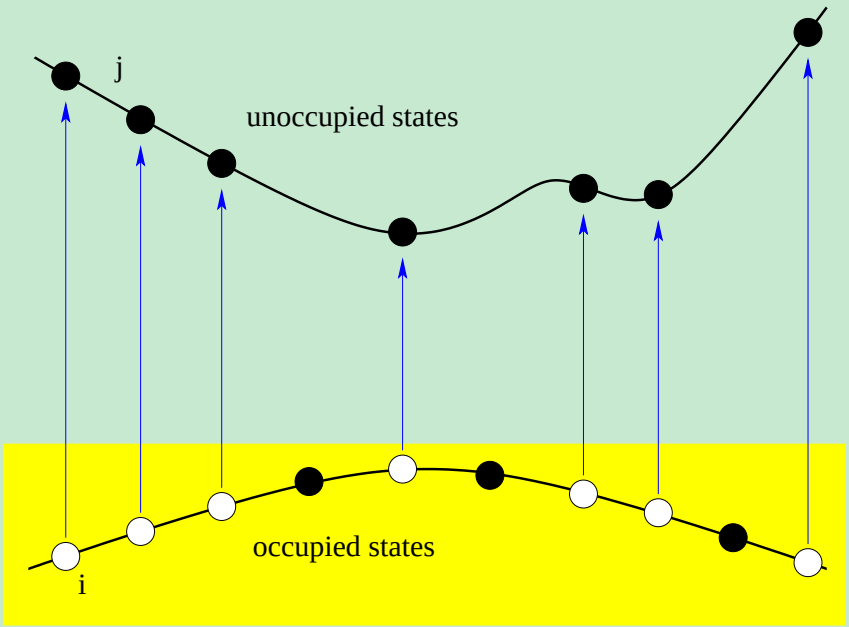
$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) \longrightarrow \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$$

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

Solids

Reciprocal space

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



Solids

Reciprocal space

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

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

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

Solids

Reciprocal space

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

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

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

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

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

Solids

Reciprocal space

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

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

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

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

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

Solids

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

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

Solids

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

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

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

Solids

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

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

$$\mathrm{ELS}(\omega) = -v_0\mathrm{Im}\left\{\chi_{00}(\omega)\right\} \; ; \; \mathrm{Abs}(\omega) = -\mathrm{v}_0\mathrm{Im}\left\{\frac{1}{1+\mathrm{v}_0\chi_{00}(\omega)}\right\}$$

Solids

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

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

$$\mathrm{ELS}(\omega) = -v_0 \mathrm{Im}\left\{\chi_{00}(\omega)\right\} \; ; \; \mathrm{Abs}(\omega) = -\mathrm{v}_0 \mathrm{Im}\left\{\frac{1}{1+\mathrm{v}_0\chi_{00}(\omega)}\right\}$$

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

Solids

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

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

$$\mathrm{ELS}(\omega) = -v_0 \mathrm{Im}\left\{\chi_{00}(\omega)\right\} \; ; \; \mathrm{Abs}(\omega) = -\mathrm{v}_0 \mathrm{Im}\left\{\frac{1}{1+\mathrm{v}_0\chi_{00}(\omega)}\right\}$$

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

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

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

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

Solids

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

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

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

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

Exercise

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

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 $\bar{v}$

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

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

Solids

Microscopic components $\bar{v}$

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

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

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

Solids

Microscopic components $\bar{v}$

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

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

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

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

Solids

Microscopic components $\bar{v}$

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

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

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

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

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

Solids

Microscopic components $\bar{v}$

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

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

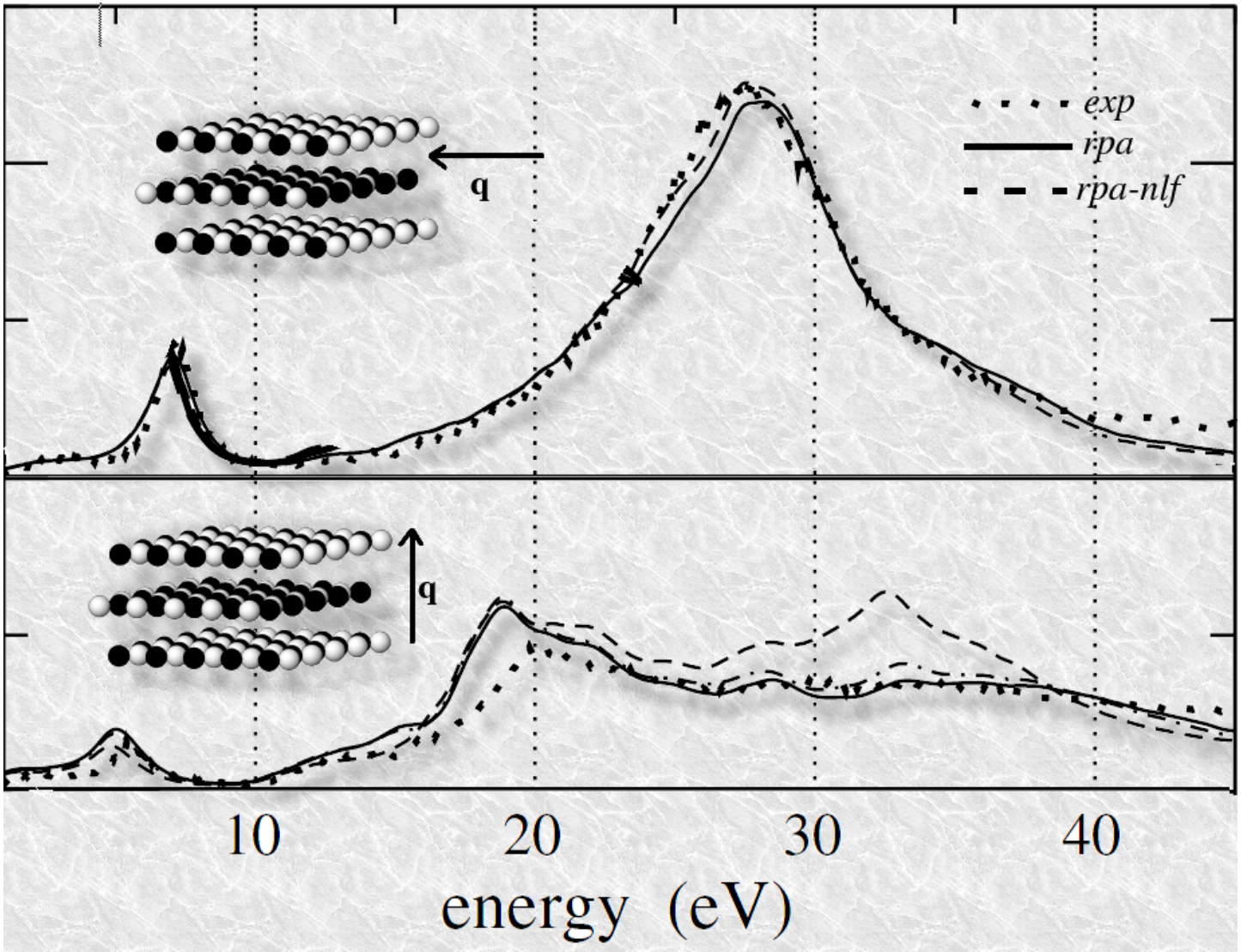
$$\text{Abs}^{\text{NLF}} = -v_0 \, \text{Im} \left\{ \bar{\chi}^{\text{NLF}} \right\}$$

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

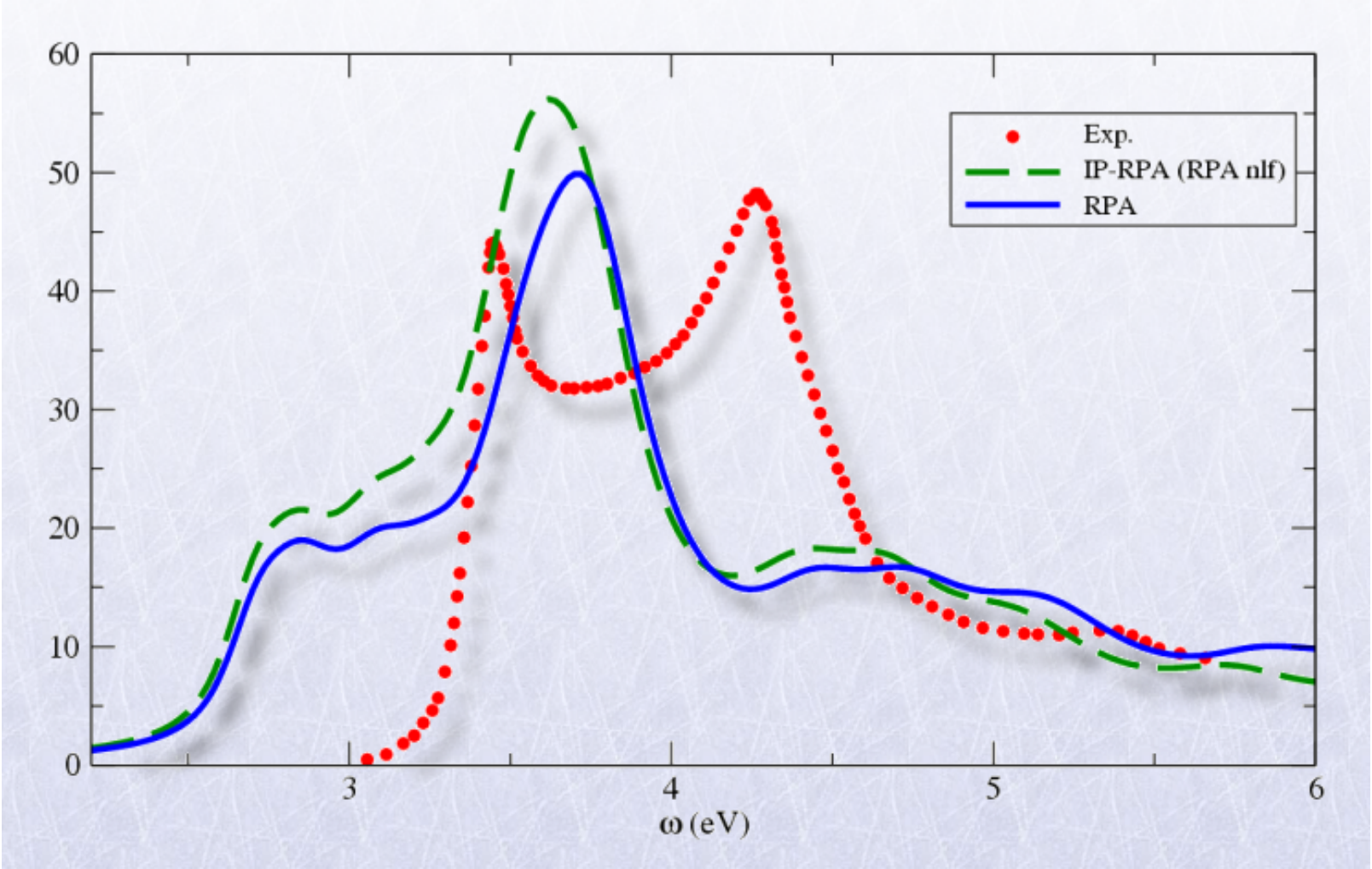
Exercise

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

EELS of Graphite



Absorption of Silicon



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

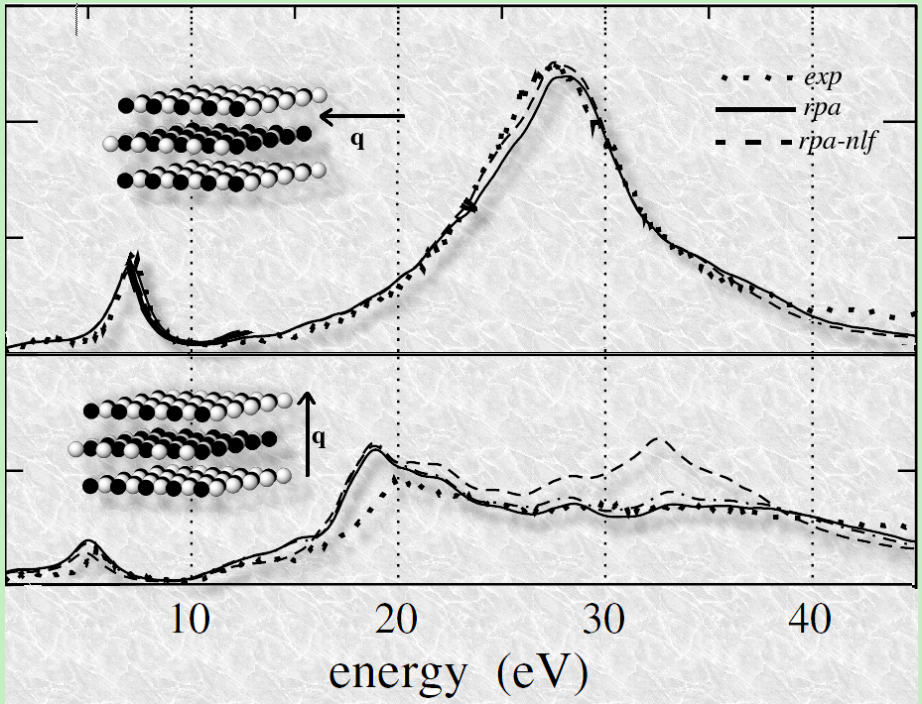
Electron Energy Loss Spectrum of Graphite

RPA vs EXP

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

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

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



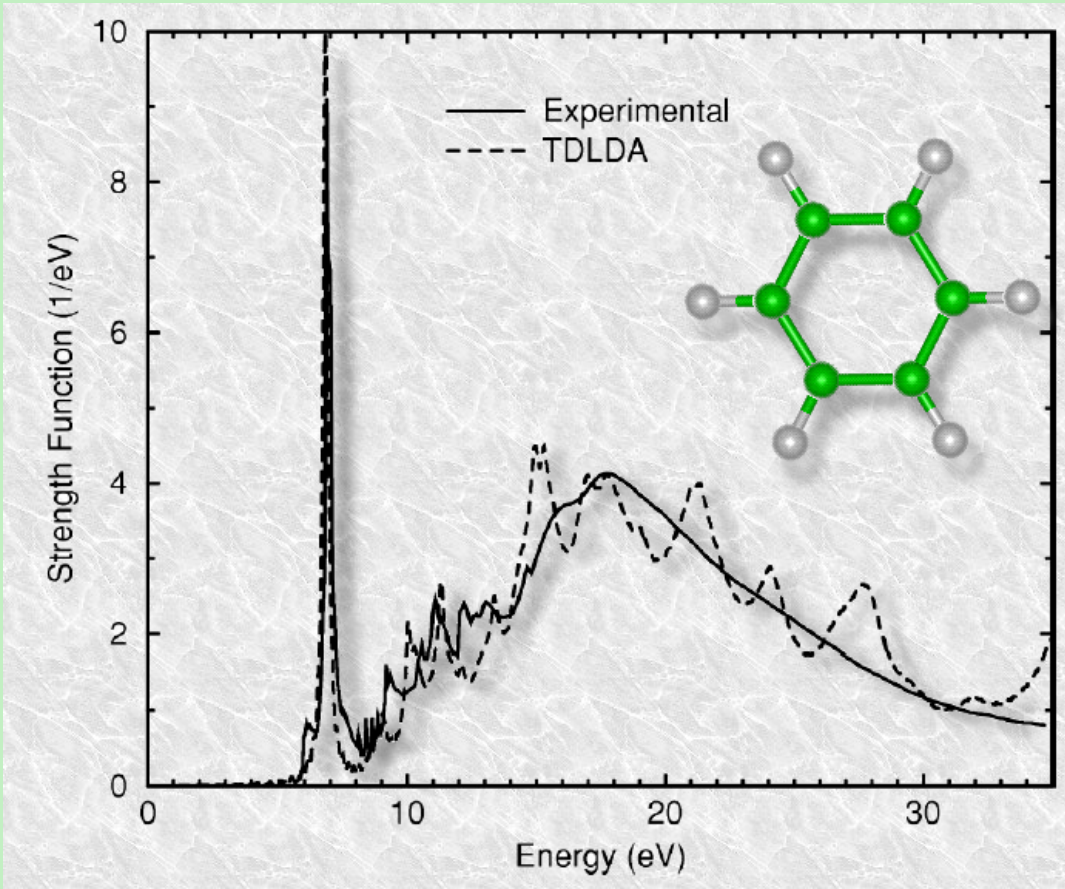
A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ALDA: Achievements and Shortcomings

Photo-absorption cross section of Benzene

ALDA vs EXP

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



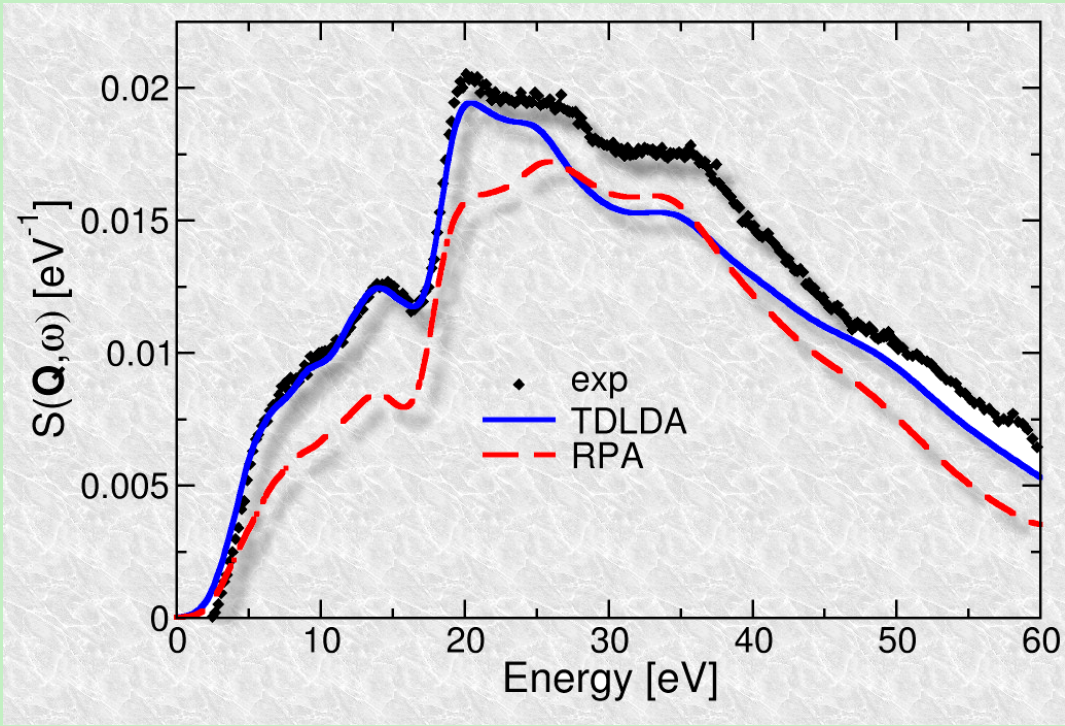
K.Yabana and G.F.Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

ALDA: Achievements and Shortcomings

Inelastic X-ray scattering of Silicon

ALDA vs RPA vs EXP

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



Weissker *et al.*, PRL **97**, 237602 (2006)

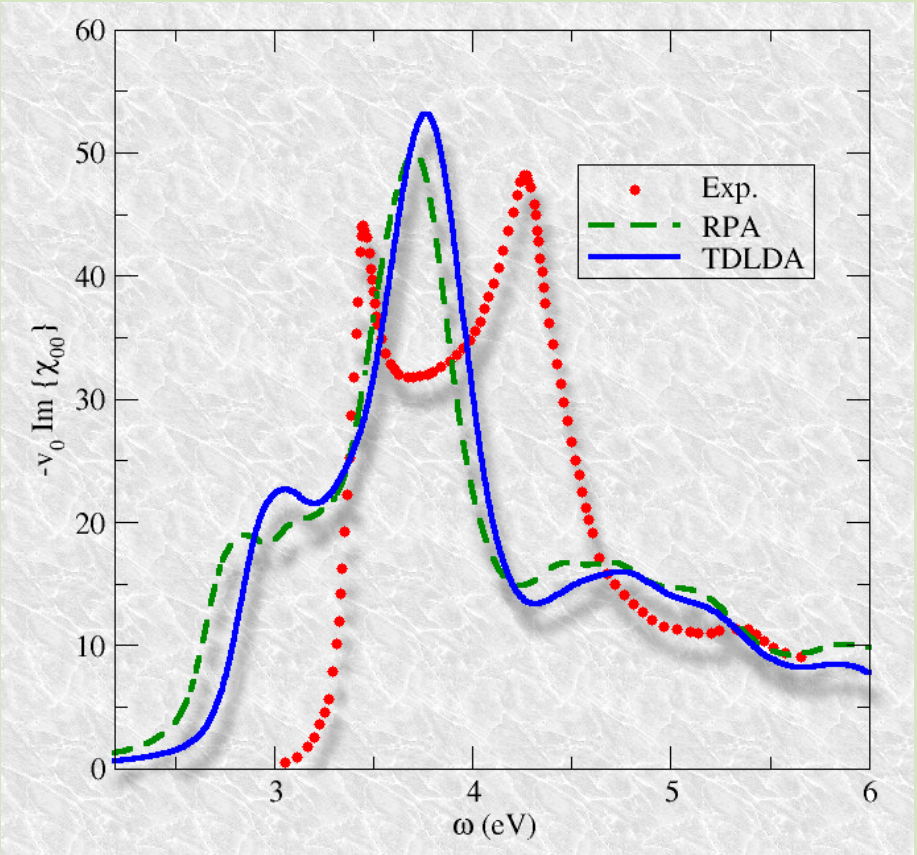
ALDA: Achievements and Shortcomings

Absorption Spectrum of Silicon

ALDA vs RPA vs EXP

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

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



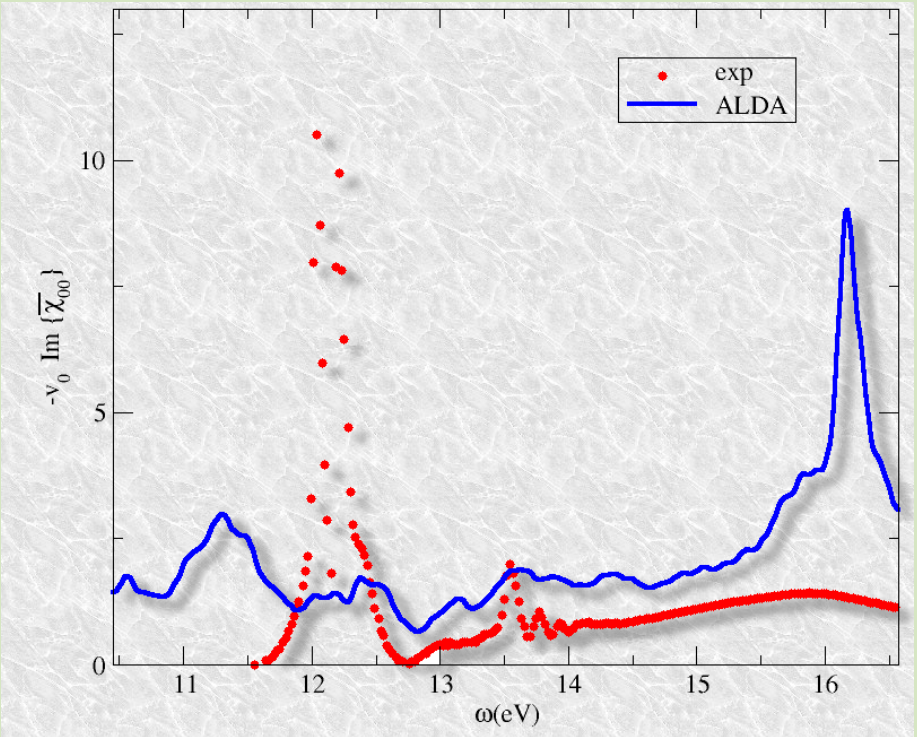
ALDA: Achievements and Shortcomings

Absorption Spectrum of Argon

ALDA vs EXP

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

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



ALDA: Achievements and Shortcomings

Good results

- Photo-absorption of small molecules
- ELS of solids

Bad results

- Absorption of solids

ALDA: Achievements and Shortcomings

Good results

- Photo-absorption of small molecules
- ELS of solids

Bad results

- Absorption of solids

Why?

ALDA: Achievements and Shortcomings

Good results

- Photo-absorption of small molecules
- ELS of solids

Bad results

- Absorption of solids

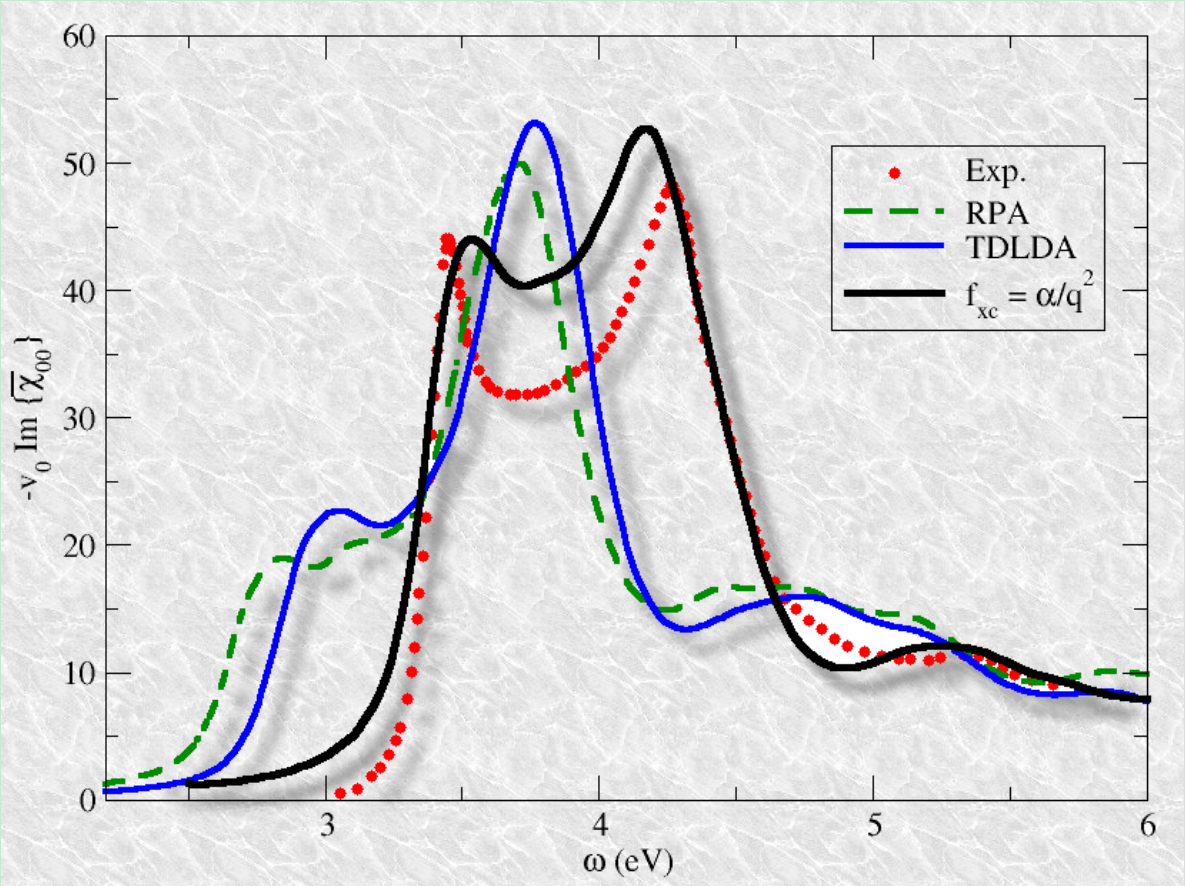
Why?

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

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

ALDA: Achievements and Shortcomings

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



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

find better fxc for solids

Outline

Resources

Codes (more or less) available for TDDFT

- Octopus (Marques,Castro,Rubio) -(real space, real time) - mainly finite systems - GPL
  http://www.tddft.org/programs/octopus/
- DP (Olevano,Reining,Sottile) - (reciprocal space, frequency domain) - solides and finite systems - open source for academics
  http://dp-code.org
- Self (Marini) - (reciprocal space, frequency domain)
- Fleszar code
- Rehr (core excitations)
- TDDFT (Bertsch)
- VASP, SIESTA, ADF, TURBOMOLE
- TD-DFPT (Baroni)

The DP code

dp - Dielectric Properties

- Reciprocal space
- Frequency domain
- Planewave basis

- Optical absorption
- Loss Spectra (EELS,IXS)

Different approximations (RPA, ALDA, NLDA, MT, etc.)

Authors: Valerio Olevano, Lucia Reining, Francesco Sottile

Contributors:

Valérie Véniard, Eleonora Luppi non-linear

Lucia Caramella Spin

Silvana Botti kernel, Wannier functions

Margherita Marsili Mapping-Theory kernel

Christine Giorgetti metals

The DP code

The algorithm

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

The DP code

The algorithm

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

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

The DP code

The algorithm

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

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

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

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

The DP code

The algorithm

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

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

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

$$\left\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{c\mathbf{k}+\mathbf{q}} \right\rangle = \int d\mathbf{r} \phi^*_{v\mathbf{k}}(\mathbf{r}) e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \phi_{c\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) + \chi^0_{\mathbf{G}\mathbf{G}''}(\mathbf{q},\omega)\left[v_{\mathbf{G}''}(\mathbf{q}) + f^{xc}_{\mathbf{G}''\mathbf{G}'''}(\mathbf{q},\omega)\right]\chi_{\mathbf{G}'''\mathbf{G}'}(\mathbf{q},\omega)$$

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

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

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

N_t

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

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

$$N_t N_{\mathbf{G}}$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

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

$$N_t N_{\mathbf{G}} N_{\mathbf{G}}$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

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

$$N_t N_{\mathbf{G}} N_{\mathbf{G}} N_\omega$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \chi^0_{\mathbf{GG''}}(\mathbf{q},\omega)\left[v_{\mathbf{G''}}(\mathbf{q}) + f^{xc}_{\mathbf{G''G'''}}(\mathbf{q},\omega)\right]\chi_{\mathbf{G'''G'}}(\mathbf{q},\omega)$$

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

$$N_t N_{\mathbf{G}} N_{\mathbf{G}} N_\omega \quad ; \quad N_t N_r \ln N_r N_\omega$$

TDDFT vs BSE scaling

Scaling of TDDFT (DP)

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) + \chi^0_{\mathbf{G}\mathbf{G}''}(\mathbf{q},\omega)\left[v_{\mathbf{G}''}(\mathbf{q}) + f^{xc}_{\mathbf{G}''\mathbf{G}'''}(\mathbf{q},\omega)\right]\chi_{\mathbf{G}'''\mathbf{G}'}(\mathbf{q},\omega)$$

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

$$N_t N_{\mathbf{G}} N_{\mathbf{G}} N_\omega \quad ; \quad N_t N_r \ln N_r N_\omega$$

$$\text{Scaling} \lesssim N_{at}^4$$

TDDFT vs BSE scaling

Scaling of BSE (EXC)

$$H_{vc\mathbf{k}}^{v'c'\mathbf{k}'}$$

$$\text{Scaling} \quad N_t^2 N_r \lesssim N_{at}^5$$

TDDFT vs BSE scaling

Scaling of BSE (EXC)

$$H_{vc\mathbf{k}}^{v'c'\mathbf{k}'} A_{\lambda}^{v'c'\mathbf{k}'} = A_{\lambda} A_{\lambda}^{vc\mathbf{k}}$$

$$\text{Scaling} \quad N_t^2 N_r \lesssim N_{at}^5$$

$$\text{Scaling} \quad N_t^3 \lesssim N_{at}^6$$

TDDFT

Some References

- van Leeuwen, Int. J. Mod. Phys. **B15**, 1969 (2001)
- Gross and Kohn, Adv. Quantum Chem. **21**, 255 (1990)
- Marques and Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004)
- Botti *et al.* Rep. Prog. Phys. **70**, 357 (2007)
- Marques *et al.* eds. *Time Dependent Density Functional Theory*, Springer (2006)