Time Dependent Density Functional Theory

Application to Extended Systems

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Outline

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Dielectric Function in Crystals

A better representation: Fourier space

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

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

Dielectric Function in Crystals

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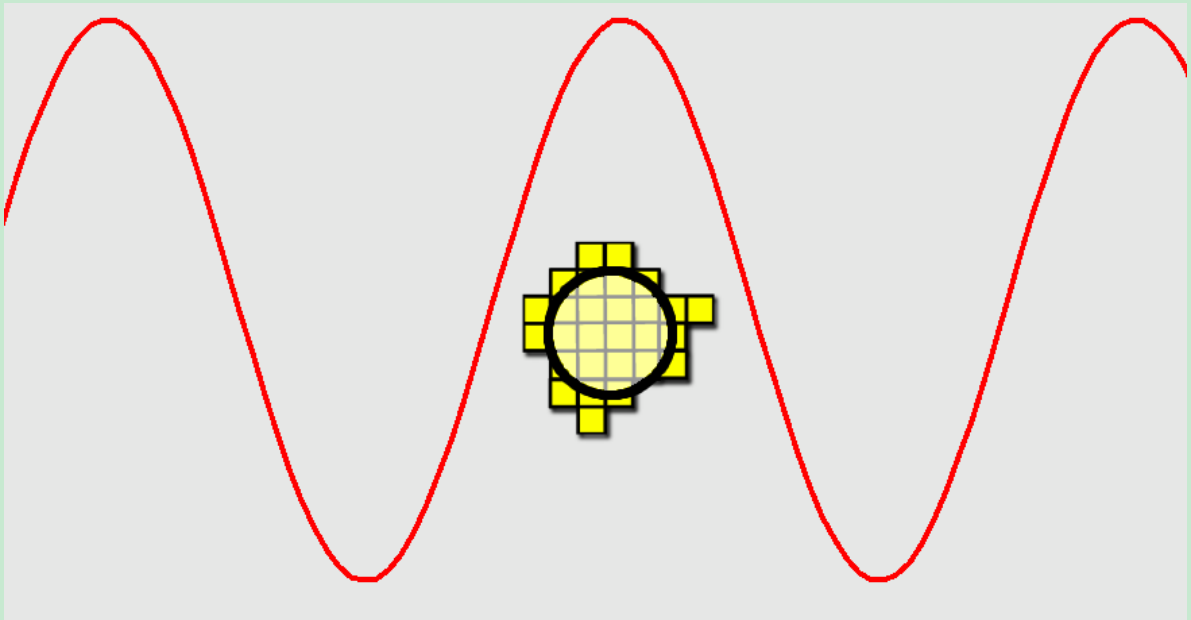
Dielectric Function in Crystals

Macroscopic average



average over distance d:

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

Dielectric Function in Crystals

Macroscopic average

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

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

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

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

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

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Absorption coefficient

General solution of Maxwell's equation

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

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

complex (macroscopic) refractive index N

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

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

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

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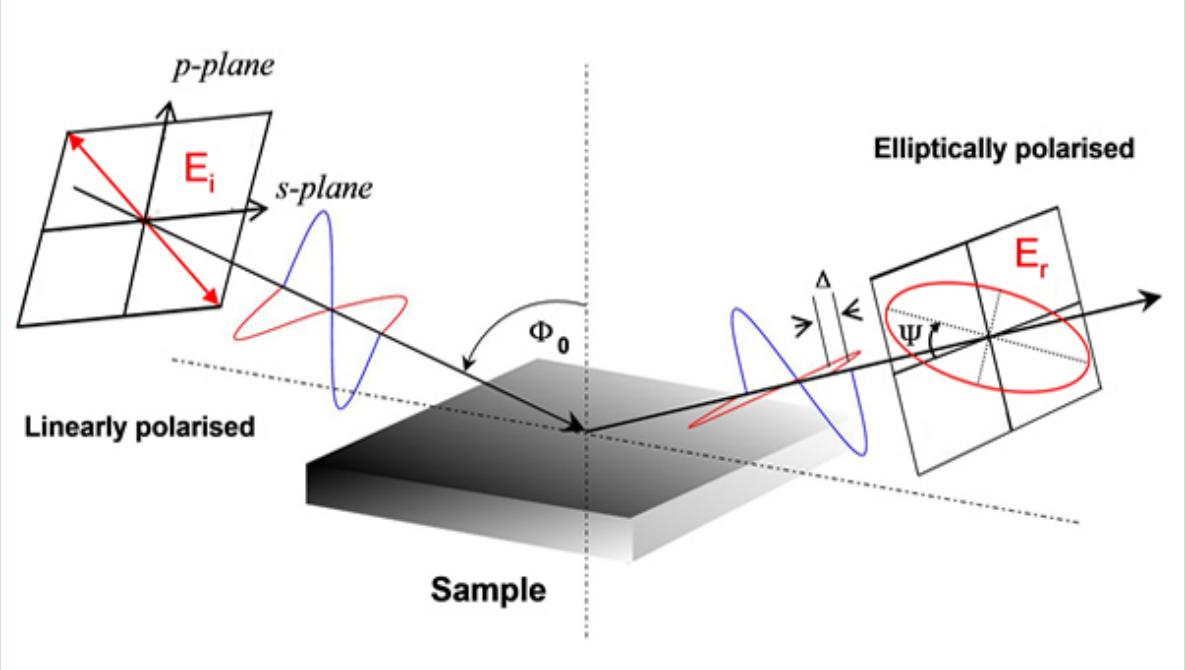
Ellipsometry Experiment



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

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

Let's calculate ε_M

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

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

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

$$\neq \varepsilon_{\mathbf{0}\mathbf{0}}(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega)$$

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

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Dielectric Function in Crystals

Let's calculate ε_M

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

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

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Dielectric Function in Crystals

The Energy Loss Spectra

Imaginary part of the macroscopic inverse dielectric function

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

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

Dielectric Function in Crystals

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Dielectric Function in Crystals

Absoprtion Spectra

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

Energy Loss Spectra

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

Dielectric Function in Crystals

Question

ε_{00} is not the macroscopic dielectric function

What is it then ?

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

without local fields.

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Solids

Reciprocal space

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

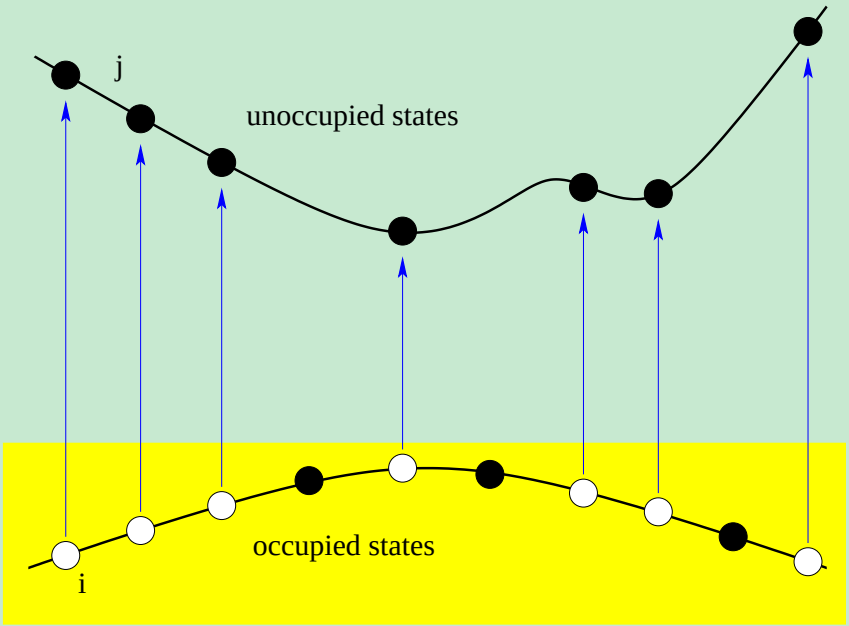
G =reciprocal lattice vector

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

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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

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

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

▸ Results

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Reciprocal space

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

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

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

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

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

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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

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

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

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

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

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

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 $\bar{v}$

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

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

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Microscopic components $\bar{v}$

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

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

Solids

Microscopic components $\bar{v}$

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

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

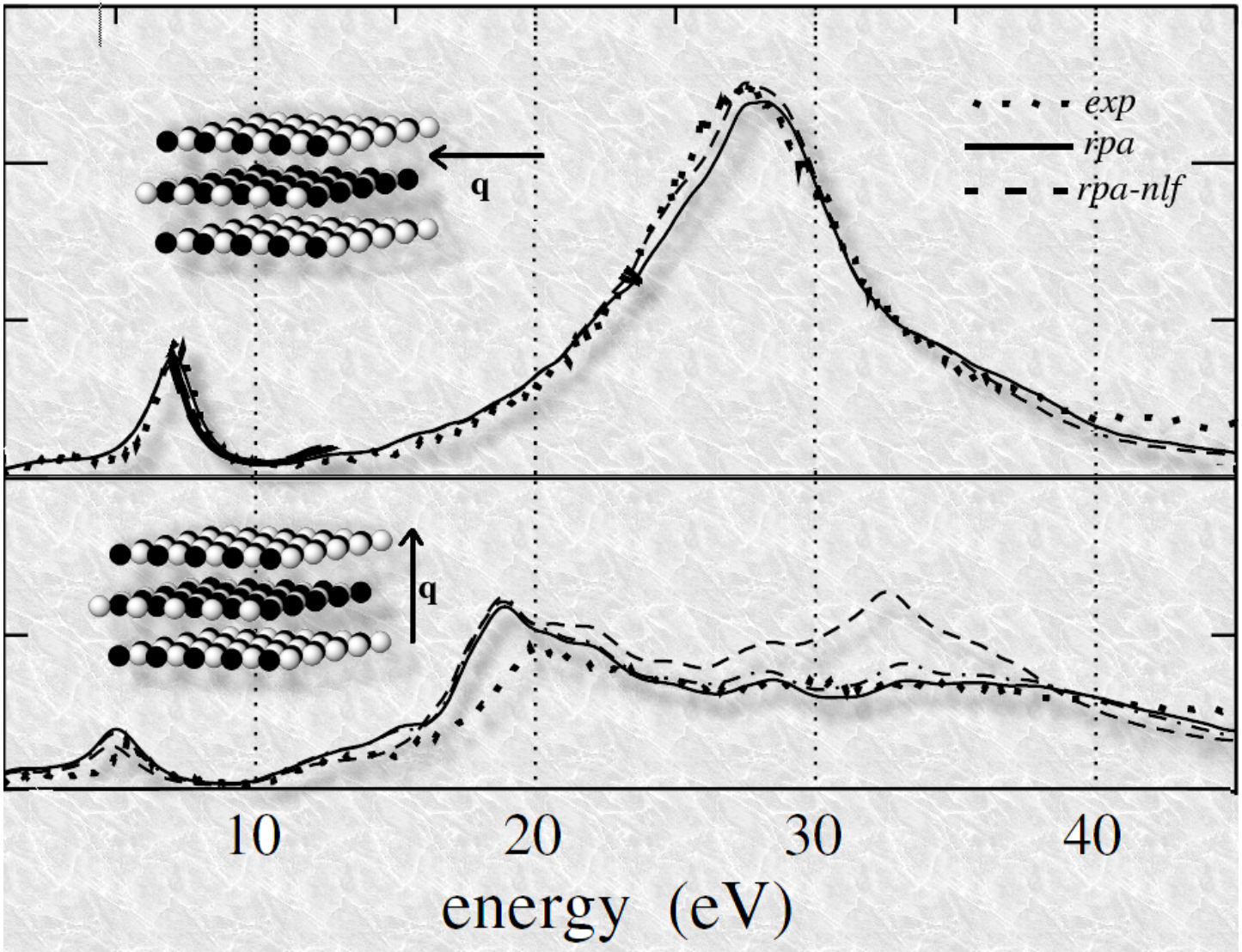
$$\text{Abs}^{\text{NLF}} = -v_0 \, \text{Im} \left\{ \bar{\chi}^{\text{NLF}} \right\}$$

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

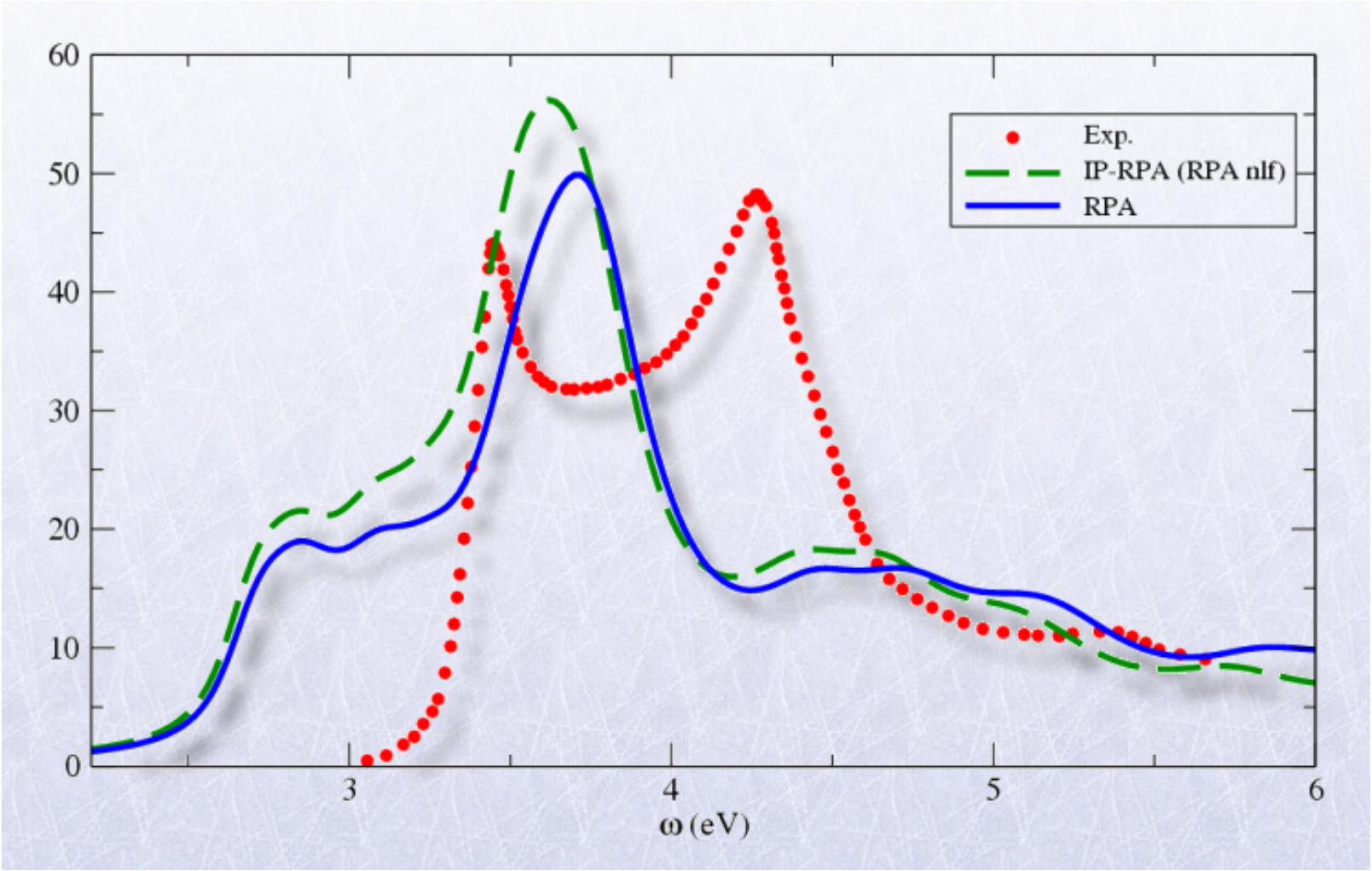
Exercise

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

EELS of Graphite



Absorption of Silicon



Outline

ALDA: Achievements and Shortcomings

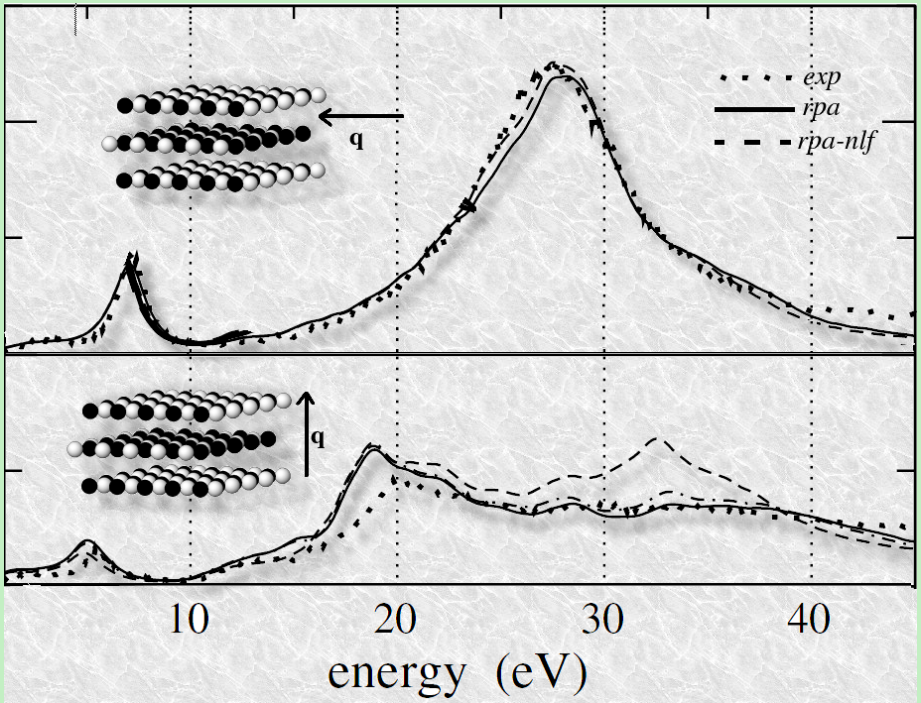
Electron Energy Loss Spectrum of Graphite

RPA vs EXP

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

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

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



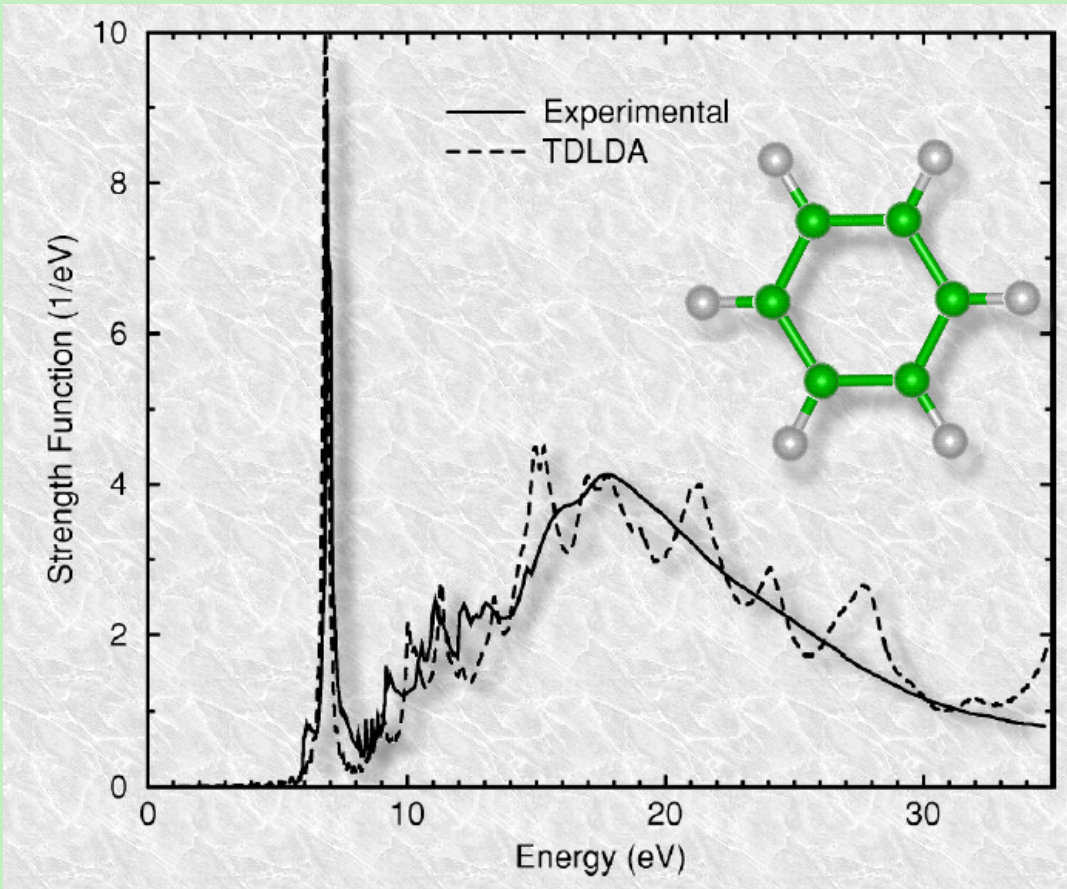
A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ALDA: Achievements and Shortcomings

Photo-absorption cross section of Benzene

ALDA vs EXP

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



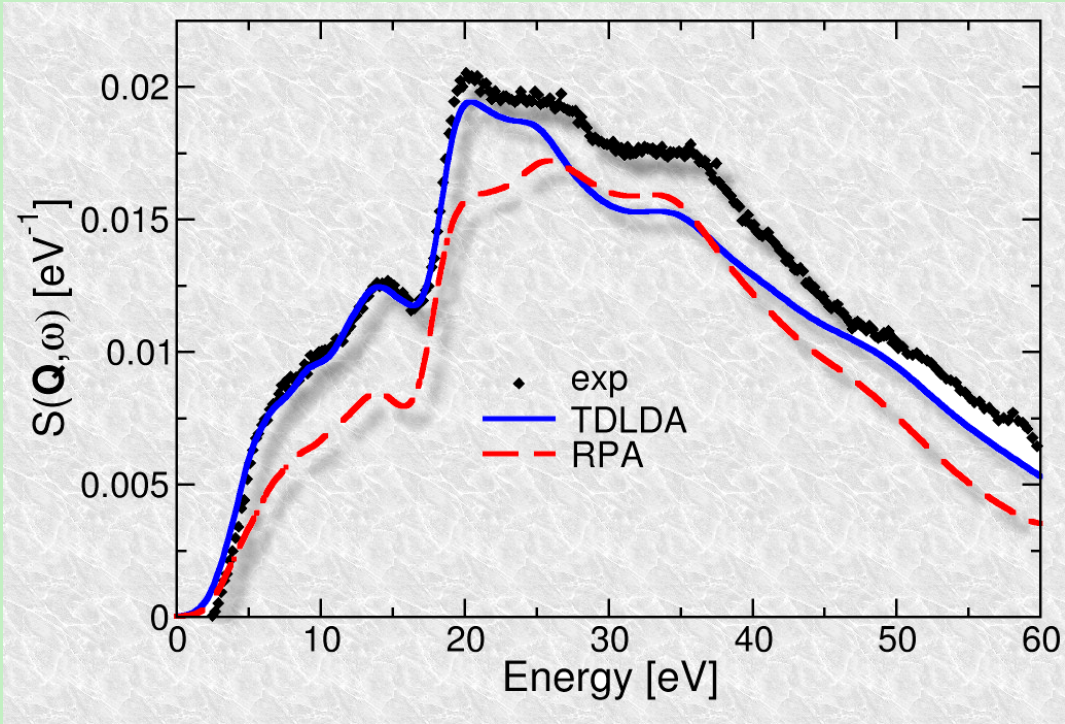
K.Yabana and G.F.Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

ALDA: Achievements and Shortcomings

Inelastic X-ray scattering of Silicon

ALDA vs RPA vs EXP

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



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

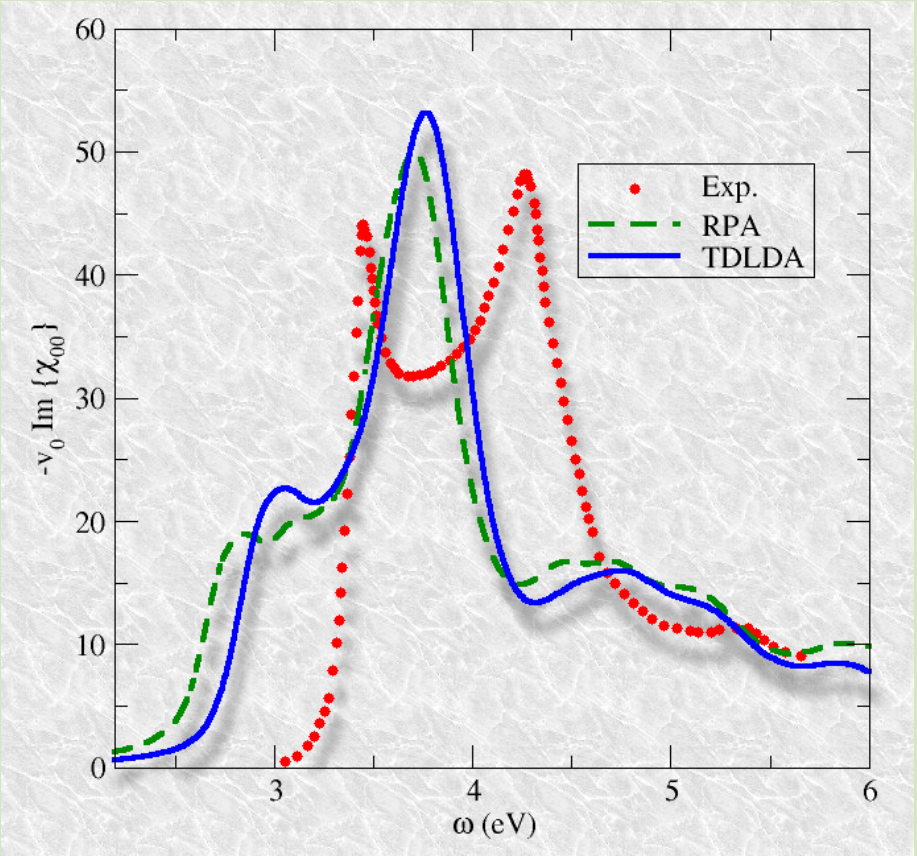
ALDA: Achievements and Shortcomings

Absorption Spectrum of Silicon

ALDA vs RPA vs EXP

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

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



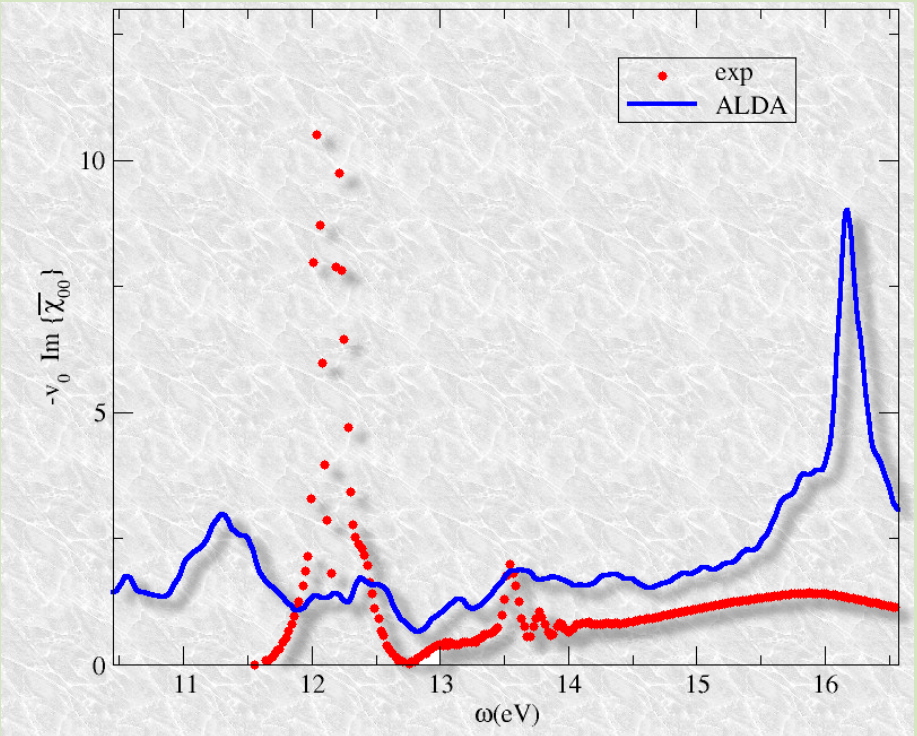
ALDA: Achievements and Shortcomings

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

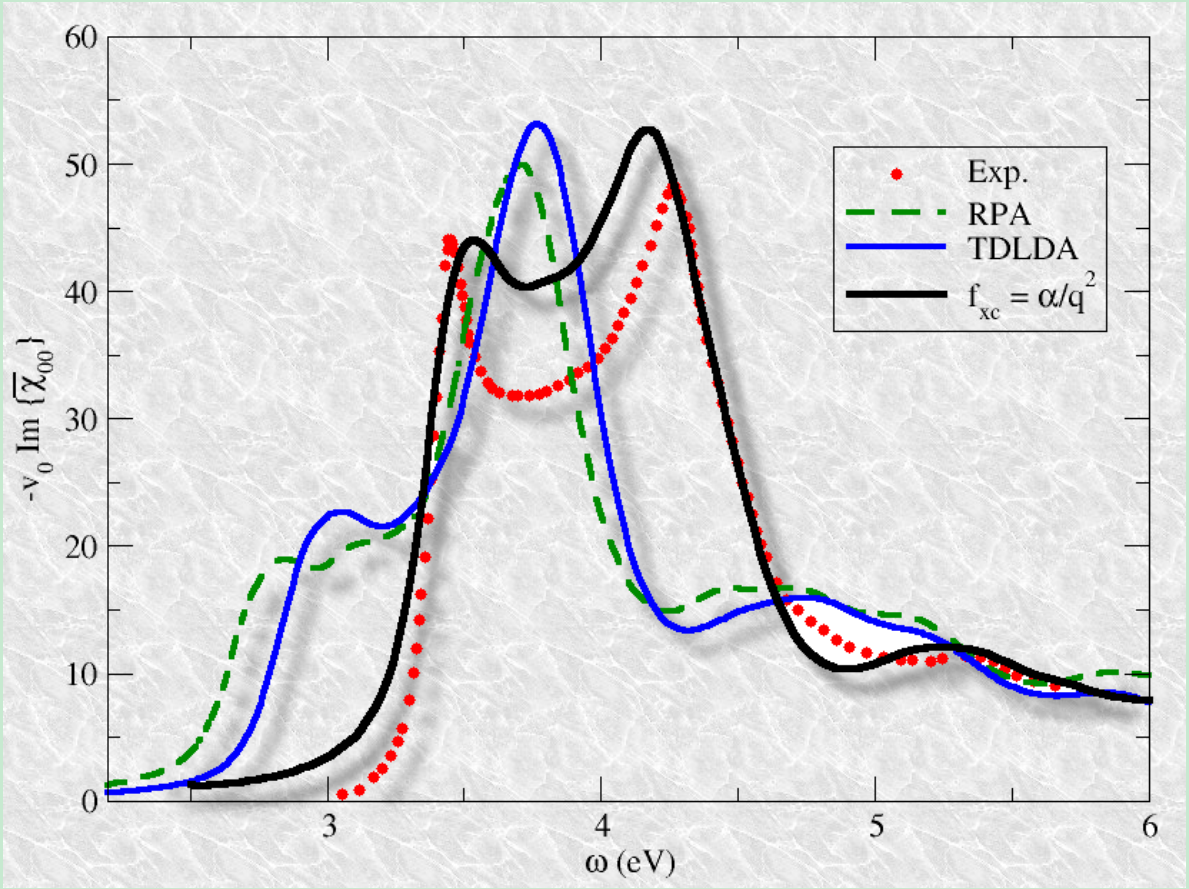
Why?

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

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

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

Parameters to fit to experiments.

Beyond ALDA approximation

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: Results

Absorption of Silicon

The Mapping Theory: Results

Absorption of Silicon

The Mapping Theory: Results

Absorption of Silicon

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

The Mapping Theory: Results

Absorption of Silicon Carbide and Diamond

last week preliminary results :-)

The Mapping Theory: Results

Absorption of Argon

The Mapping Theory: Results

Absorption of Argon

F.Sottile *et al.*, submitted to Phys.Rev.Lett.

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).

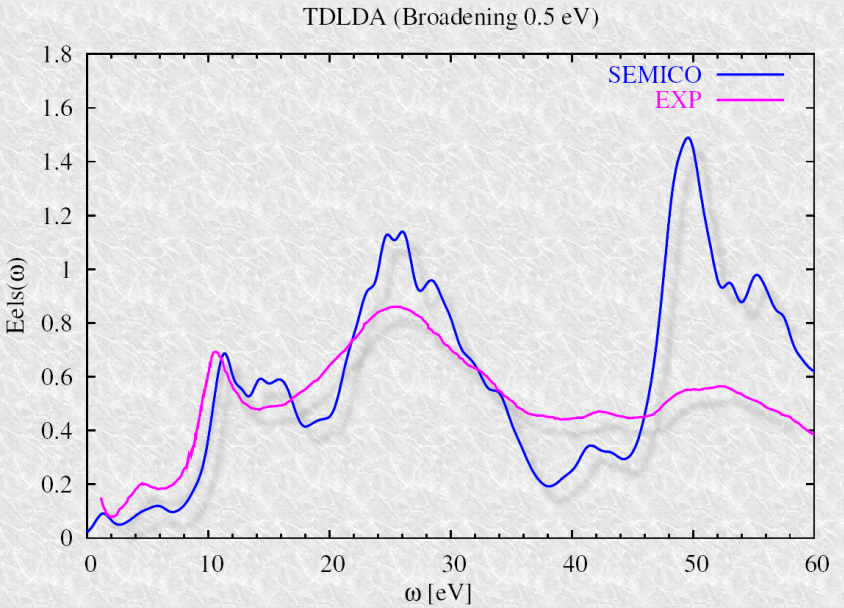
Spectra of simple systems

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

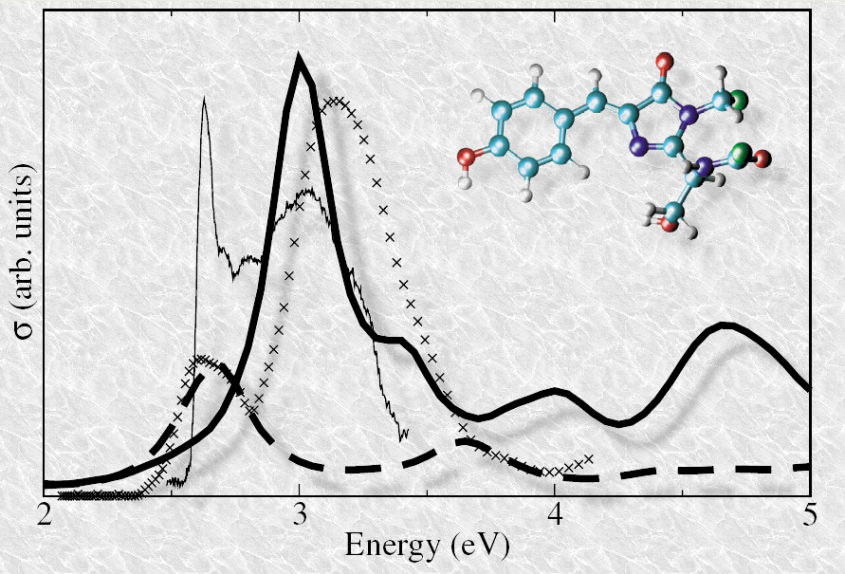
Strongly correlated systems



EEL spectrum of VO_2

M.Gatti, preliminary results

Biological systems



Abs spectrum of Green Fluorescent Protein

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