# Excitonic Effects within TDDFT


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Belfast, 29 June 2007

# Outline

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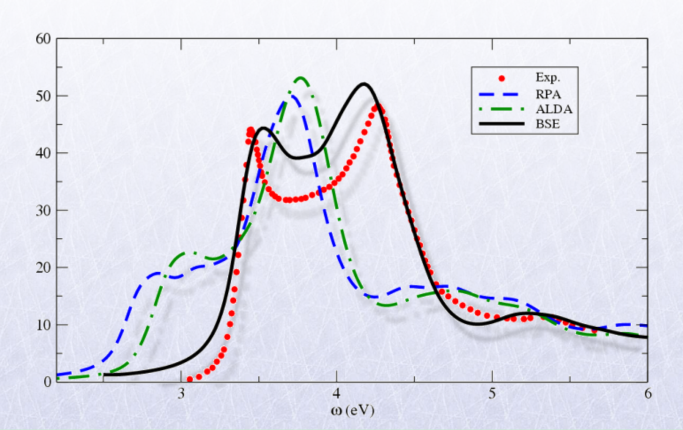
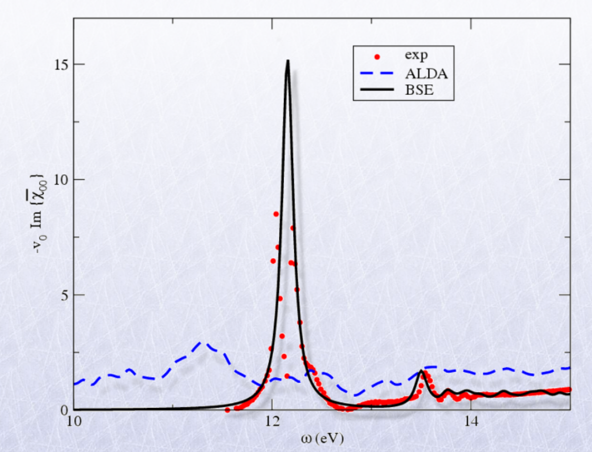
# Optical Absorption Spectra of Solids

## Semiconductors: Silicon



# Optical Absorption Spectra of Solids

## Insulators: Argon



# Optical Absorption Spectra of Solids

- ALDA bad for any solids!! though quick
- BSE good but cumbersome

# Optical Absorption Spectra of Solids

## 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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**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.

$$f_{xc} = \chi_0^{-1} GGWGG \chi_0^{-1}$$

# Outline

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# The Mapping Theory

## The idea

$$\text{BSE works} \Rightarrow \left\{ \begin{array}{c} \text{we get the ingredients of the BSE} \\ \text{and we put them in TDDFT} \end{array} \right.$$

# The Mapping Theory

**BSE: Excitonic Hamiltonian** — 4-point

$$H^{\text{BSE}}_{(vc)(v'c')} = \Big[ (E_c - E_v)\, \delta_{vv'} \delta_{cc'} + v^{v'c'}_{vc} - W^{v'c'}_{vc} \Big]$$

# The Mapping Theory

**BSE: Excitonic Hamiltonian** 4-point

$$H^{\mathrm{BSE}} = \Big[ (E_c - E_v) + \ll v \gg - \ll W \gg \Big]$$

# The Mapping Theory

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**TDDFT: Polarizability equation** 4-point

$$\chi = \chi_0 + \chi_0 \left( v + f_{xc} \right) \chi$$

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**BSE: Excitonic Hamiltonian** 4-point

$$H^{\text{BSE}} = \left[ \left( \epsilon_c + \Delta_c^{\text{GW}} - \epsilon_v - \Delta_v^{\text{GW}} \right) + \ll v \gg - \ll W \gg \right]$$

**TDDFT: written in transition space** 4-point

$$H^{\text{TDDFT}} = \left[ (\epsilon_c - \epsilon_v) + \ll v \gg + \ll f_{xc} \gg \right]$$

# The Mapping Theory

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**TDDFT: written in transition space** 4-point

$$H^{\text{TDDFT}} = \left[ (\epsilon_c - \epsilon_v) + \ll v \gg + \ll f_{xc} \gg \right]$$

**The exchange-correlation kernel $f_{xc}$ has to take into account both GW corrections and excitonic effects !!**

# The Mapping Theory

**BSE: Excitonic Hamiltonian** — 4-point

$$H^{\text{BSE}} = \left[ (E_c - E_v) + \ll v \gg - \ll W \gg \right]$$

**TDDFT: written in transition space** — 4-point

$$H^{\text{TDDFT}} = \left[ (E_c - E_v) + \ll v \gg + \ll f_{xc} \gg \right]$$

**Same starting point for both BSE and TDDFT: the GW band-structure.**

# The Mapping Theory

**BSE: Excitonic Hamiltonian** 4-point

$$H^{\text{BSE}} = \left[ (E_c - E_v) + \ll v \gg - \ll W \gg \right]$$

**TDDFT: written in transition space** 4-point

$$H^{\text{TDDFT}} = \left[ (E_c - E_v) + \ll v \gg + \ll f_{xc} \gg \right]$$

**We concentrate, then, only on the excitonic effects.**

# The Mapping Theory

**BSE: Excitonic Hamiltonian** — 4-point

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**TDDFT: written in transition space** — 4-point

$$H^{\text{TDDFT}} = \left[ (E_c - E_v) + \ll v \gg - \ll W \gg \right]$$

**We substitute the ‘unknown’ $\ll f_{xc} \gg$ with $\ll W \gg$.**

# The Mapping Theory

## The idea

**We want to use $\ll W \gg$, but in a 2-point equation.**

$$\chi(12,\omega) = \chi_0(12,\omega) + \chi_0(13,\omega)\left(v(34) + f_{xc}(34,\omega)\right)\chi(42,\omega)$$

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# The Mapping Theory

$$\chi = \chi_0 + \chi_0 \left( v + f_{xc} \right) \chi$$

$$\chi = \left( 1 - \chi_0 v - \chi_0 f_{xc} \right)^{-1} \chi_0$$

Let's define an invertible matrix $X(12,\omega) = \sum_{vc} \phi_v(1)\phi_c(1) g_{vc}(2,\omega)$

$$\chi = X X^{-1} \left( 1 - \chi_0 v - \chi_0 X^{-1} X f_{xc} \right)^{-1} \chi_0$$

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$$T(12,\omega) = \sum_{\substack{vc \\ v'c'}} g_{vc}(1,\omega) \ll f_{xc} \gg g_{v'c'}(2,\omega)$$

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## TDDFT 2-point equation containing $\ll W \gg$

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**What about the application ??**

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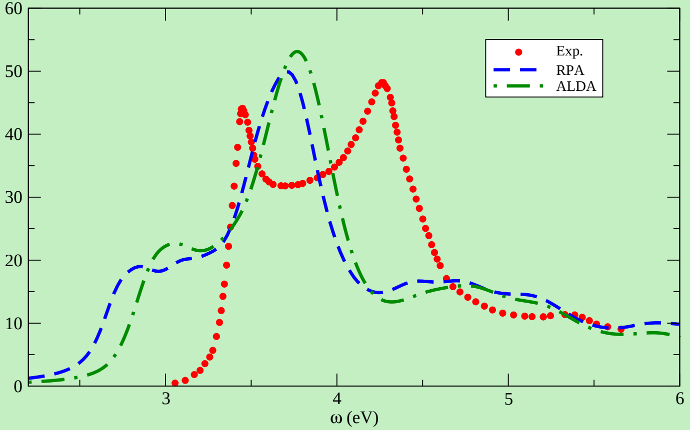
# Outline

# The Mapping Theory: Results

## Absorption of Silicon



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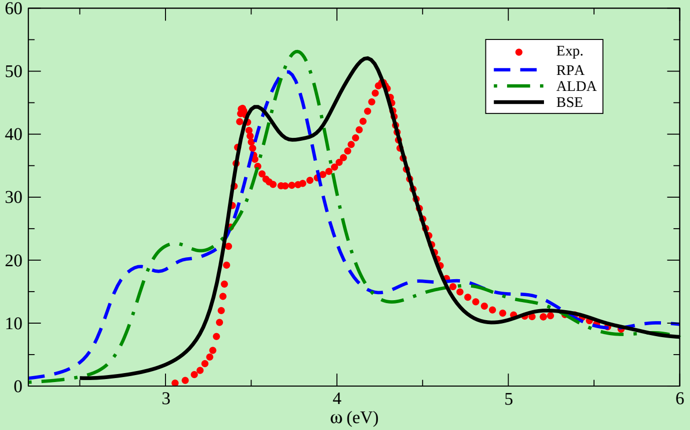

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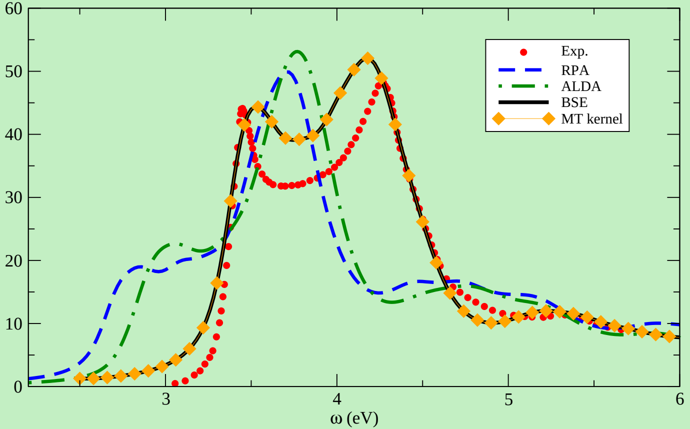
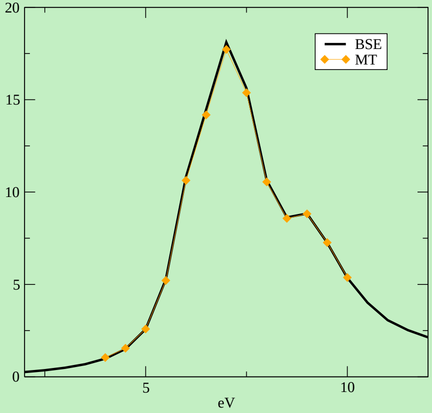
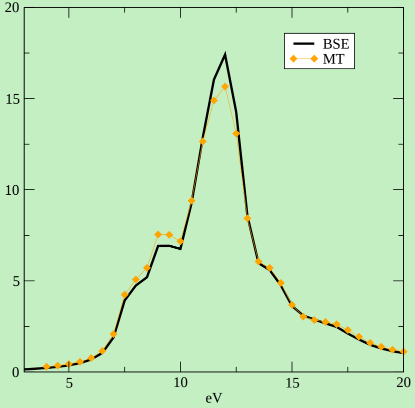



F.Sottile *et al.* Phys.Rev.Lett **91**, 56402 (2003)

# The Mapping Theory: Results

## Absorption of Silicon Carbide and Diamond

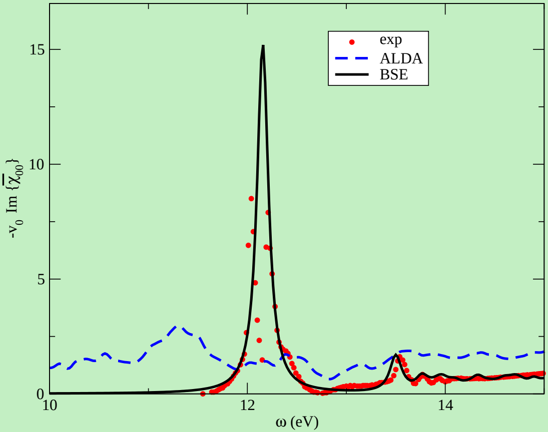



last week preliminary results :-)

# The Mapping Theory: Results

## Absorption of Argon



# The Mapping Theory: Results

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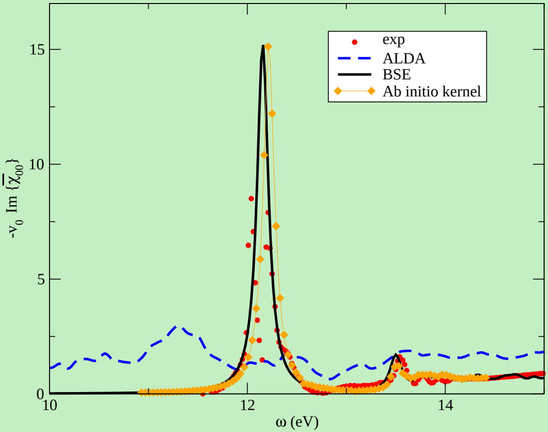



F.Sottile *et al.*, submitted to Phys.Rev.Lett.

# 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).

# Outline

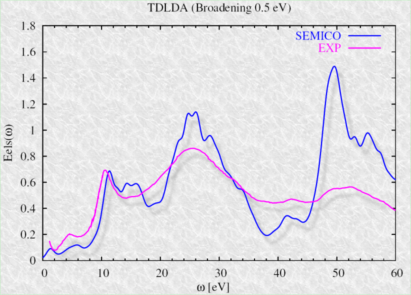
# Conclusions

## TDDFT is the method of choice

- $\surd$ Absorption spectra of simple molecules
- $\surd$ Electron energy loss spectra
- $\surd$ Inelastic X-ray scattering spectroscopy
- $\surd$ Absorption of Solids (BSE-like scaling)

# Towards new applications

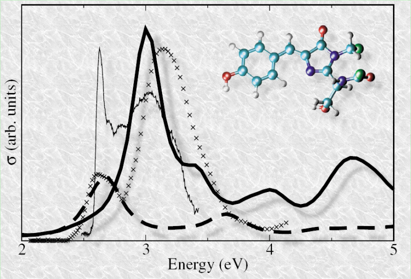
## Strongly correlated systems




EEL spectrum of $VO_2$

M.Gatti, preliminary results

## Biological systems

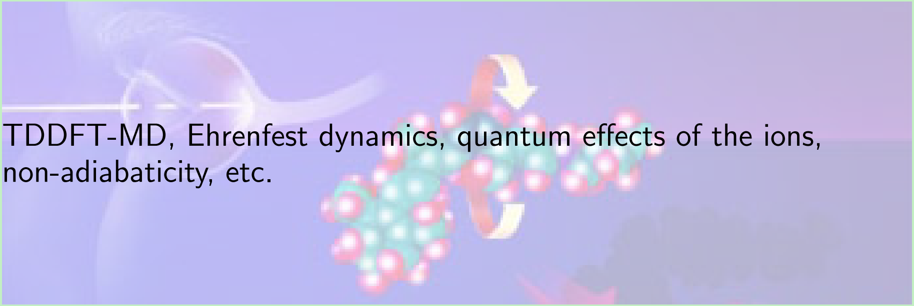



Abs spectrum of Green Fluorescent Protein

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

# New Frontiers

## Excited-State Dynamics



TDDFT-MD, Ehrenfest dynamics, quantum effects of the ions, non-adiabaticity, etc.

Sugino and Miyamoto, Phys.Rev.B **59**, 2579 (1999)

# New Frontiers

## TDDFT concept into MBPT

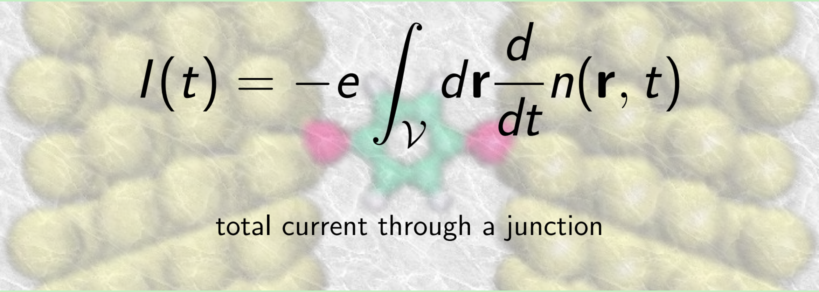
$$\Sigma = GW\Gamma$$

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)

# Conclusions

## TDDFT is the method of choice

- √ Absorption spectra of simple molecules
- √ Electron energy loss spectra
- √ Inelastic X-ray scattering spectroscopy
- √ Absorption of Solids (BSE-like scaling)
- √ Promising for new applications.

## Open problems

- open-shell atoms
- charge-transfer excitations
- *really* efficient calculations of solids

**approximation for $f_{xc}$**

# Conclusions

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- √ Inelastic X-ray scattering spectroscopy
- √ Absorption of Solids (BSE-like scaling)

- √ Promising for new applications.

## Open problems

- open-shell atoms
- charge-transfer excitations
- *really* efficient calculations of solids

**approximation for** $f_{xc}$

# *Thank you for your attention during these three days*