Excitonic Effects within TDDFT

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Outline

1. BSE and TDDFT up to 2002
2. The Mapping Theory Kernel
   - Theory
   - Results
3. Conclusions and Perspectives
Optical Absorption Spectra of Solids

Semiconductors: Silicon

![Graph showing optical absorption spectra for silicon, comparing experimental data (Exp.), RPA, ALDA, and BSE calculations.](image-url)
Optical Absorption Spectra of Solids

Insulators: Argon

![Graph showing optical absorption spectra for Argon. The graph compares experimental data (exp), ALDA, and BSE results.](image-url)
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

  Long-range kernel

  Polarization density functional. Long-range.

  Exact-exchange

  Long-range and contact exciton.

  Dynamic long-range component

Parameters to fit to experiments.
The problem of Abs in solids. Towards a better understanding

  - Long-range kernel

  - Polarization density functional. Long-range.

  - Exact-exchange

  - Long-range and contact exciton.

  - Dynamic long-range component

**Parameters to fit to experiments.**
Beyond ALDA approximation

Abs in solids. Insights from MBPT

Parameter-free Ab initio kernels

Full many-body kernel. Mapping Theory.

Full many-body kernel. Perturbation Theory.

\[ f_{xc} = \chi_0^{-1} GGWGG \chi_0^{-1} \]
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1. BSE and TDDFT up to 2002

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3. Conclusions and Perspectives
The Mapping Theory

The idea

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

**BSE: Excitonic Hamiltonian**

\[
H_{(vc)(v'c')}^{\text{BSE}} = \left[ (E_c - E_v) \delta_{vv'} \delta_{cc'} + v_{vc}^{v'c'} - W_{vc}^{v'c'} \right]
\]
BSE: Excitonic Hamiltonian

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

**BSE: Excitonic Hamiltonian**

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

BSE: Excitonic Hamiltonian

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

TDDFT: Polarizability equation

\[ \chi = \chi_0 + \chi_0 (v + f_{xc}) \chi \]
The Mapping Theory

**BSE: Excitonic Hamiltonian**

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

**TDDFT: written in transition space**

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

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

TDDFT: written in transition space

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

The exchange-correlation kernel \( f_{xc} \) has to take into account both GW corrections and excitonic effects!!
The Mapping Theory

BSE: Excitonic Hamiltonian

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

TDDFT: written in transition space

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

Same starting point for both BSE and TDDFT: the GW band-structure.
## The Mapping Theory

### BSE: Excitonic Hamiltonian

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

### TDDFT: written in transition space

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

We concentrate, then, only on the excitonic effects.
The Mapping Theory

BSE: Excitonic Hamiltonian 4-point

\[ H_{\text{BSE}} = \left[ (E_c - E_v) + \ll \nu \gg - \ll W \gg \right] \]

TDDFT: written in transition space 4-point

\[ H_{\text{TDDFT}} = \left[ (E_c - E_v) + \ll \nu \gg - \ll W \gg \right] \]

We substitute the ‘unknown’ \( \ll f_{xc} \gg \) with \( \ll W \gg \).
The Mapping Theory

The idea

We want to use $W$, but in a 2-point equation.

$$\chi(12, \omega) = \chi_0(12, \omega) + \chi_0(13, \omega) (\nu(34) + f_{xc}(34, \omega)) \chi(42, \omega)$$
The Mapping Theory

The idea

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

$$\chi(12, \omega) = \chi_0(12, \omega) + \chi_0(13, \omega) (v(34) + f_{xc}(34, \omega)) \chi(42, \omega)$$
The Mapping Theory

$$\chi = \chi_0 + \chi_0 (\nu + f_{xc}) \chi$$

$$\chi = (1 - \chi_0 \nu - \chi_0 f_{xc})^{-1} \chi_0$$

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

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

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

$$\chi = X \left(X - \chi_0 \nu X - \chi_0 X^{-1} T \right)^{-1} \chi_0$$
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\[ T(12, \omega) = X(13, \omega) f_{xc}(34, \omega) X(42, \omega) = \sum_{vc} \int d(34) g_{vc}(1, \omega) \phi_v(3) \phi_c(3) f_{xc}(34, \omega) \phi_{v'}(4) \phi_{c'}(4) g_{v'c'}(2, \omega) \]

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

\[ T_{BSE}(12, \omega) = \sum_{vc} g_{vc}(1, \omega) \ll W \gg g_{v'c'}(2, \omega) \]
The Mapping Theory

\[ \chi = X \left( X - \chi_0 \nu X - \chi_0 X^{-1} T \right)^{-1} \chi_0 \]

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The Mapping Theory

TDDFT 2-point equation containing $\ll \mathbf{W} \gg$

$$\chi = X \left( X - \chi_0 \nu X - \chi_0 X^{-1} T \right)^{-1} \chi_0$$

$$T_{BSE}(12, \omega) = \sum_{v'c'} g_{vc}(1, \omega) \ll \mathbf{W} \gg g_{v'c'}(2, \omega)$$

$$X(12, \omega) = \sum_{vc} \phi_v(1) \phi_c(1) g_{vc}(2, \omega)$$

What about the application ??
The Mapping Theory

TDDFT 2-point equation containing \( \ll W \rr \)

\[
\chi = X \left( X - \chi_0 \nu X - \chi_0 X^{-1} T \right)^{-1} \chi_0
\]

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T_{\text{BSE}}(12, \omega) = \sum_{v'c'} g_{vc}(1, \omega) \ll W \rr g_{v'c'}(2, \omega)
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What about the application??
The Mapping Theory

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

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What about the application ??
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The Mapping Theory: Results

Absorption of Silicon

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Excitonic Effects within TDDFT

Francesco Sottile
The Mapping Theory: Results

Absorption of Silicon

![Graph showing absorption of silicon with various theoretical models compared to experimental data. The graph plots energy (ω) against optical response, with different lines representing Exp., RPA, ALDA, and BSE calculations. The graph highlights the excitonic effects within TDDFT.](image-url)
The Mapping Theory: Results

Absorption of Silicon

The Mapping Theory: Results

Absorption of Silicon Carbide and Diamond

last week preliminary results :-)
Absorption of Argon

The Mapping Theory: Results

Excitonic Effects within TDDFT
The Mapping Theory: Results

Absorption of Argon

![Graph showing absorption of argon](image)

The Mapping Theory: Results

Tested also on absorption of SiO$_2$, DNA bases, Ge-nanowires, RAS of diamond surface, and EELS of LiF.

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)
Towards new applications

**Strongly correlated systems**

TDLDA (Broadening 0.5 eV)

- EEL spectrum of VO$_2$
  - M.Gatti, preliminary results

**Biological systems**

Abs spectrum of Green Fluorescent Protein

New Frontiers

Excited-State Dynamics

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

New Frontiers

**TDDFT concept into MBPT**

\[ \Sigma = GW \Gamma \]

i.e. a promising path to go beyond GW approx through TDDFT

Quantum Transport in TDDFT

\[ I(t) = -e \int_V \frac{d}{dt} n(r, t) \]

total current through a junction

New Frontiers

Let’s go back to Ground-State

Total energies calculations via TDDFT

\[ E = T_{KS} + V_{\text{ext}} + E_{H} + E_{xc} \]

\[ E_{xc} \propto \int dr dr' \int_{0}^{1} d\lambda \int_{0}^{\infty} du \chi^{\lambda}(r, r', iu) \]

adiabatic connection fluctuation-dissipation theorem

- M. Lein et al. 61, 13431 (2000)
Conclusions

TDDFT is the method of choice

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- 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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**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