



Introduction to TDDFT

Linear-Response TDDFT in Frequency-Reciprocal space on a Plane-Waves basis: the DP (Dielectric Properties) code

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Résumé

- Motivation
- TDDFT
- Linear-Response TDDFT
- Frequency-Reciprocal space TDDFT
- TDDFT on a PlaneWaves basis: the DP code
- Approximations: RPA, ALDA, new kernels
- Results
- Conclusions

Condensed Matter Theories

- Models:
 - Jellium
 - Anderson
 - Hubbard -> DMFT

analytic
(but C-DMFT medium numerical)

- Semi-Empirical and Phenomenological Theories:
 Tight Binding
 lightly numerical
- *Ab Initio* First-Principles or Microscopical Theories:
 CI
 - OM(
 - QMC
 - DFT, TDDFT
 - MBPT (GW and Bethe-Salpeter Equation)

heavy numerical

What DFT **can** predict

(normal error 1~2% in the 99% of cond-mat systems)

- Atomic Structure, Lattice Parameters (XRD)
- Total Energy, Phase Stability
- Electronic Density (STM, STS)
- Elastic Constants
- Phonon Frequencies (IR, Neutron scattering, Raman)

that is, all **Ground State** Properties!

Vanadium Oxide, VO	n	DFT-LDA nlcc D	FT-LDA semic	EXP [Longo et al.]
lattice parameters	^z a	5.659 Å	5.549 Å	5.7517 ± 0.0030 Å
	b	4.641 Å	4.522 Å	4.5378 ± 0.0025 Å
	С	5.420 Å	5.303 Å	5.3825 ± 0.0025 Å
M. Gatti et al., PRL accepted	α	121.46	121.73°	$122.646^{\circ} \pm 0.096$

What DFT **cannot** predict

- Electronic Structure, Bandplot
- Bandgap, Metal/Insulator/Semiconductor
- Optical and Dielectric properties
- that is, all **Excited State** Properties!

You may use DFT to predict all such properties but it cannot be blamed if it does not succeed.



Optical Spectroscopies



Why we need ab initio theories to calculate spectra

To understand and explain observed phenomena
 To offer experimentalists reference spectra
 To predict properties before the synthesis, the experiment

Excitations: Charged vs Neutral

Charged Excitations N -> N+1 (or N-1) (Photoemission Spectroscopy)

Neutral Excitations N -> N (Optical and Dielectric Spectroscopy)

Inverse Photoemission

Optical Absorption

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Excitations: Charged vs Neutral

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Photoemission Spectroscopy

Optical Spectroscopy

Dielectric, Energy-Loss Spectroscopy (EELS)

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Possible *ab-initio* Theories for the Excited States

- **TDDFT** (Time-Dependent Density-Functional Theory) in the Approximations:
 - RPA
 - TDLDA
 - beyond
- **MBPT** (Many-Body Theory) in the Approximations:
 - **GW Charged** Excitations
 - BSE (Bethe-Salpeter Equation approach)
 Neutral

 Excitations

What is TDDFT?

• TDDFT is an extension of DFT; it is a DFT with time-dependent external potential:

 Fundamental degree of freedom: Time-Dependent electronic Density ρ(r,t) (instead of the total many-body wavefunction Ψ(r₁,...,r_N,t))

TDDFT milestones

- Runge and Gross (1984): rigorous basis of TDDFT.
- Gross and Kohn (1985): TDDFT in Linear Response.

The Runge Gross theorem

$$\begin{split} &i\partial_t \Psi_1(t) \!=\! (\hat{T} \!+\! \hat{V}_1(t) \!+\! \hat{W}) \Psi_1(t) \\ &i\partial_t \Psi_2(t) \!=\! (\hat{T} \!+\! \hat{V}_2(t) \!+\! \hat{W}) \Psi_2(t) \end{split}$$

 $v_1(t) \neq v_2(t) + c(t) \implies \rho_1(t) \neq \rho_2(t)$

Any observable is functional of the (time-dependent) density:

PRL 52, 997 (1984)

$$ar{o}(t) = \langle \Psi(t) | \hat{o} | \Psi(t)
angle = o[
ho](t)$$

Runge Gross theorem caveats

- 1) Any observable is functional of the density **and of the initial state** $\Psi_0 = \Psi(t_0)$
- 2) The Runge-Gross theorem has been proven for v(t) Taylor expandable around t₀. And if you run into problems already in describing the (nonequilibrium) initial state, you can't go on with TDDFT. Previous demonstrations required periodic v(t) or a small td perturbation (linear response), or later (Laplace transformable switch-on potentials+initial ground-state). But there is no very general prove of the Runge Gross theorem.

$$ar{o}(t) = o[
ho, \Psi_0](t)$$

TDDFT vs DFT Zoological Comparative Anatomy

DFT V Hohenberg-Kohn:	TDDFT Runge-Gross:
$\mathbf{v}(\mathbf{r}) \Leftrightarrow \rho(\mathbf{r})$	$\mathbf{v}(r,t) \Leftrightarrow ho(r,t)$
The Total Energy: $\langle \Phi \hat{H} \Phi \rangle = E[\rho]$	The Action: $\int_{t_0}^{t_1} dt \ \langle \Phi(t) i \partial_t - \hat{H}(t) \Phi(t) \rangle = A[\rho]$
are unique functiona	ls of the density.
The extrema of the:	The stationary points of the:
Total Energy	Action
$\frac{\delta E[\rho]}{\delta \rho(r)} = 0$ give the exact dense	$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0$ Sity of the system:
ho(r)	ho(r , $t)Valerio Olevano, Introduction to TDDFT$

DFT VS TDDFT
Kohn-Sham:

$$\rho(r) = \sum_{i=1}^{N} |\phi_{i}^{KS}(r)|^{2}$$

$$\nu^{KS}(r) = \nu(r) + \int dr' \frac{\rho(r')}{|r-r'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$

$$H^{KS}(r) \phi_{i}^{KS}(r) = \epsilon_{i}^{KS} \phi_{i}^{KS}(r)$$

$$i\partial_{t} \phi_{i}^{KS}(r, t) = H^{KS}(r, t) \phi_{i}^{KS}(r, t)$$

$$H^{KS}(r) \phi_{i}^{KS}(r) = \epsilon_{i}^{KS} \phi_{i}^{KS}(r)$$

$$For the equations$$

$$\rho(t) = \frac{1}{2} \int_{0}^{1} \frac{1}{\sqrt{1 + \frac{1}{2}}} \int_{0$$

TDDFT further caveats

- 1) The functional $A_{xc}[\rho]$ is defined only for **vrepresentable densities**. It is undefined for ρ which do not correspond to some potential $v \rightarrow$ problems when variations $\delta A[\rho]$ with respect to **arbitrary** densities are required in order to search for stationary points.
- 2) A functional A[ρ] with ρ(t) on the real time, is hill defined, since we would run in a causality-symmetry paradox -> we can solve the problem by declaring t on the Keldysh contour. Response functions are symmetric on the contour and become causal on physical time.

$$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0 \qquad \frac{\delta A_{xc}[\rho]}{\delta \rho(r,t)}$$

If exists $\frac{\delta A_s[\rho]}{\delta \rho(r,t)} = v_s(r,t)$

Then we can define the Lagrange transform:

$$\tilde{A}[v] = -A[\rho] + \int dr dt \rho(r,t) v(r,t)$$

$$\frac{\delta \tilde{A}[v]}{\delta v(r,t)} = \rho(r,t)$$

$$\frac{\delta \tilde{A}}{\delta v(r,t) \delta v(r't')} = \frac{\delta \rho(r,t)}{\delta v(r't')}$$
Symmetric causal (=0 for t'>t)

Van Leeuwen, PRL 80, 1280 (1998).

TDDFT in Linear Response

Gross and Kohn (1985)

• If:

$$\mathbf{v}(r,t) = \mathbf{v}(r) + \delta \mathbf{v}(r,t)$$

• with:

$$\delta v(r,t) \ll v(r)$$

Strong (Laser) perturbations excluded!

TDDFT = DFT + Linear Response (to the time-dependent perturbation) Hohenberg-Kohn Theorem for Linear Response TDDFT

DFT: $v(r) \Leftrightarrow \rho(r)$

TDDFT: $v(r,t) \Leftrightarrow \rho(r,t)$

$$\mathbf{v}(r) + \delta \mathbf{v}(r,t) \Leftrightarrow \rho(r) + \delta \rho(r,t)$$

$$\mathbf{LR-TDDFT:} \quad \delta \mathbf{v}(r,t) \Leftrightarrow \delta \rho(r,t)$$

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Calculation Scheme

Polarizability χ

$\delta v_{ext} \quad \begin{array}{l} \text{External Perturbation} \\ \text{(variation in the external potential)} \end{array}$

$\delta \rho \qquad \frac{\text{Induced Density}}{(\text{variation in the density induced by } \delta v_{ext})}$

implicit definition of the *polarizability* χ :

$$\delta \rho = \chi \, \delta \, \mathbf{v}_{ext}$$

Polarizability χ

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Variation in the Total Potential

The variation in the density induces a variation in the Hartree and in the exchange-correlation potentials which screen the external perturbation:

So that the variation in the total potential (external + screening) is:

$$\delta v_{tot} = \delta v_{ext} + \delta v_H + \delta v_{xc}$$

Total Perturbation

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LR-TDDFT Kohn-Sham scheme: the Independent Particle Polarizability $\chi^{(0)}$

Let's introduce a ficticious *s*, Kohn-Sham non-interacting system such that:

$$\delta \rho_s = \delta \rho$$

Then, instead of calculating χ , we can more easily calculate the polarizability $\chi^{(0)}$ (also χ_s or χ^{KS}) of this non-interacting system, called independent-particle polarizability and defined:

$$\delta
ho = \chi^{(0)} \delta \nu_{tot}$$

Independent Particle Polarizability $\chi^{(0)}$

the Independent Particle Polarizability $\chi^{(0)}$

By variation $\delta v_{tot} (= \delta v_s = \delta v^{KS})$ of the Kohn-Sham equations, one obtains the Linear-Response variation of the density $\delta \rho$ and then an expression for $\chi^{(0)}$ in terms of the Kohn-Sham energies and wavefunctions:

$$\chi^{(0)}(r,r',\omega) = \sum_{ij} (f_i - f_j) \frac{\phi_i(r)\phi_j(r)\phi_i(r')\phi_j(r')}{\omega - (\epsilon_i - \epsilon_j) - i\delta}$$

Independent-Particle Polarizability (Adler-Wiser)

In Frequency-Reciprocal space:

$$\chi_{GG'}^{(0)}(q,\omega) = \sum_{ij} (f_i - f_j) \frac{\langle \phi_j | e^{-i(q+G)r} | \phi_i \rangle \langle \phi_i | e^{+i(q+G')r} | \phi_j \rangle}{\omega - (\epsilon_i - \epsilon_j) - i\delta}$$

χ as a function of $\chi^{(0)}$

From:

$$\delta \rho = \chi \delta v_{ext}$$
$$\delta \rho = \chi^{(0)} \delta v_{tot}$$

The polarizability in terms of the independent-particle polarizability is:

$$\chi = \chi^{(0)} + \chi^{(0)} (v_c + f_{xc}) \chi$$
Polarizability χ
Coulombian (Local-Fields)
Exchange-Correlation Kernel

change-Correlation Kernel

Also explicitly:

$$\chi = (1 - \chi^{(0)} \nu_c - \chi^{(0)} f_{xc})^{-1} \chi^{(0)}$$

Dielectric Function

$$\delta v_{tot} = \varepsilon^{-1} \delta v_{ext}$$

definition of the Dielectric Function ϵ

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

Test-Particle Dielectric Function

 $\varepsilon_{te}^{-1} = 1 + (v_c + f_{xc})\chi$ Test-Electron Dielectric Function

 $\varepsilon_{GG'}^{-1}(\boldsymbol{q}, \boldsymbol{\omega})$ In a periodic system

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Macroscopic Dielectric Function

$$\varepsilon_{M}(r,r') = \overline{\varepsilon(r,r')}$$

$$\varepsilon_{M}(q,\omega) = \frac{1}{\varepsilon_{00}^{-1}(q,\omega)}$$
Macroscopic Dielectric Function ε_{M}

$$\begin{array}{ll} \text{Macroscopic} \\ \text{Dielectric} \\ \text{Function } \boldsymbol{\varepsilon}_{M} \end{array} \rightarrow \begin{array}{ll} \text{Observables} \rightarrow & ABS = \Im \, \boldsymbol{\varepsilon}_{M} \\ & EELS = -\Im \, \boldsymbol{\varepsilon}_{M}^{-1} \end{array}$$

$$\varepsilon_M^{LF} \neq \varepsilon_{00} = \varepsilon_M^{NLF}$$

TDDFT: fundamental equations

Local-Fields Effects (LF)

$$\delta \mathbf{v}_{G}^{tot} = \sum_{G'} \varepsilon_{GG'}^{-1} \delta \mathbf{v}_{G'}^{ext}$$

Effect of the ε non diagonal elements (density inhomogeneities)

$$\bigvee \bigvee \bigvee \rightarrow \int & & & & \\ \varepsilon^{-1} \sim \rho & & & & \delta v_{tot} \end{pmatrix}$$

 $\epsilon_{\scriptscriptstyle M}^{\scriptscriptstyle NLF}(q\, {\scriptstyle,}\omega){=}\epsilon_{\scriptscriptstyle 00}(q\, {\scriptstyle,}\omega)$

Macroscopic Dielectric Function ε without local-fields effects (NLF)

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LR-TDDFT Calculation Scheme Résumé

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dp code (dielectric properties)

- The thing: **Linear-Response TDDFT** code in **Frequency-Reciprocal** Space on **PW** basis.
- Purpose: Dielectric and Optical Properties (Absorption, Reflectivity, Refraction, EELS, IXSS, CIXS,..
- Systems: bulk, surfaces, clusters, molecules, atoms (through supercells) made of insulator, semiconductor and metal elements.
- Approximations: RPA, ALDA, GW-RPA, LRC, non-local kernels, ..., with and without LF (Local Fields).
- Machines: Linux, Compaq, IBM, SG, Nec (6GFlop), Fujitsu.
- Libraries: BLAS, Lapack, CXML, ESSL, IMSL, ASL, Goedecker, FFTW.
- Interfaces: ABINIT, Milan-CP, PWSCF, SPHINGx

http://www.dp-code.org

Frequency-Reciprocal space: why and where could be convenient

- Reciprocal Space -> Infinite Periodic Systems (Bulk, but also Surfaces, Wires, Tubes with the use of Supercells);
- Frequency Space -> Spectra.

In the case of isolated systems (atoms, molecules) it is more convenient a real space-time approach (e.g. Octopus code)

DP tricks

If we only need $\varepsilon_{00}^{-1} = 1 - v_0 X_{00}$ that is only X_{00} then instead of solving (inverting a full matrix):

$$x_{GG'} = (1 - x^{(0)} v_c - x^{(0)} f_{xc})_{GG''}^{-1} x_{G''G'}^{(0)}$$

we solve the **linear system** for only the first column of $\chi_{G'0}$

$$(1 - X^{(0)} v_c - X^{(0)} f_{xc})_{GG'} X_{G'0} = X^{(0)}_{G0}$$

O(N²) instead of O(N³)

DP performances: CPU scaling and Memory usage

- CPU scaling for
- CPU scaling for
- Memory occupation

$$\chi^{(0)} : N_b N_k (N_\omega N_G^2 + N_r \log N_r)$$

$$\varepsilon^{-1} : N_\omega N_G^2$$

$$N_\omega N_G^2 + N_r N_k N_b$$

Exchange-Correlation Kernel f_{xc}: the RPA approximation

• Random Phase Approximation = neglect of the exchange-correlation effects (in the response)

– RPA

$$f_{xc}^{RPA}=0$$

RPA Approximation

RPA (without Local Fields) = sum over independent transitions (application of Fermi's Golden Rule to an independent particle system)

Adiabatic Local Density Approximation (TDLDA)

• The Adiabatic Local Density Approximation

- ALDA
$$f_{xc}^{ALDA} = \frac{\delta v_{xc}^{LDA}}{\delta \rho}_{\omega=0}$$

$$f_{xc}^{ALDA}(r,r') = A(r)\delta(r,r')$$
 local in r-space
no memory effect

TDDFT: Results

Energy Loss->-Im ε^{-1} Optical Properties->Im ε

TDDFT: Results

Energy Loss

TDDFT and EELS in Solids

- TDLDA (but also RPA) in good agreement with experiment;
- Importance of Local-Field (LF) effects.

Local Field Effects in EELS

- RPA is enough. But when inhomogeneities are present, Local-Field effects should be absolutely taken into account.
- **Quantitative** Agreement

IXSS and CIXS and other synchrotron-radiation spectroscopies

• In Solids all Dielectric Properties related to the Energy-Loss function are well described by TDDFT in RPA with an improvement in ALDA.

IXSS synchrotron-radiation spectroscopy

• In Solids all Dielectric Properties related to the Energy-Loss function are well described by TDDFT in RPA with an improvement in ALDA.

TDDFT: Results

Optical Properties

TDDFT RPA Optical Properties in Nanotubes

Nanotubes parallel polarization

• RPA is qualitatively able to interpret observed structures in optical spectra

LF Effects in in C and BN Nanotubes

• LF explain depolarization effects both for C and BN Nanotubes in perpendicular polarization optical spectra

Optical Absorption in Clusters

Fair agreement (improvable) of the TDLDA result with the Experiment.

G. Onida et al, Rev. Mod. Phys. 74, 601 (2002).

Optical Properties in Solids: Si

- The TDLDA **cannot** reproduce Optical Properties in Solids.
- We miss both:
 - 1 **Self-Energy (electron-electron) effects** (red shift of the entire spectrum)
 - 2 **Excitonic (electron-hole) effects** (underestimation of the low-energy part)

GW: optical properties in Solids

• GW corrects the red-shift but still misses the Excitonic Effects

MBPT: GW, BSE and Excitonic Effects

Bethe-Salpeter Equation: optical properties in Solids

• Almost quantitative agreement of BSE with the experiment

- Exciton ~ Hydrogen atom \rightarrow $E_n \sim 1/n^2$ Balmer-like series
- BSE can reproduce even **bound Excitons**

What can we do to solve the TDDFT kernel problem?

- If a new Approximation in TDDFT could be established, combining TDDFT's simplicity with MBPT's reliability...
- Hints for this new Approximation: compare critically MBPT with TDDFT fundamental equations.

New Approximations:

LRC (Long Range Contribution only)

Nanoquanta kernel (or mapping BSE on TDDFT)

LRC Approximation

long-range coulombian

$$X = X^{(0)} + X^{(0)} (v_c + f_{xc}) X$$

ALDA: local kernel

$$f_{xc}^{LRC} = lim_{q \to 0} f_{xc}^{MT} = -\frac{\alpha}{(q+G)^2}$$

Long Range Contribution only

 $\alpha = 4.6 \varepsilon_{\infty}^{-1}$ Inversely proportional to the screening

TDDFT, LRC approximation

• The LRC approximation makes TDDFT work also on Optical Properties in Solids

Nanoquanta kernel

- L. Reining, V. Olevano, A. Rubio and G. Onida, (2001)
- G. Adragna and R. Del Sole, (2001)
- F. Sottile, V. Olevano and L. Reining, (2004)
- A. Marini, R. Del Sole, A. Rubio, (2004)
- U. Von Barth, N. E. Dahlen, R. Van Leeuwen and G. Stefanucci, (2006)
- R. Stubner, I. Tokatly and O. Pankratov, (2006)

TDDFT vs BSE

$$F^{TDDFT}(x_{1}, x_{2}, x_{3}, x_{4}) = \delta(x_{1}, x_{2}) \delta(x_{3}, x_{4}) f_{xc}(x_{1}, x_{3})$$

$$F^{BSE}(x_{1}, x_{2}, x_{3}, x_{4}) = -\delta(x_{1}, x_{3}) \delta(x_{2}, x_{4}) f_{xc}(x_{1}, x_{2})$$

Nanoquanta $f_{\rm xc}$

$$f_{xc}(q,G,G') = \sum_{n_{1}n_{2}n_{3}n_{4}} \frac{1}{(f_{n_{1}} - f_{n_{2}})} \Phi^{-1}(n_{1},n_{2};G) K_{(n_{1}n_{2})(n_{3}n_{4})}(\Phi^{*})^{-1}(n_{3},n_{4};G')$$
Where:
$$\Phi(n_{1},n_{2};r) = \phi_{n_{1}}(r) \phi_{n_{2}}^{H}(r)$$
Kohn-Sham bilinear
$$K_{(n_{1}n_{2})(n_{3}n_{4})} = (\Delta \epsilon_{n_{2}}^{GW} - \Delta \epsilon_{n_{1}}^{GW}) \delta_{n_{1}n_{3}} \delta_{n_{2}n_{4}} + (f_{n_{1}} - f_{n_{2}}) F_{(n_{1}n_{2})(n_{3}n_{4})}^{BSE}$$

$$F_{(n_{1}n_{2})(n_{3}n_{4})}^{BSE} = -\int dr dr' \Phi(n_{1},n_{3};r) W(r',r) \phi^{*}(n_{2},n_{4};r')$$
Excitonic

WARNING: f_{xc} could not exist due to invertibility problems of Φ ! PRL 88, 066404 (2002).

Solid Argon: Bound Excitons

• The Nanoquanta kernel makes TDDFT reproduce even Bound Exciton

TDDFT Excitation Energies and the Casida Equations

eigenvalues = poles of
$$\chi$$

$$\sum_{t'} \Omega_{tt'}(\omega) a_{t'} = \omega^2 a_{t'}$$
eigenvectors = oscillator strengths

$$\Omega_{tt'} = \omega_t^2 \,\delta_{tt'} + 2 \sqrt{\omega_t \omega_{t'}} f_{tt'}^{Hxc}$$

 $\omega_t = \epsilon_c - \epsilon_v$ Kohn-Sham excitation energies

 $f_{tt'}^{Hxc} = \int dr_1 dr_2 \phi_c^*(r_1) \phi_v(r_1) [v_c(r_1, r_2) + f_{xc}(r_1, r_2, \omega)] \phi_{v'}^*(r_2) \phi_{c'}(r_2)$ 4-points Hartree+xc kernel

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Conclusions

- TDDFT is a valid tool of Condensed Matter Theoretical Physics to calculate from first principles excited-state properties;
- The agreement with the experiment is good, but the choice of the right xc-approximation with respect to the given excited state property is crucial:
 - **RPA** with **LF** is able to reproduce **EELS** spectra at q=0;
 - **TDLDA** improves upon **RPA** on **EELS** (and also **IXSS**, **CIXS**) spectra at high q;
 - **TDLDA** seems also to improve upon **RPA** on optical spectra in finite systems;
 - More refined kernels (LRC, MT) are required to reproduce optical spectra in solids, especially in presence of strong excitonic effects and bound excitons.
- Perspectives:
 - Improve the algorithms, simplify the orbital expressions of the kernel, find a density-functional dependent kernel.