

# MBPT and TDDFT Theory and Tools for Electronic-Optical Properties Calculations in Material Science

Dott.ssa Letizia Chiodo

Nano-bio Spectroscopy Group &

ETSF - European Theoretical Spectroscopy Facility,

Dipartimento de Física de Materiales, Facultad de Químicas,

Universidad del País Vasco UPV/EHU,

San Sebastián-Donostia, Spain

# Outline of the Lectures

- Many Body Problem
- DFT elements; examples
- DFT drawbacks
- excited properties:  
electronic and optical spectroscopies. elements of theory
- Many Body Perturbation Theory: GW
- codes, examples of GW calculations
- Many Body Perturbation Theory: BSE
- codes, examples of BSE calculations
- **Time Dependent DFT**
- **codes, examples of TDDFT calculations**
- state of the art, open problems

# Time Dependent Density Functional Theory

# Outline

- **phenomena described by TDDFT**
- **basic theorems of TDDFT: Runge – Gross theorem**
- **Exchange-Correlation kernel**
- **TDDFT in the linear-response regime:**
  - **Casida approach**
  - **Time Propagation approach**
  - **Calculation of optical excitation spectra**
  
- **a TDDFT implementation: OCTOPUS**
- **features of the code**
- **typical calculation**
- **results and examples**
  
- **ref:** M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, E. K. U. Gross, Time-Dependent Density Functional Theory. (Springer-Verlag, 2006). (in the following, TDDFT-book)

# phenomena described with TDDFT

generic situation:  
molecule in laser field

- Strong laser ( $v_{\text{laser}}(t) \geq v_{\text{en}}$ ) :  
→ Non-perturbative solution of full TDSE required
- Weak laser ( $v_{\text{laser}}(t) \ll v_{\text{en}}$ ) :  
Calculate
  - 1. Linear density response
  - 2. Dynamical polarizability!
  - 3. Photo-absorption cross section

# Many Body Problem

Time Dependent Schroedinger Equation:

$$\hat{H}(t)\Psi(t) = i \frac{d\Psi(t)}{dt} \quad \text{with} \quad \Psi(0) \text{ given}$$

we assume:

N nonrelativistic electrons, Coulomb repulsion, external time dependent potential

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad \text{kinetic energy}$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{electron-electron Coulomb repulsion}$$

$$\hat{V}_{ext} = \sum_{i=1}^N v_{ext}(\mathbf{r}_i, t) \quad \text{one body potential: it may vary depending on the problem}$$

in the various many problems, we change:

N electrons

$$v_{ext}(\mathbf{r}, t)$$

$t = 0 \rightarrow t$  evolving

wavefunctions and charge density of the system change

$$n(\mathbf{r}, t) = N \int d^3 r_2 \dots \int d^3 r_N |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2 \quad \int d^3 r n(\mathbf{r}, t) = N$$

idea:

as it is possible to establish a correspondance between

the density and the **STATIC** external potential

in the Density Functional Theory (Theorem of Hohenberg and Kohn, 1964),

we would like to find an analogous theorem for the case of a

**TIME DEPENDENT** external potential

# Runge-Gross Theorem

E. Runge, E.K.U. Gross, *Phys. Rev. Lett.* **52**, 997-1000 (1984)  
analogous to the K-S theorem for GS density

statement: two densities evolving from a common initial state under the influence of two potentials differing more than a time-dependent function

one-to-one mapping Density-Potential  $\rightarrow$  Functional of the Density

proof

1- potential  $\longleftrightarrow$  current density

2- density and initial state  $\longleftrightarrow$  operators expectation value,  
by using a surface condition (surface integral)



# Time Dependent Kohn-Sham Equations

auxiliary and fictitious non interacting particles system,  
satisfying the **KS time dependent equations**

$$i \frac{\partial \varphi_i(\mathbf{r}, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}[n](\mathbf{r}, t) \right] \varphi_i(\mathbf{r}, t)$$

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}, t)|^2$$

**exchange-correlation potential is unique**

$$v_{KS}(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t)$$

how to find exchange-correlation action, to obtain the functional?

the one proposed in RG '84 was wrong

- Van Leeuwen, how to find the potential (TDDFT-book, ch. 2)
- the surface condition makes difficult to use TDDFT for extended systems (non locality)
- effect of initial state (memory) (TDDFT-book, ch. 4)

# Linear Response and TDDFT

TDKS  $\rightarrow$  electronic excitations  
absorption, photoluminescence, etc

imagine to perturb at  $t = 0$ , weak  $\mathbf{E}$   
propagate, and follow the system dipole evolution  
FT of dipole  $\rightarrow$  optical absorption spectrum

# Linear Response and TDDFT

density is slowly changing with time  $\rightarrow$  density close to the initial state

$$n(\mathbf{r}, t) = n_{GS}(\mathbf{r}, t) + \delta n(\mathbf{r}, t)$$

perturbation theory for the potential

$$v_{KS}[n_{GS}](\mathbf{r}, t) = v_{xc}[n_{GS}](\mathbf{r}) + \int dt' \int d^3r' f_{xc}[n_{GS}](\mathbf{r}, \mathbf{r}', t - t') \delta n(\mathbf{r}', t')$$

**exchange-correlation kernel**  $\longrightarrow$  **linear response**

$$f_{xc}[n_{GS}](r, r', t - t') = \left. \frac{\delta v_{xc}[r, t]}{\delta n(r', t')} \right|_{n=n_{GS}}$$

# Main Equation of TDDFT in Linear Response

susceptibility

$$\delta n(\mathbf{r}, t) = \int dt' \int d^3 r' \chi[n_{GS}](\mathbf{r}, \mathbf{r}', t - t') \delta v_{ext}(\mathbf{r}', t')$$

||

$$\delta n(\mathbf{r}, t) = \int dt' \int d^3 r' \chi_{KS}[n_{GS}](\mathbf{r}, \mathbf{r}', t - t') \times \{ \delta v_{ext}(\mathbf{r}', t') + \delta v_H(\mathbf{r}', t') + \delta v_{xc}(\mathbf{r}', t') \}$$

main equation of TDDFT linear response (in frequency)

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) +$$

$$\int d^3 r_1 \int d^3 r_2 \chi_{KS}(\mathbf{r}, \mathbf{r}_1, \omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right\} \chi(\mathbf{r}_2, \mathbf{r}', \omega)$$

# Casida's Method

if the kernel is frequency independent, find the poles is equivalent to solve an eigenvalue problem

$$\sum_{q'} R_{qq'} F_{q'} = \Omega_q^2 F_q$$

eigenvalues and eigenvectors

low transitions

just diagonal matrix elements: Petersilka

"Time-Dependent Density Functional Response Theory of Molecular Systems: Theory, Computational Methods, and Functionals" M. E. Casida in Recent Development and Applications of Modern Density Functional Theory, edited by J.M. Seminario (Elsevier, Amsterdam, 1996), p. 391.

"Molecular excitation energies to high-lying bound states from TDDFT " M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub J. Chem. Phys. 108, 4439 (1998)

# Adiabatic Approximation

exchange-correlation potential:  
depends on history of density, initial state of real and KS systems

if nondegenerate GS, this dependence is removed

but: MEMORY!

adiabaticity: dependence on past  $t$  is removed  
just dependence on instantaneous density (local in time)

# ALDA

adiabatic LDA

kernel local in space and time

## TDDFT and DFT

KS eigenvalues are zero-order approximation to optical excitation energies



# Kernel Problem: Many Body Perturbation Theory

## ETSF Kernel

use of the MBPT data, to build a kernel for TDDFT

from V. Olevano:

... TDDFT kernel able to reproduce excitonic effects on optical spectra, at a level of accuracy comparable to Bethe-Salpeter results. This kernel was a derivation done by Lucia Reining starting from a **comparison between the Bethe-Salpeter equation and the TDDFT Casida's equation**. But I must say that the same kernel was also previously derived by Rodolfo Del Sole along **perturbation theory approximations holding into many-body theory**. He showed me, before to leave to Palaiseau, this kernel and the promising results he got together with Gianni Adragna using a Tight Binding approach. But at that time the statistics was only on Silicon and GaAs and I was erroneously believing that the Tight-Binding adjustable parameters could do most of the job.

When we realized that the two kernels were in fact the same, we started to believe that an ab initio implementation was really worth to. This kernel has a really **complicated, orbital dependent, shape**. --- the surprising nice result was that TDDFT and the DP code were even able to reproduce in solid Argon a series of three bound excitons within the photoemission band-gap, in agreement with the experiment and the Bethe-Salpeter result.

Well so far TDDFT was considered to be the future. But now TDDFT is the present!

computationally very demanding

# Technical Features

$$i \frac{\partial \varphi_i(\mathbf{r}, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}[n](\mathbf{r}, t) \right] \varphi_i(\mathbf{r}, t)$$

work in frequency or time domain

by propagating, beyond linear response

propagation in time of SE

# Propagators for TD-KS Equations

evolution operator

$$i \frac{d\hat{U}(t, t_0)}{dt} = \hat{H}(t)\hat{U}(t, t_0)$$



$$\varphi(t) = \hat{U}(t, t_0)\varphi_0(t_0)$$

Dyson equation

best algorithm for TDDFT implementation: depends on physics of the system, and on frequency and intensity of the external field

# Time vs Frequency Space Techniques

which is the best approach to TDDFT calculations?

efficiency:

size

memory

- GS occupied states
- phase multiplying each KS state → polarization evolving in time
- propagation up to T
- calculation of D on TDKS states
- FT to have optics

• CPU & memory as  $N^2_{\text{atoms}}$

# CASIDA

matrix diagonalization

low lying excitations → reduction of cost

needing of empty states to calculate transitions, because the matrix elements between empty and occupied states are needed

# OCTOPUS

- Fortran 95 and C
- 0-3 D systems, but focused on finite systems
- norm-conserving pseudo-potentials
- real-space grid representation
- features:
  - Ground state DFT
  - TDDFT
  - Time propagation
    - Linear response and strong fields.
    - Ehrenfest molecular dynamics.
  - Casida LR-TDDFT
  - Sternheimer linear response
  - Optimal control theory
  - Real-time quantum transport
- linear and non linear absorption spectra, harmonic spectra, laser induced fragmentation, photoemission, etc.



# Real Grid Space

- Functions are represented by their value over a set of points.
- Uniform space grid.
- Distance between points is constant: Spacing.
- Non-uniform grids.
- Finite region of the space: Box



# Boundary Conditions

For finite systems functions go to zero.

Impose functions to be zero over the border of the box.

The box has to be large enough to contain the functions.

Other BCs are possible: periodic, zero derivative, open.

Optimize the shape of the box to minimize the number of points.

General box shape:

Minimum box: a sphere around each atom.

Sphere.

Cylinder.

Parallelepiped.

Arbitrary.

Natural boundary conditions for different problems.

Systematically improve discretisation quality:

Decrease the spacing.

Increase the box size.

Orthogonal “basis set”.

Independent of atomic positions (no Pulay forces).

Problems:

Breaking of translational invariance: egg-box effect.

Breaking of rotational invariance.

# Parallelization

- **Parallelization in domains:**

Each processor handles points in a region of space.

Points in the boundaries of each region must be copied to other nodes.

Integrals are performed locally and summed over all domains.

Efficient and scalable scheme.

- **Parallelization in states:**

Each processor handles a group of states.

Efficient scheme for time propagation.

Work in progress for the ground state.

Combined parallelization.

Scales to hundreds of processors (development version).

# Example of a TDDFT Calculation

```
XYZCoordinates = "adjusted.xyz"
```

```
Units = ev_angstrom
```

```
%Species
```

```
"Ti" | 44 | spec_ps_upf | 22 | 3 | 1
```

```
%
```

```
CalculationMode = gs
```

```
Spacing = 0.15
```

```
Radius = 6.3
```

```
SpinComponents = 2
```

```
Smearing = 0.1
```

```
SmearingFunction = 3
```

```
ExtraStates = 5
```

```
NumberUnoccStates = 50
```

```
ExcessCharge = -1
```

```
11/2/2009
```

GS calculation

output

```
XYZCoordinates = "03-adjusted.xyz"

Units = ev_angstrom

ParallelizationStrategy = par_domains

%Species
"Ti" | 44 | spec_ps_cpi | 22 | 3 | 1
%
CalculationMode = unocc

Spacing = 0.15

Radius = 6.3

SpinComponents = 2

EigenSolverMaxIter = 4000

#Eigensolver = rmmdiis

Smearing = 0.01

SmearingFunction = 2

ExtraStates = 10

NumberUnoccStates = 100
```

UNOCC calculation

```
XYZCoordinates = "03-adjusted.xyz"

Units = ev_angstrom

ParallelizationStrategy = par_domains

%Species
"Ti" | 44 | spec_ps_cpi | 22 | 3 | 1
%
CalculationMode = casida

Spacing = 0.15

Radius = 6.3

SpinComponents = 2

#Eigensolver = rmmdiis

Smearing = 0.01

SmearingFunction = 2

ExtraStates = 10

NumberUnoccStates = 100

LinearResponseKohnShamStates = "01-100"
```

CASIDA calculation

```
XYZCoordinates = "03-adjusted.xyz"
Units = ev_angstrom
ParallelizationStrategy = par_domains
%Species
  "Ti" | 44 | spec_ps_cpi | 22 | 3 | 1
%
  CalculationMode = td
  Spacing = 0.15
  Radius = 6.3
  SpinComponents = 2

  #Eigensolver = rmmdiis

  Smearing = 0.01

  SmearingFunction = 2

  ExtraStates = 10

  NumberUnoccStates = 100

  TDTimeStep = 0.001

  TDDeltaStrength = 0.01

  TDPolarizationDirection = 1

  TDMaximumIter = 25 / TDTimeStep

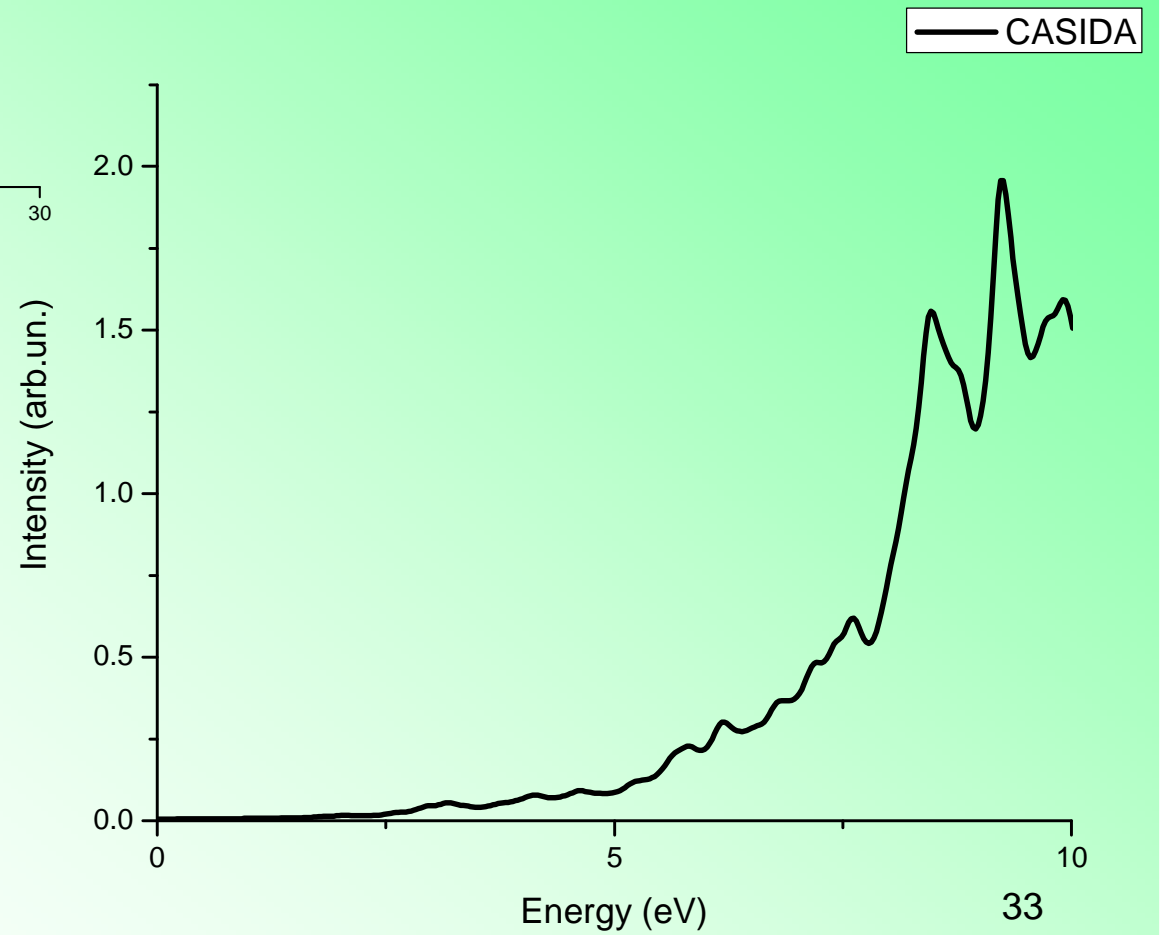
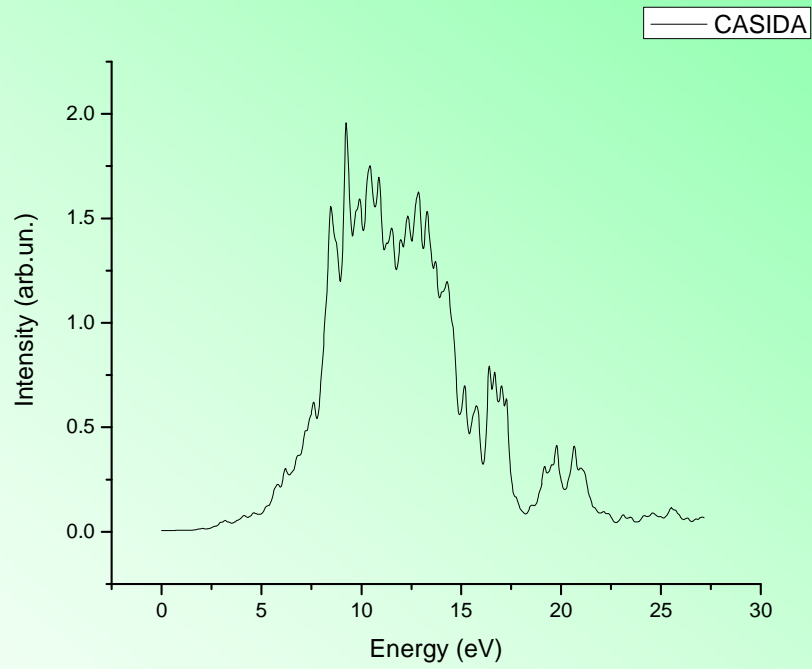
  OutputEvery = 1000
```

TD calculation

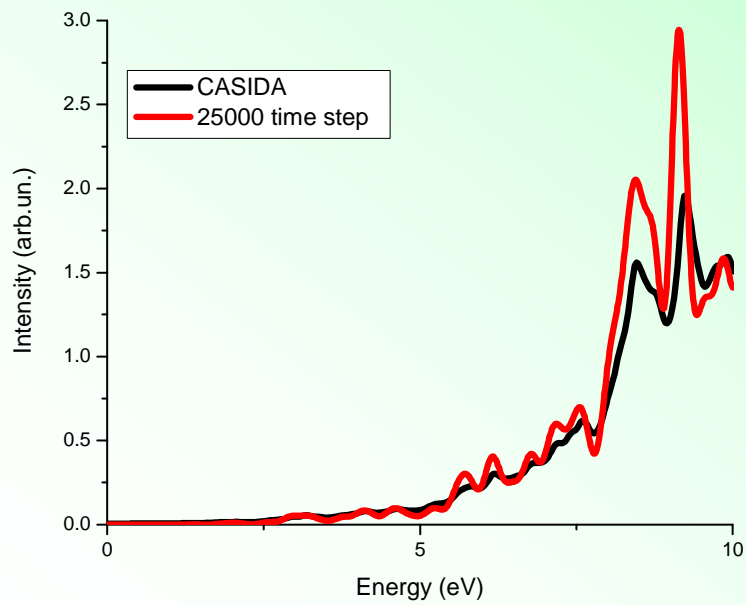
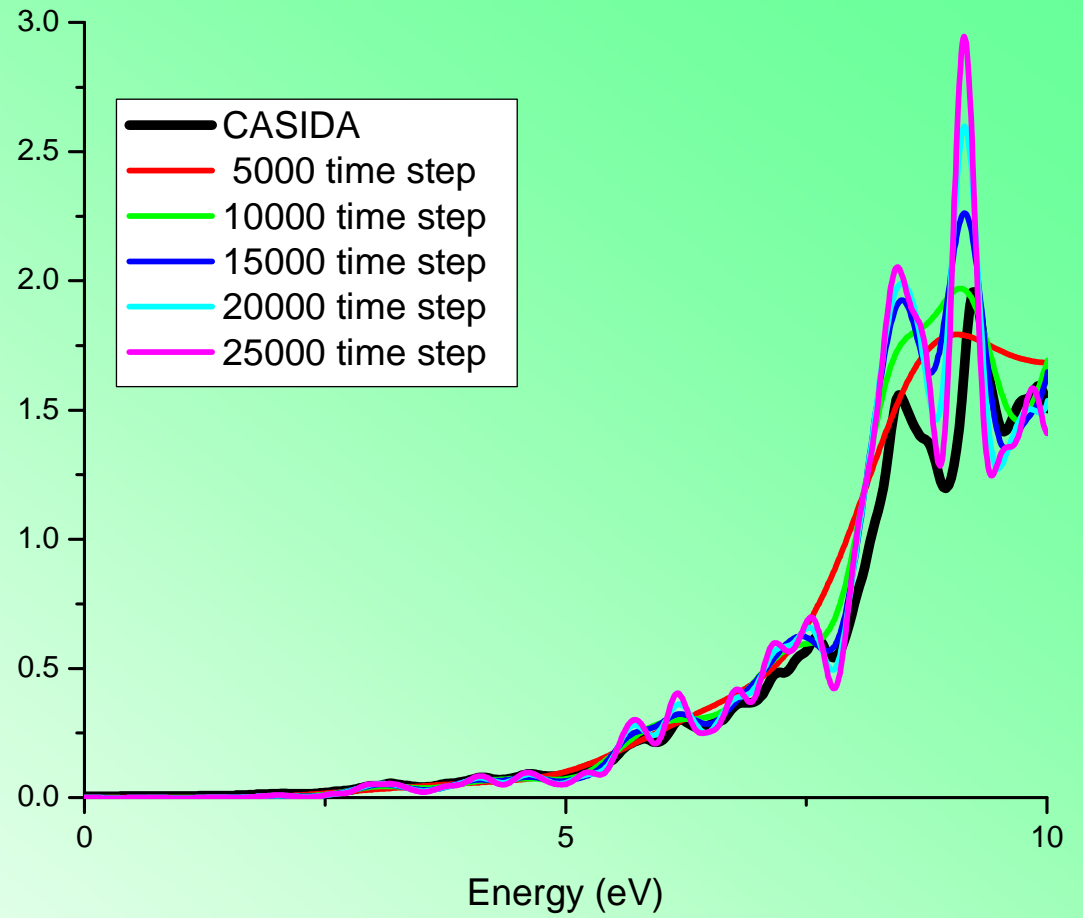
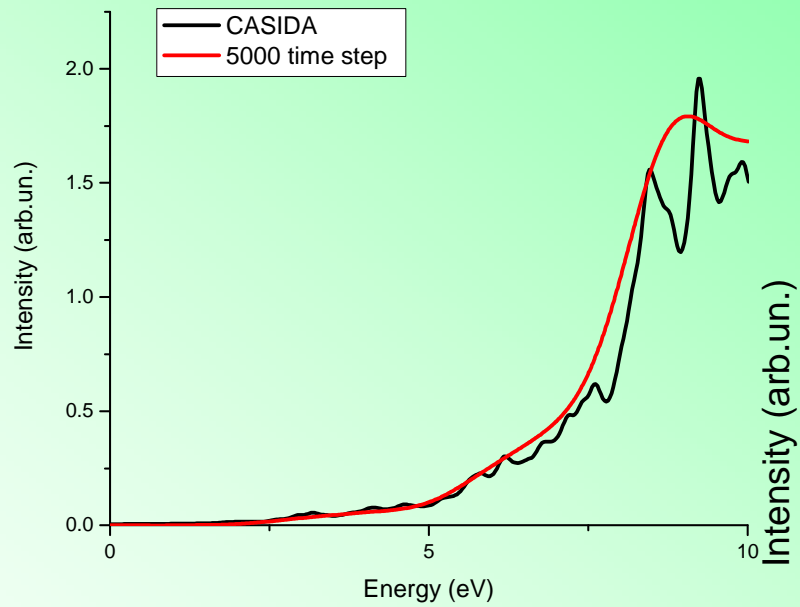
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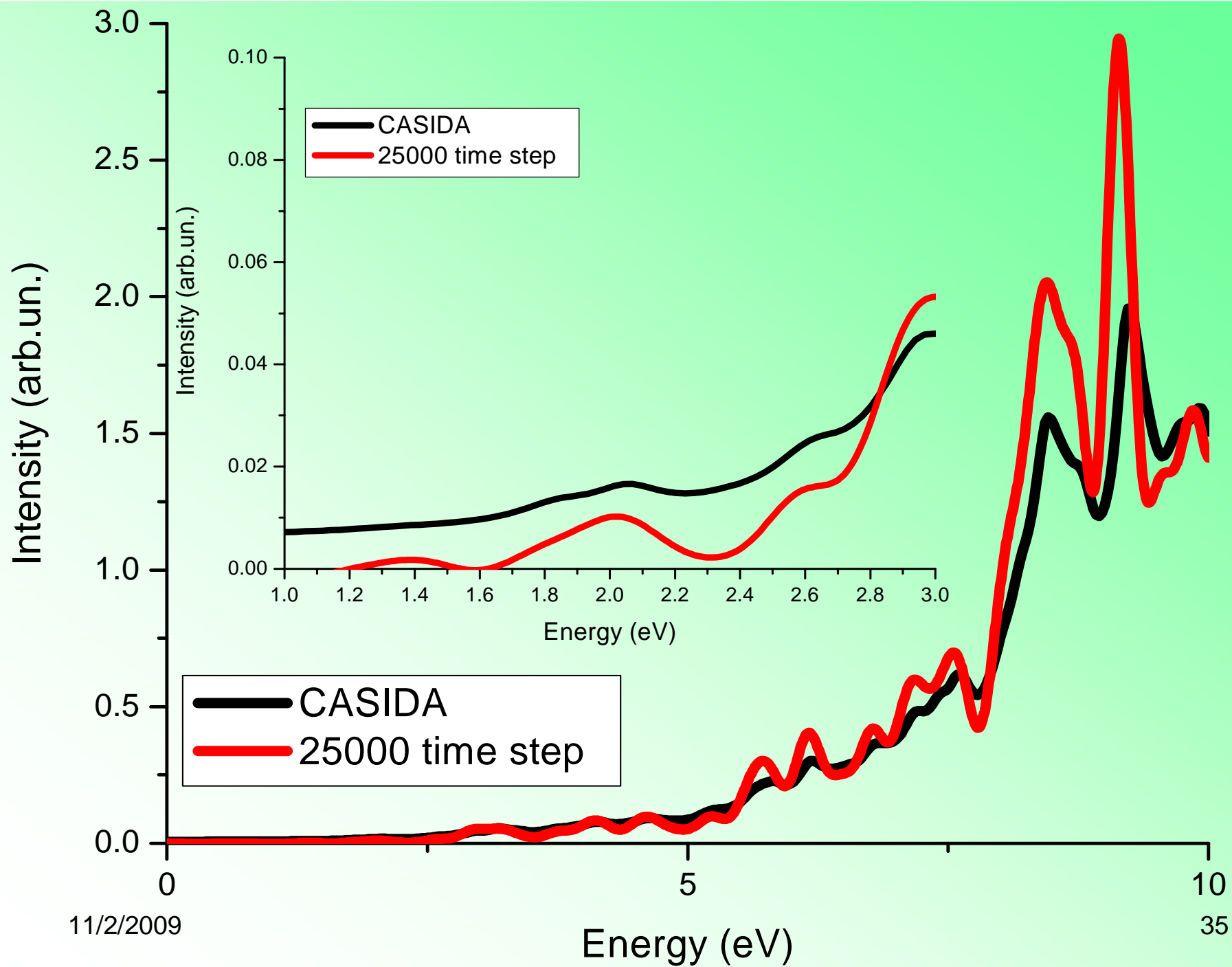
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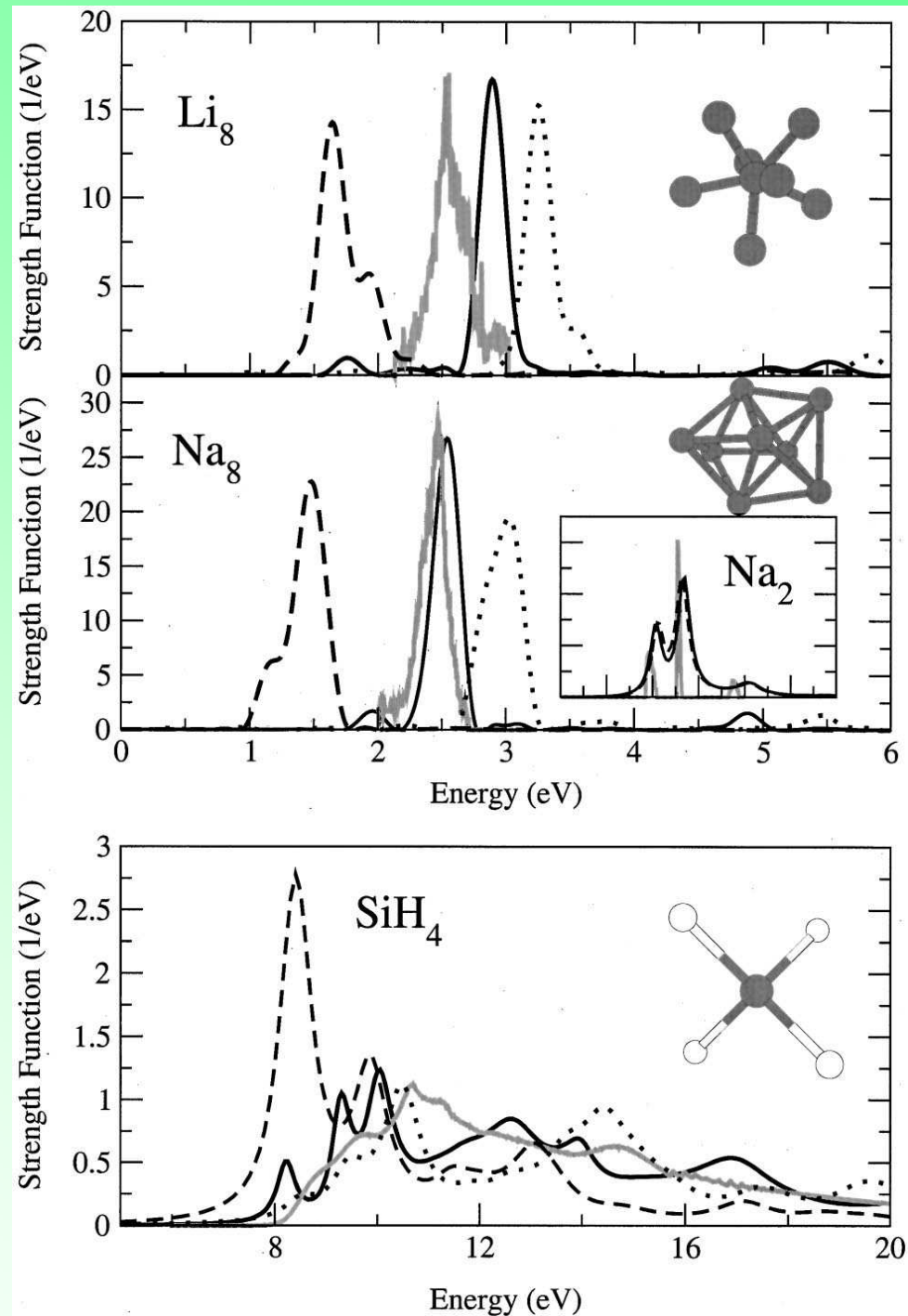


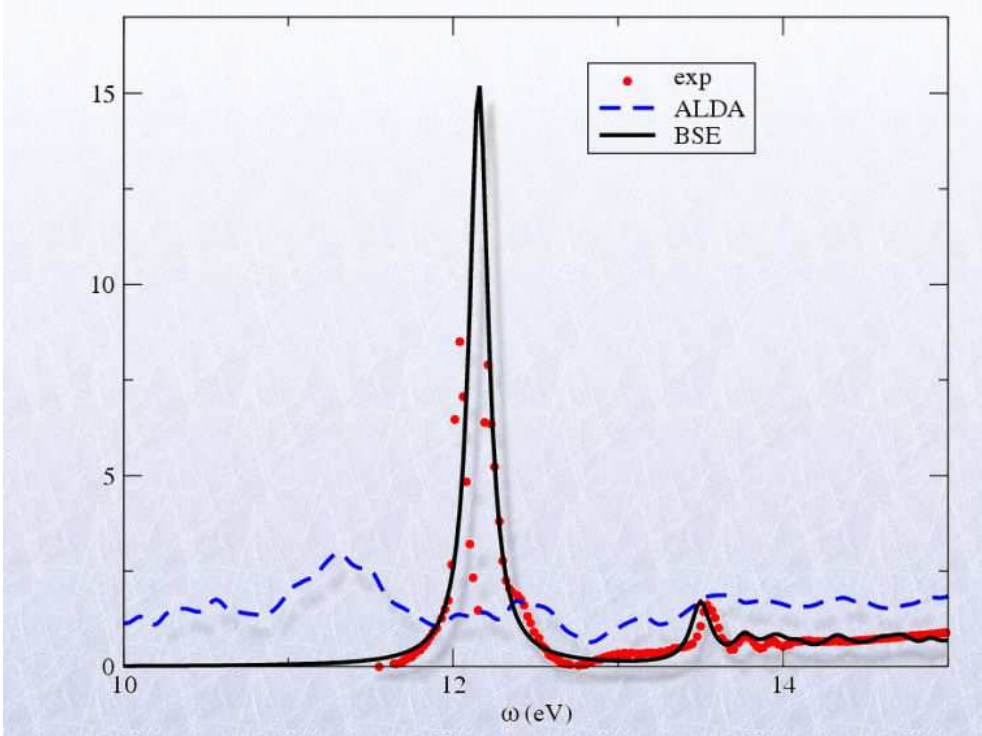
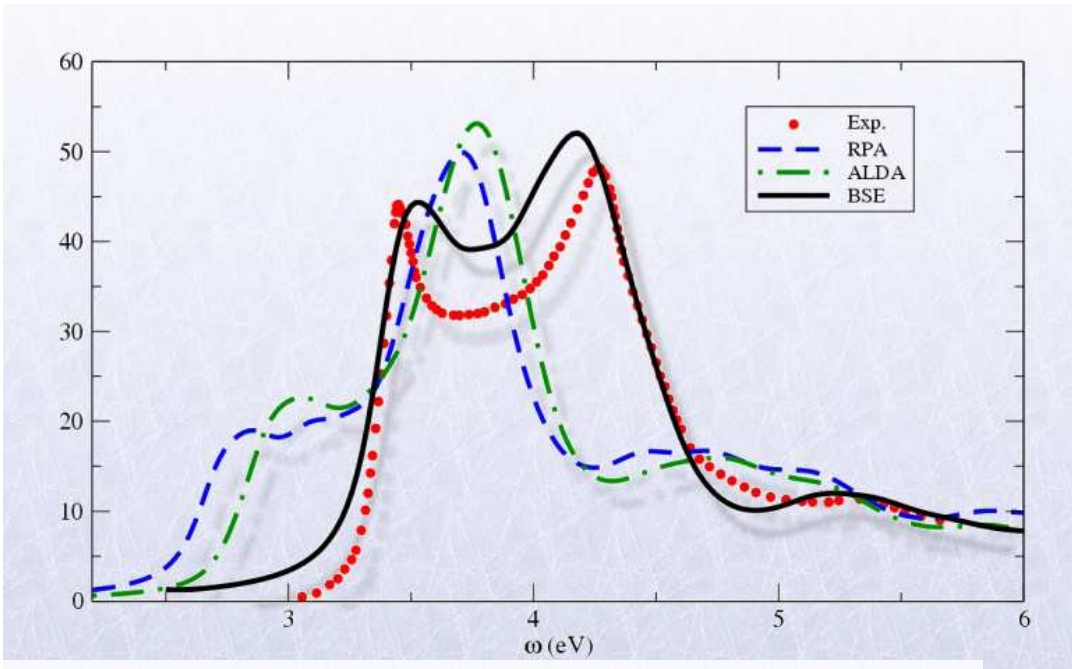
# Linear Response Applications

in Literature, you can find results on

- atoms and clusters  $\text{Ti}_8\text{C}_{12}$  and  $\text{V}_8\text{C}_{12}$ , fullerene-like CdSe
- solids
- polymers
- biochromophores
- excited states, photochemistry, charge transfer

TDDFT allows calculation of (bound and unbound) excited-state energies and transition probabilities of a many-body system





nanoquanta  $f_{xc}$



