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Time-Dependent Density-Functional Theory

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Plan

1. Time-Dependent Kohn-Sham equation
2. Runge-Gross theorem
3. Approximate XC action and TD potential
4. The linear regime
5. Casida's approach to excitation energies

References :

E. Runge and E.K.U. Gross, *Phys. Rev. Lett.* 52, 997 (1984)
M.E. Casida, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J.M. Seminario (Elsevier Science, Amsterdam), p. 391 (1995).
G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* <u>74</u> , 601 (2002)

Back to undergrad Quantum Mechanics (I)

Starting point : the Time-Dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

e.g. for 1 particle

$$i\hbar \frac{\partial \psi}{\partial t}\bigg|_{(\vec{r},t)} = -\frac{\hbar^2}{2m}\bar{\nabla}^2\psi\bigg|_{(\vec{r},t)} + V(\vec{r},t)\psi(\vec{r},t)$$

If the Hamiltonian does not depend on time,

$$\hat{H} = \sum_{i=1,n} -\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_i} + V(\vec{r}_1,...,\vec{r}_n)$$

we have the following ansatz

$$\psi(\vec{r}_1,...\vec{r}_n,t) = \varphi(\vec{r}_1,...\vec{r}_n).f(t)$$

Back to undergrad Quantum Mechanics (II)

$$\psi(\vec{r}_1,...\vec{r}_n,t) = \varphi(\vec{r}_1,...\vec{r}_n).f(t)$$

$$i\hbar\frac{\partial\psi}{\partial t} = \varphi.i\hbar\frac{\partial f}{\partial t}$$

$$\hat{H}\psi = f.\hat{H}\varphi$$

Now,

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \qquad \Rightarrow \qquad \underbrace{i\hbar\frac{\partial f}{\partial t}\frac{1}{f}}_{\substack{\text{depend}\\\text{only on time}}} = \underbrace{\frac{1}{\varphi}(\hat{H}\varphi)}_{\substack{\text{does not}\\\text{depend on time}}} = K$$

Identify K with the energy $\qquad \psi(\vec{r}_1,...\vec{r}_n,t) = \varphi(\vec{r}_1,...\vec{r}_n).e^{-i\frac{Et}{\hbar}}$

$\varphi_m(\vec{r}_1,...\vec{r}_n) \qquad$ such that $\qquad \boxed{\hat{H}\varphi_m = E_m\varphi_m}$

General solutions $\qquad \boxed{\psi(\vec{r}_1,...\vec{r}_n,t) = \sum_m c_m\varphi_m(\vec{r}_1,...\vec{r}_n)\exp\left(-\frac{iE_m.t}{\hbar}\right)}$

Why are we interested by time dependence ?

Electrons do not stay in a stationary (eigen) state ! (except GS)
Spontaneously emit photon => ground state

Time-dependent perturbations of a system :
typically time-dependent electric field (photons)
-small perturbations (linear regime for electric field)
-large perturbations (LASER field)

Also, some adiabatic (« slow ») changes, like ion-molecule collisions (or ion-surface interaction)

Induced electronic transitions to excited states !

Time-dependent Kohn-Sham equation (I)

Started early 80's :
-Stott and Zaremba, Phys. Rev. A 21, 12 (1980)
-Zangwill and Soven, Phys. Rev. A 21, 1561 (1980)

Computed photoabsorption cross section of atoms $\sigma(\omega)$

Time-dependent Hartree-Fock already existed
but quite inaccurate !
They generalised LDA ... without a formal justification

Time-dependent Kohn-Sham equation (II)

(using atomic units)

LDA equations

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}\text{-}\vec{r}'|} d\vec{r}' + V_{XC}(\rho(\vec{r})) \right) \psi_\alpha(\vec{r}) = \varepsilon_\alpha \psi_\alpha(\vec{r})$$

$$\rho(\vec{r}) = \sum_\alpha^{occ} \psi_\alpha^*(\vec{r})\psi_\alpha(\vec{r}) \qquad \int \psi_\alpha(\vec{r})\, \psi_\beta(\vec{r}) d\vec{r} = \delta_{\alpha\beta}$$

become ...

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r},t) + \int \frac{\rho(\vec{r}',t)}{|\vec{r}\text{-}\vec{r}'|} d\vec{r}' + V_{XC}(\rho(\vec{r},t)) \right) \psi_\alpha(\vec{r},t) = i\frac{\partial}{\partial t} \psi_\alpha(\vec{r},t)$$

$$\rho(\vec{r},t) = \sum_\alpha^{occ} \psi_\alpha^*(\vec{r},t)\psi_\alpha(\vec{r},t) \qquad \int \psi_\alpha(\vec{r},t)\, \psi_\beta(\vec{r},t) d\vec{r} = \delta_{\alpha\beta}$$

Is this valid ?

In search of a Time-Dependent Dependent Density Functional Theory ...

In DFT, we have ...

$\rho(\vec{r})$ determines $v(\vec{r})$,

up to an overall constant

for the Ground State

There is an universal
functional of the density $F[\rho]$
such that

$E[\rho, v] = F[\rho] + \int \rho(\vec{r}) v(\vec{r}) d\vec{r}$

and $E[v] = \min_{\rho} E[\rho, v]$

In TD-DFT, what could we have ?

$\rho(\vec{r}, t)$ determines $v(\vec{r}, t)$?

up to an overall constant?

for ...?

The quantum − mechanical action

$A = \int_{t_0}^{t_1} dt \left\langle \Psi(t) \middle| i \frac{\partial}{\partial t} - H(t) \middle| \Psi(t) \right\rangle$

is not extremal, but only

stationary for fixed $\Psi(t_0)$ and $\Psi(t_1)$

The Runge-Gross theorems (I)

For every single-particle potential $v(\vec{r},t)$
which can be expanded into a Taylor series with respect to
the time coordinate around $t=t_0$,
a map $G : v(\vec{r},t) \rightarrow \rho(\vec{r},t)$

is defined by solving the TD Schrödinger equation with a
fixed initial state $\Phi(t_0) = \Phi_0$ and calculating the
corresponding densities $\rho(\vec{r},t)$.

This map can be inverted up to an additive merely
TD function in the potential : $v'(\vec{r},t) = v(\vec{r},t) + C(t)$

Note : fixed initial state ;
global TD of the map (not isolated times) ;
the overall additive TD function in the potential

The Runge-Gross theorems (II)

For a fixed initial state, $\Phi(t_0) = \Phi_0$
and a given TD density, $\rho(\vec{r}, t)$

The wavefunction $\Phi(t)$ can be determined, within a TD phase factor $\Phi(t) = e^{-i\alpha(t)} \Phi'[\rho](t)$

Note : the phase factor comes from the overall additive
TD function in the potential $\dot{\alpha}(t) = C(t)$;
no problem of degeneracy (but the initial WF is known)

Also, several maps can be defined for a same fixed initial state,
corresponding to larger and larger time regions :
if $t_0 < t_1 < t_2 < t_3 \dots$, then
$\rho(t)$ within $[t_0, t_1]$ gives $v(t)$ and $\Phi(t)$ within $[t_0, t_1]$
$\rho(t)$ within $[t_0, t_2]$ gives $v(t)$ and $\Phi(t)$ within $[t_0, t_2]$ etc

The time-dependence is non-local, albeit causal

Time-Dependent Density Functional Theory

The Runge-Gross theorems (III)

The quantum-mechanical action,

$$A[\rho, \Phi_0, v] = \int_{t_0}^{t_1} dt \left\langle \Phi[\rho](t) \left| i\frac{\partial}{\partial t} - \hat{T} - \boxed{v(t)} - \hat{W} \right| \Phi[\rho](t) \right\rangle$$

is a functional of the TD density between the initial and final times (the phase factor C(t) cancels out) and of the initial wavefunction. It is stationary at the TD density corresponding to the TD potential.

$$\frac{\delta A}{\delta \rho(\vec{r}, t)} = 0$$

The following functional is an universal functional of the TD density and the initial wavefunction

$$B[\rho, \Phi_0] = \int_{t_0}^{t_1} dt \left\langle \Phi[\rho](t) \left| i\frac{\partial}{\partial t} - \hat{T} - \hat{W} \right| \Phi[\rho](t) \right\rangle$$

The Runge-Gross theorems (IV)

Now we introduce, in the Kohn-Sham spirit, the possibility to compare the behaviour of density functionals for electrons interacting with the physical Coulomb interaction, and for non-interaction electrons. This leads to the TD exchange-correlation action, a functional of the TD density and the initial wavefunction.

$$\Rightarrow A_{xc}\left[\rho, \Phi_0\right] \quad \text{and} \quad v_{xc}\left[\rho, \Phi_0\right](\vec{r}, t) = \frac{\delta A}{\delta \rho(\vec{r}, t)}$$

Exact framework :

was $V_{XC}\left(\rho(\vec{r}, t)\right)$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}, t) + \int \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{XC}\left[\rho, \Phi_0\right](\vec{r}, t)\right)\psi_\alpha(\vec{r}, t) = i\frac{\partial}{\partial t}\psi_\alpha(\vec{r}, t)$$

$$\rho(\vec{r}, t) = \sum_\alpha^{occ} \psi_\alpha^*(\vec{r}, t)\psi_\alpha(\vec{r}, t) \qquad \int \psi_\alpha(\vec{r}, t)\ \psi_\beta(\vec{r}, t)\, d\vec{r} = \delta_{\alpha\beta}$$

Approximate XC action and TD potential (I)

$$A_{xc}[\rho, \Phi_0] \qquad v_{xc}[\rho, \Phi_0](\vec{r},t) = \frac{\delta A}{\delta \rho(\vec{r},t)}$$

Formally, the action (and TD potential) is defined for an interval of times, and, at initial time, depends on the full many-body wavefunction

Approximation 1 : at initial time, we choose the ground-state, and thus, can start with the usual XC potential, a functional of the density at that initial time

Approximate XC action and TD potential (II)

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

There is still a causal « non-local » time-dependence,
as the action and XC potential at time t depends (in principle)
on the GS density, and on the TD density
between initial time and present time : this is a memory effect.

Approximation 2 : suppress the memory effect !
Adiabatic approximation => left with only usual spatial
non-locality (leading to LDA, GGA, etc)

$$A_{xc}[\rho] = \int_{t_0}^{t_1} a_{XC}[\rho(t)]\,dt \qquad\qquad v_{xc}[\rho(t)](\vec{r},t) = \left.\frac{\delta a_{XC}}{\delta\rho(\vec{r})}\right|_{(\vec{r},t)}$$

Approximate XC action and TD potential (III)

Beyond adiabatic approximation : active research field
Sum rules / constraints exist
The adiabatic approximation fulfills many of them
 (compare with LDA !)

Hydrodynamic formulation of TDDFT => Current DFT
Add spin also ...

Combine corrected -1/r XC potential with simple
TD behaviour

Implementations

1) Treatment in real time domain

K. Yabana and G.F. Bertsch, Phys. Rev. B 54, 4484 (1996)
M. Marques et al, Comput. Physics Commun. 151, 60 (2002)

OCTOPUS : also GPL, we share the Nanoquanta lib XC
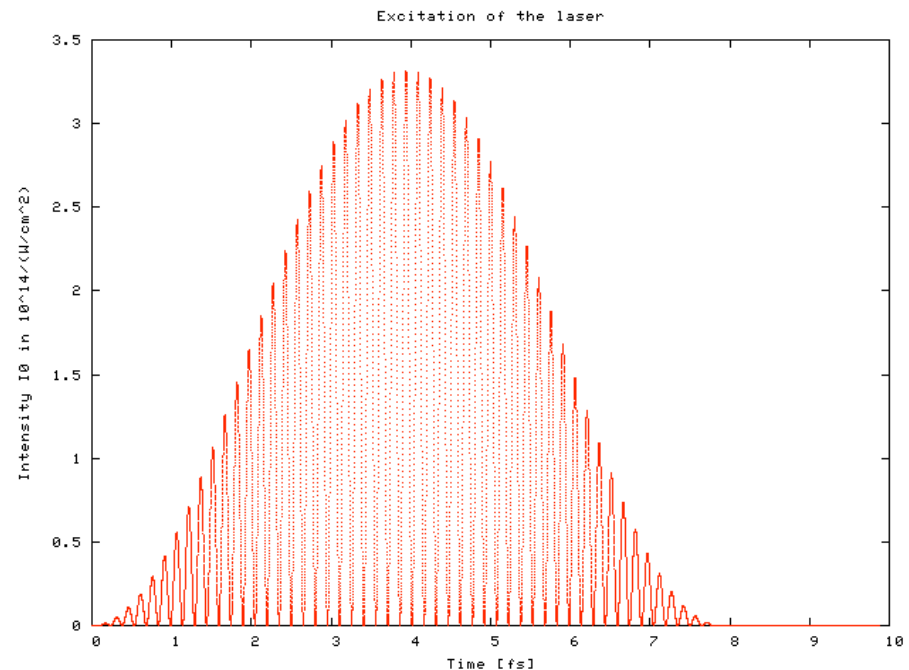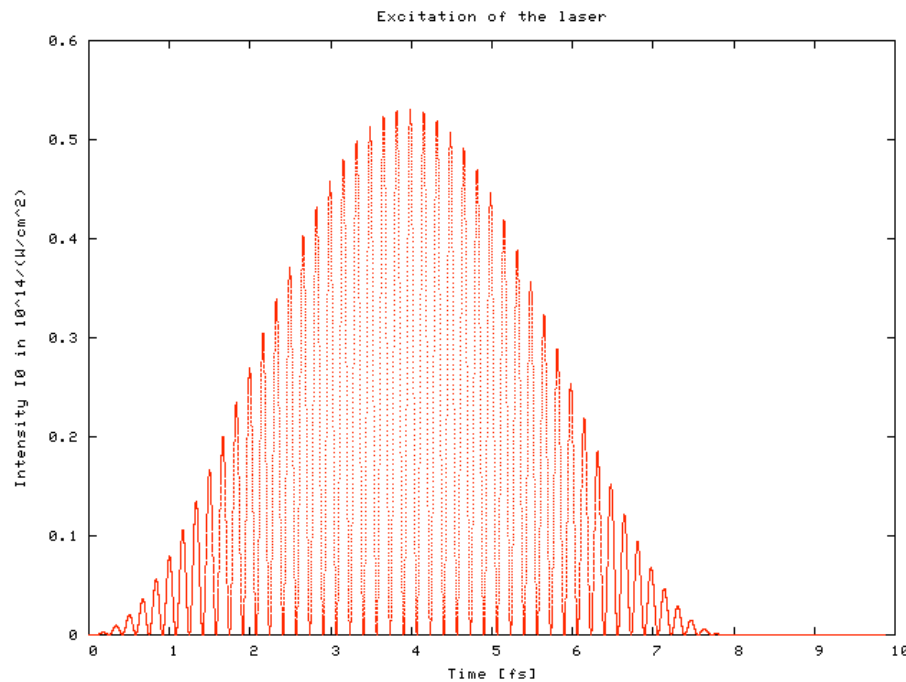
2) Treatment in frequency domain

Linear and non-linear response : frequency dependent
susceptibilities
Direct computation of the excitation energies
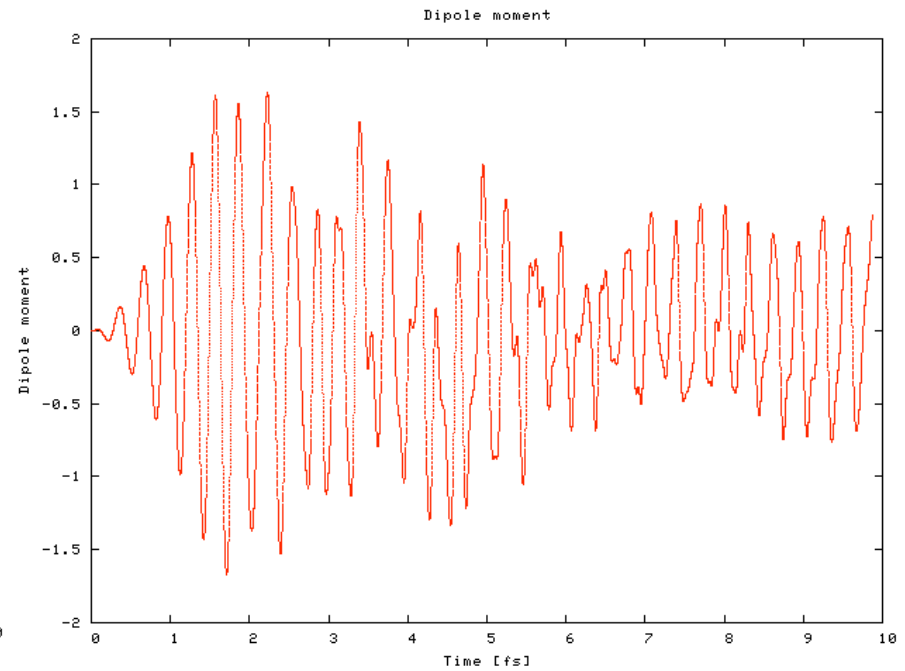
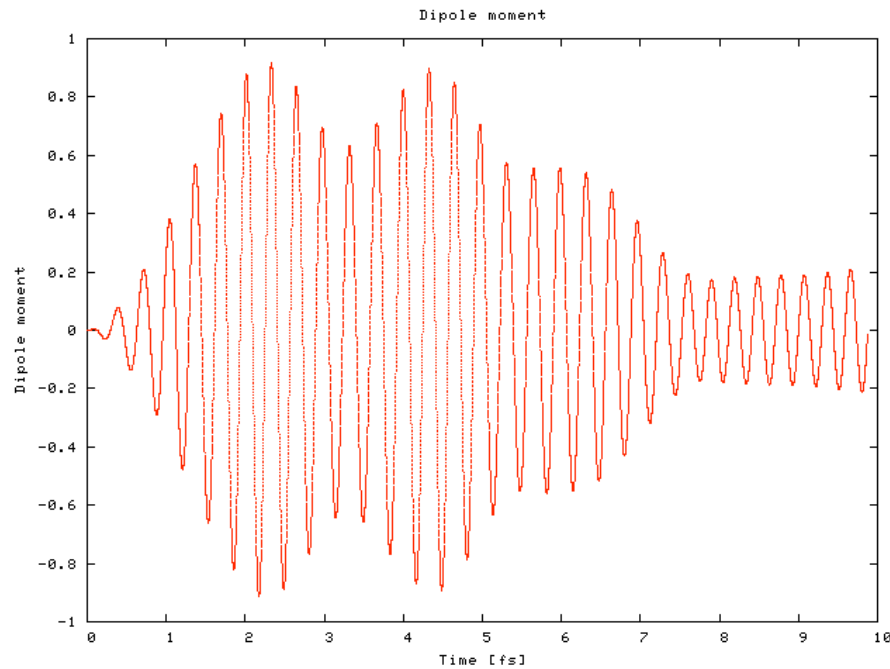# The Nitrogen molecule under intense laser (I)

from the Octopus code, http://www.tddft.org/td-elf/

and T. Burnus, M. Marques, and E.K.U. Gross.Phys. Rev. A 71, 10501 (2005)

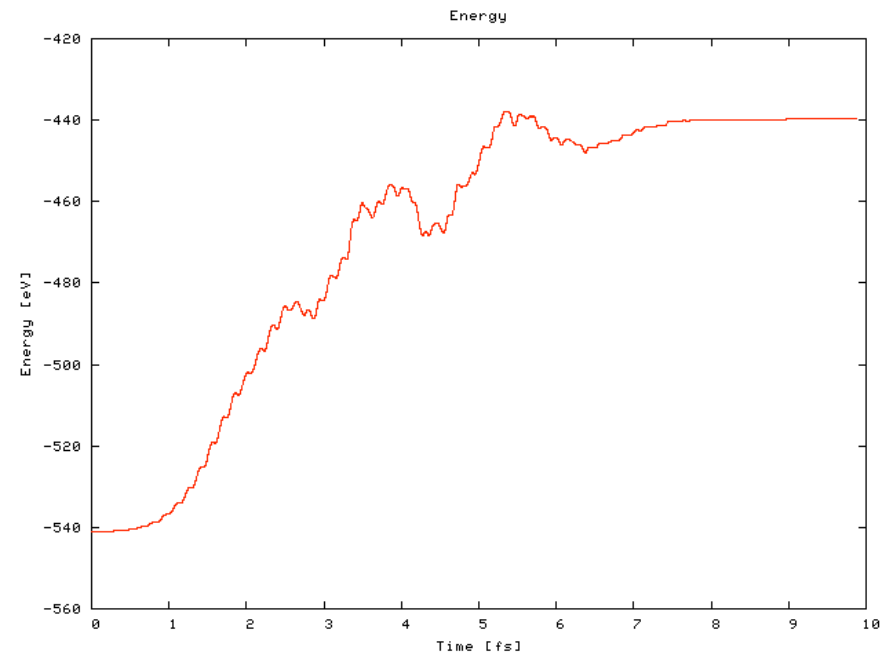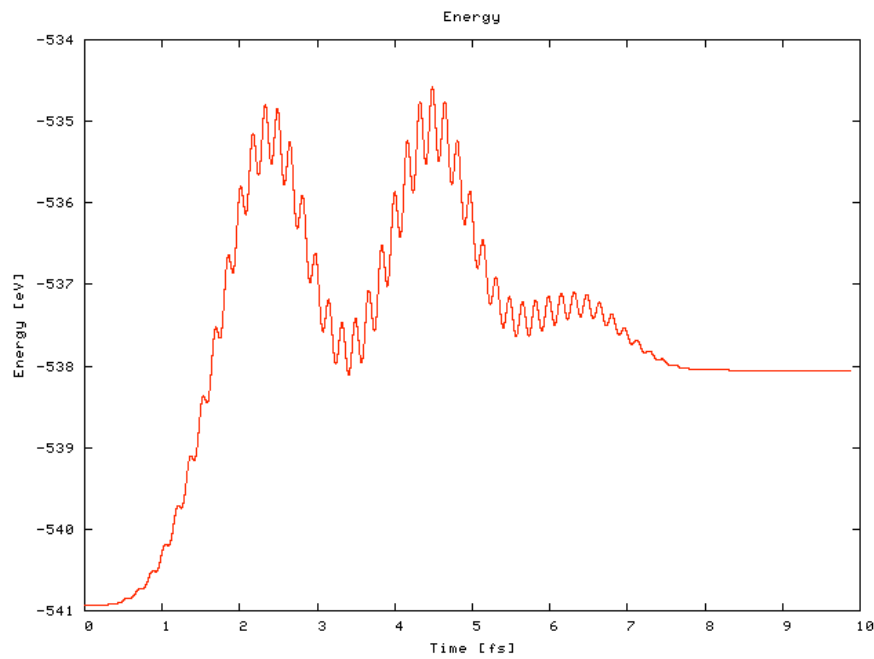

LASER Excitation fields : right-hand side is 5 times bigger than left-hand side

The Nitrogen molecule under intense laser (II)

Dipole moment : on the right figure, observe the non-linearities seen
as higher frequency Fourier components

Time-Dependent Density Functional Theory

The Nitrogen molecule under intense laser (III)

Total energy of the system : compare the different scales

Linear response

Consider some system in its GS, and apply a small
TD perturbation characterized by some frequency.
Watch the density change.
In the linear regime, the associated Fourier components
are related by the frequency-dependent susceptibility
or density-density response function

$$\rho^{(1)}(\vec{r},\omega) = \int \chi(\vec{r},\vec{r}';\omega) v_{ext}^{(1)}(\vec{r}',\omega) \, d\vec{r}'$$

This susceptibility can be computed within TD-DFT,
for a given choice of TD-XC functional

The TD Hartree and XC kernels

A change of the external potential induces a change of density, that induces a change of Hartree and XC potential.
For the Hartree potential, we have :

$$v_H^{(1)}(\vec{r},\omega) = \int \frac{1}{\left|\vec{r}\text{-}\vec{r}\,'\right|} \rho^{(1)}(\vec{r}\,',\omega)\,d\vec{r}\,'$$

Supposing that the TD XC functional is known, we have an explicit expression for the change, in term of the TD XC kernel

$$v_{XC}^{(1)}(\vec{r},\omega) = \int K_{XC}(\vec{r},\vec{r}\,',\omega)\rho^{(1)}(\vec{r}\,',\omega)\,d\vec{r}\,'$$

XC kernels : local / adiabatic approximation

Combining local approximation and adiabatic
approximation, the expression of the
TD XC kernel is particularly simple. It is independent
of the frequency (local in time), local in space, and
is determined by a local XC energy density,
a function of the local unperturbed density.

$$K_{XC}(\vec{r},\vec{r}',\omega) = \left.\frac{d^2 e_{XC}}{d\rho}\right|_{\rho^{(0)}(\vec{r})} \delta\left(\vec{r}\text{-}\vec{r}'\right)$$

Note : It might be that the local XC energy density is
the ground state one, but this is not mandatory.
Example : LB94 / ALDA

The independent-particle susceptibility

The TD external, Hartree, and XC changes of potential combine to give a total change of Kohn-Sham potential seen by independent electrons :

$$v_{KS}^{(1)}(\vec{r},\omega) = v_{ext}^{(1)}(\vec{r},\omega) + v_H^{(1)}(\vec{r},\omega) + v_{XC}^{(1)}(\vec{r},\omega)$$

The change of density due to this potential can be computed from the independent-particle susceptibility $\chi_0(\vec{r},\vec{r}';\omega)$

$$\rho^{(1)}(\vec{r},\omega) = \int \chi_0(\vec{r},\vec{r}';\omega) v_{KS}^{(1)}(\vec{r}',\omega) \, d\vec{r}'$$

Adler and Wiser have given an explicit expression for $\chi_0(\vec{r},\vec{r}';\omega)$ in terms of the one-particle occupied and unoccupied eigenfunctions, and eigenenergies

$$\chi_0(\vec{r},\vec{r}';\omega) = 2\Re e \sum_{\sigma} \sum_{n}^{occ.} \sum_{m}^{empty} \frac{\varphi_{n\sigma}^*(\vec{r})\varphi_{m\sigma}(\vec{r})\varphi_{m\sigma}^*(\vec{r}')\varphi_{n\sigma}(\vec{r}')}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega}$$

The Dyson equation for the susceptibility (I)

One combines these equations or their inverse (assuming they can be inverted) :

$$v_{KS}^{(1)}(\vec{r},\omega) = v_{ext}^{(1)}(\vec{r},\omega) + v_{H}^{(1)}(\vec{r},\omega) + v_{XC}^{(1)}(\vec{r},\omega)$$

$$v_{KS}^{(1)}(\vec{r}',\omega) = \int \chi_0^{-1}(\vec{r},\vec{r}';\omega)\rho^{(1)}(\vec{r},\omega)d\vec{r}'$$

$$v_{ext}^{(1)}(\vec{r}',\omega) = \int \chi^{-1}(\vec{r},\vec{r}';\omega)\rho^{(1)}(\vec{r},\omega)d\vec{r}'$$

$$v_{H}^{(1)}(\vec{r},\omega) = \int \frac{1}{|\vec{r}-\vec{r}'|}\rho^{(1)}(\vec{r}',\omega)d\vec{r}'$$

$$v_{XC}^{(1)}(\vec{r},\omega) = \int K_{XC}(\vec{r},\vec{r}',\omega)\rho^{(1)}(\vec{r}',\omega)d\vec{r}'$$

They are valid for all perturbations, thus we must have:

$$\chi_0^{-1}(\vec{r},\vec{r}';\omega) = \chi^{-1}(\vec{r},\vec{r}';\omega) + \frac{1}{|\vec{r}-\vec{r}'|} + K_{XC}(\vec{r},\vec{r}',\omega)$$

$$\boxed{\chi^{-1}(\vec{r},\vec{r}';\omega) = \chi_0^{-1}(\vec{r},\vec{r}';\omega) - \frac{1}{|\vec{r}-\vec{r}'|} - K_{XC}(\vec{r},\vec{r}',\omega)}$$

The Dyson equation for the susceptibility (I)

This is an exact formula for the inverse of the susceptibility

$$\chi^{-1}(\vec{r},\vec{r}';\omega) = \chi_0^{-1}(\vec{r},\vec{r}';\omega) - \frac{1}{|\vec{r}-\vec{r}'|} - K_{XC}(\vec{r},\vec{r}',\omega)$$

Exact XC kernel,
to be approximated

$$\chi_0(\vec{r},\vec{r}';\omega) = 2\Re e \sum_{\sigma} \sum_{n}^{occ.} \sum_{m}^{empty} \frac{\varphi_{n\sigma}^*(\vec{r})\varphi_{m\sigma}(\vec{r})\varphi_{m\sigma}^*(\vec{r}')\varphi_{n\sigma}(\vec{r}')}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega}$$

The latter is an exact expression for the independent-particle susceptibility, if the exact KS eigenenergies and eigenfunctions (occ/unocc) are known. In practice these must be approximated.

Photoabsorption cross section

For a finite system, the polarizability tensor is given by

$$\alpha_{ij}(\omega) = -\int \vec{r}_i \; \chi(\vec{r},\vec{r}';\omega) \; \vec{r}_j \; d\vec{r}d\vec{r}'$$

and the photoabsorption cross section corresponds to its imaginary part, with suitable coefficients

$$\sigma_{ij}(\omega) = \frac{4\pi\omega}{c} \Im m \; \alpha_{ij}(\omega + i\delta^+)$$

Independently of the TDDFT formulation of the susceptibility, it is known (in the many-body theory), that the systems can absorb energy at the frequencies corresponding to transitions to excited states, and that the polarizability can be formulated as a sum over states of the many-body system.
This is the basis of the Casida technique to find excitation energies.

Casida's approach to excitation energies (I)

For a finite system, the polarizability must be given by

$$\alpha_{ij}(\omega) = \sum_{I} \frac{f_{I,ij}}{\omega_I^2 - \omega^2}$$

where the I index labels different excited states, ω_I and $f_{I,ij}$ are the corresponding excitation energy and oscillator strength. After some non-trivial mathematics, for adiabatic XC kernels, Casida (1995) deduced that the square of the excitation energies were all eigenvalues of a specific matrix equation

$$\underline{\underline{\Omega}}\, \underline{F}_I = \omega_I^2\, \underline{F}_I$$

while the oscillator strengths could be deduced from the eigenvectors $\underline{F}_I$ of the same equation.

Casida's approach to excitation energies (II)

This matrix $\underline{\underline{\Omega}}$ is defined in the space of electron-hole excitations, namely, products of one occupied and one unoccupied wavefunction.

One line (or one row) of the matrix is a composite index, i.e. kl (k unoccupied and l occupied), associated to energy change $\omega_{kl} = \varepsilon_k - \varepsilon_l$

and spatial electron-hole wavefunction product $\phi_k(\vec{r})\phi_l(\vec{r})$

Note : for a finite system, all wavefunctions can be taken real.

$$\Omega_{ij,kl} = \omega_{ij}^2\left(\delta_{ik}\delta_{jl}\right) + \sqrt{\omega_{ij}}\,K_{ij,kl}\,\sqrt{\omega_{kl}}$$

$$K_{ij,kl} = \iint \phi_i(\vec{r})\phi_j(\vec{r})\left(\frac{1}{|\vec{r}\text{-}\vec{r}'|} + \frac{\delta v_{XC}(\vec{r})}{\delta\rho(\vec{r}')}\right)\phi_k(\vec{r}')\phi_l(\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'$$

Casida's approach to excitation energies (III)

(1) Until now, no change of spin was considered : the computed excitation energies correspond to spin-singlet excited states.
This formalism can be trivially extended to spin-flipping TD potentials, and give access also to spin-triplet excited states.

(2) Knowing the excitation energies allows to compute Born-Oppenheimer hypersurfaces for excited states, as

$$E_I\{R\} = E_{GS}\{R\} + \omega_I\{R\}$$

(3) Casida's formalism allows to identify well-separated excitation eigenenergies. OK for finite systems, not for bulk, periodic chains or slabs.
More fundamentally, kernels based on LDA/GGA are unable to modify band edges within TDDFT, they are only able to shift oscillator strength.

Implementation of Casida's formalism (I)

Restricted to finite systems :
- big supercell
- nkpt=1

Restricted to spin-unpolarized ground-state + no spinor
- nsppol=1
- nspinor=1

First dataset

Second dataset

iscf=-1

Ground State SCF (with occupied bands)	→	Non-SCF calculation (with many bands) +TDDFT

Implementation of Casida's formalism (II)

If you need the dynamical polarisability, you need
to give the supercell a « box center », so that there
is vacuum at the discontinuity of the r potential.

The spectrum is to be produced by yourself, on the basis
of excitation energies and oscillator strength

(old utility, not maintained : ~ABINIT/Utilities/dynamic_pol.f)

Parallelism present (although not properly documented).

Nitrogen molecule : tight-binding analysis

Diagram of molecular orbitals

Atom   Diatomic molecule   Atom
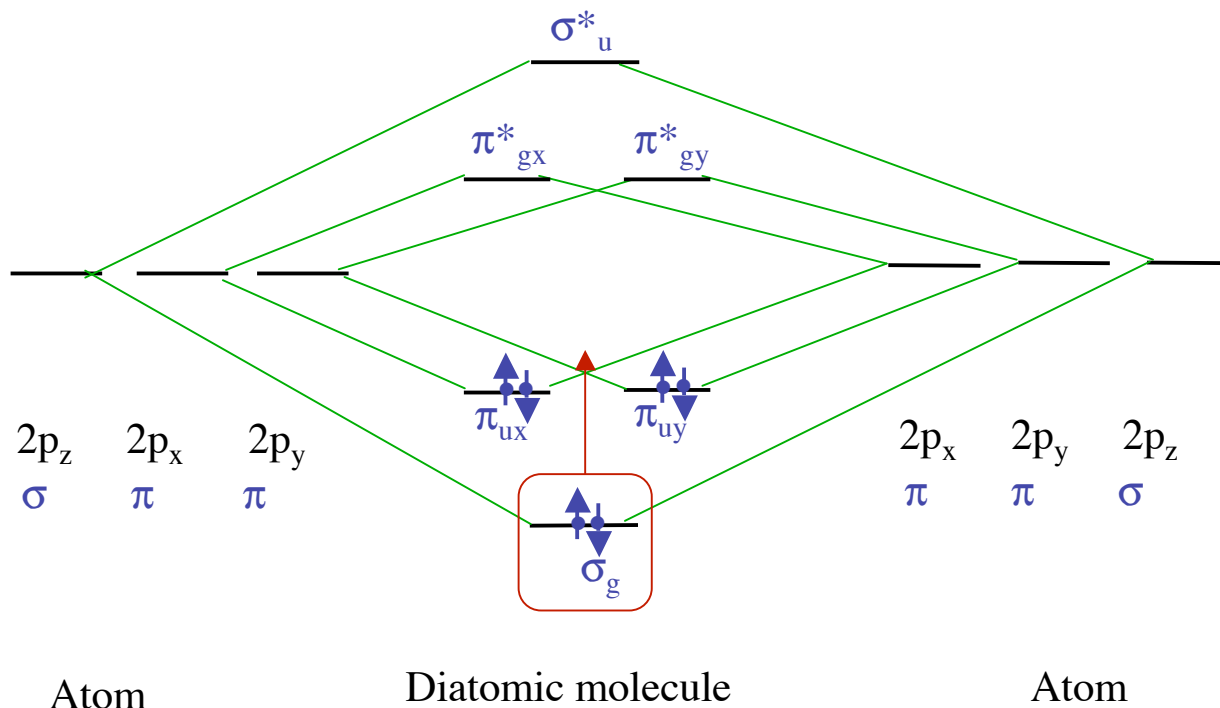
However, due to repulsion with the lower lying states, generated by the 2s orbitals, the σ_g orbital is pushed above the π_u orbitals, and the σ^*_u is also repelled.

Nitrogen molecule : Kohn-Sham energies

(from the tutorial : non-converged values)

σ_g 0.40 eV

π^*_{gx} π^*_{gy} -0.50 eV

2p

-8.96 eV

σ_g

π_{ux} π_{uy} -10.41 eV

σ^*_u

-12.18 eV

2s

-27.11 eV

σ_g

KS energies

$2\Sigma_u + \Delta_u$

9.91 eV

Π_g

8.46 eV

9.36 eV

Σ_g

10.81 eV

Π_u

lowest KS transitions

Time-Dependent Density Functional Theory

Nitrogen molecule : TDDFT

(from the tutorial : non-converged values)

	Kohn-Sham		TDDFT triplet	TDDFT singlet
Π_u	10.81 eV		9.91 eV	10.79 eV
		Σ_u	(ionized)	(ionized)
$2\Sigma_u + \Delta_u$	9.91 eV	Δ_u	9.08 eV	10.46 eV
		Σ_u	8.16 eV	9.91 eV
Σ_g	9.36 eV		9.16 eV	9.86 eV
Π_g	8.46 eV		7.85 eV	9.47 eV

Time-Dependent Density Functional Theory

Discussion

TDDFT formalism well-established

Approximations : adiabatic OK ;
        beyond is still an active research area

In the Casida formalism, need good starting XC potential
            and XC kernel

Powerful for finite systems

Accuracy : might be as good as 0.1 eV, but as bad as 1 eV.

Not useful (at present) for bulk solids, surfaces and chains.