Time-dependent density functional theory

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### OUTLINE

- Phenomena to be described by TDDFT: Matter in weak and strong laser fields
- Basic theorems of TDDFT
- Approximate xc functionals of TDDFT the “exact adiabatic” approximation
- TDDFT in the linear-response regime
  - Optical excitation spectra of molecules
  - Excitonic effects in the optical spectra of solids
  - Charge-transfer excitations in molecules and the discontinuity of the xc kernel

### THANKS

- Manfred Lein
- Volker Engel
- Erich Runge
- Stephan Kümmel
- M. Thiele
- Martin Petersilka
- Ulrich Gossmann
- Tobias Grabo
- Sangeeta Sharma
- Kay Dewhurst
- Antonio Sanna
- Maria Hellgren
Time-dependent systems

**Generic situation:**
Molecule in laser field

\[
\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} - \frac{Z_{\alpha}e^2}{|r_j-R_{\alpha}|} + \hat{E} \cdot \hat{r}_j \cdot \sin \omega t
\]

**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 \(\rho_1(\vec{r}, t)\)
2. Dynamical polarizability \(\alpha(\omega) = -\frac{e}{E} \int z \rho_1(\vec{r}, \omega) d^3r\)
3. Photo-absorption cross section \(\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im} \alpha\)
Weak lasers: Optical spectra of finite systems (atoms, molecules)

- Continuum states
- Unoccupied bound states
- Occupied bound states

Laser frequency $\omega$

Photo-absorption cross section $\sigma(\omega)$
Standard linear response formalism

\[ H(t_0) = \text{full static Hamiltonian at } t_0 \]

\[ H(t_0)|m\rangle = E_m|m\rangle \leftarrow \text{exact many-body eigenfunctions and energies of system} \]

**Full response function**

\[ \chi(r, r'; \omega) = \lim_{\eta \to 0^+} \sum_m \left( \frac{\langle 0|\hat{\rho}(r)|m\rangle\langle m|\hat{\rho}(r)|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{\rho}(r')|m\rangle\langle m|\hat{\rho}(r')|0\rangle}{\omega + (E_m - E_0) + i\eta} \right) \]

⇒ The exact linear density response

\[ \rho_1(\omega) = \chi(\omega)v_1 \]

has poles at the exact excitation energies \( \Omega = E_m - E_0 \)
Weak lasers: Optical spectra of periodic solids (insulators)
Strong Laser Fields

Intensities in the range of $10^{13} \ldots 10^{16}$ W/cm$^2$
Comparison: Electric field on 1st Bohr-orbit in hydrogen

$$E = \frac{1}{4\pi\varepsilon_0} \frac{e}{a_0^2} = 5.1 \times 10^9 \text{ V/m}$$

$$I = \frac{1}{2} \varepsilon_0 c E^2 = 3.51 \times 10^{16} \text{ W/cm}^2$$

Three quantities to look at:

I. Emitted ions
II. Emitted electrons
III. Emitted photons
I. Emitted Ions

Walker et al.,
PRL 73, 1227 (1994)

\[ \lambda = 780 \text{ nm} \]
Momentum Distribution of the He$^{2+}$ recoil ions

![Graph showing momentum distribution of He$^{2+}$ recoil ions](image)
$\left| \Psi(p_1, p_2, t) \right|^2$ of the He atom

$|\Psi(p_1, p_2, t)|^2$ of the He atom

Wigner distribution $W(Z,P,t)$ of the electronic center of mass for He atom

$\nu_{\text{Laser}}(z,t) = E_z \sin \omega t \quad I = 10^{15} \text{ W/cm}^2 \quad \lambda = 780 \text{ nm}$

II. Electrons: Above-Threshold-Ionization (ATI)

Ionized electrons absorb more photons than necessary to overcome the ionization potential (IP)

Photoelectrons: \[ E_{\text{kin}} = (n + s) \hbar \omega - \text{IP} \]

\[ \Rightarrow \text{Equidistant maxima in intervals of } \hbar \omega: \]

Agostini et al., PRL 42, 1127 (1979)
III. Photons: High-Harmonic Generation

Emission of photons whose frequencies are integer multiples of the driving field. Over a wide frequency range, the peak intensities are almost constant (plateau).

\[ \text{IP} + 3.17 U_p \]
Even harmonic generation due to nuclear motion

(a) Harmonic spectrum generated from the model HD molecule driven by a laser with peak intensity $10^{14}$ W/cm$^2$ and wavelength 770 nm. The plotted quantity is proportional to the number of emitted phonons. (b) Same as panel (a) for the model H$_2$ molecule.

**Dream:** Use single molecules as basic units (transistors, diodes, …) of electronic devices
Molecular Electronics

**Dream:** Use single molecules as basic units (transistors, diodes, …) of electronic devices

Bias between L and R is turned on: $U(t) \rightarrow V$ for large $t$

A steady current, $I$, may develop as a result.

- Calculate current-voltage characteristics $I(V)$
- Investigate cases where no steady state is achieved
Hamiltonian for the complete system of \( N_e \) electrons with coordinates \((r_1 \cdots r_{N_e}) \equiv \underline{r}\) and \( N_n \) nuclei with coordinates \((R_1 \cdots R_{N_n}) \equiv \underline{R}\), masses \( M_1 \cdots M_{N_n} \) and charges \( Z_1 \cdots Z_{N_n} \).

\[
\hat{H} = \hat{T}_n (\underline{R}) + \hat{W}_{nn} (\underline{R}) + \hat{T}_e (\underline{r}) + \hat{W}_{ee} (\underline{r}) + \hat{U}_{en} (\underline{R}, \underline{r})
\]

with

\[
\hat{T}_n = \sum_{v=1}^{N_n} -\frac{\nabla_v^2}{2M_v}, \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}, \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\mu,v}^{N_n} \frac{Z_\mu Z_v}{|R_\mu - R_v|},
\]

\[
\hat{W}_{ee} = \frac{1}{2} \sum_{j,k}^{N_e} \frac{1}{|r_j - r_k|}, \quad \hat{U}_{en} = \sum_{j=1}^{N_e} \sum_{v=1}^{N_n} -\frac{Z_v}{|r_j - R_v|}
\]

Time-dependent Schrödinger equation

\[
i \frac{\partial}{\partial t} \Psi (r, R, t) = \left( H (r, R) + V_{\text{external}} (r, R, t) \right) \psi (r, R, t)
\]
Example: Oxygen atom (8 electrons)

\[ \Psi(\vec{r}_1, \cdots, \vec{r}_8) \] depends on 24 coordinates

rough table of the wavefunction

10 entries per coordinate: \( \Rightarrow 10^{24} \) entries
1 byte per entry: \( \Rightarrow 10^{24} \) bytes
10\(^{10}\) bytes per DVD: \( \Rightarrow 10^{14} \) DVDs
10 g per DVD: \( \Rightarrow 10^{15} \) g DVDs
\[ = 10^9 \text{ t DVDs} \]
Every observable quantity of a quantum system can be calculated from the density of the system ALONE.

The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles.
Ground-State Density Functional Theory
compare ground-state densities $\rho(r)$ resulting from different external potentials $v(r)$.

**QUESTION:** Are the ground-state densities coming from different potentials always different?
single-particle potentials having nondegenerate ground state

ground-state wavefunctions

ground-state densities

**Ground-State Density Functional Theory**

\[ G: v(r) \rightarrow \rho (r) \text{ is invertible} \]
For any observable $\hat{O}$

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = O[\rho]$$

is functional of the density
For any observable $\hat{O}$

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = O[\rho]$$

is functional of the density

For general observables: Need to find approximations for the functionals $O[\rho]$ representing the observables.
For any observable \( \hat{O} \)

\[
\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle = O[\rho]
\]

is functional of the density

For general observables: Need to find approximations for the functionals \( O[\rho] \) representing the observables.

Easy observables: \( E_{\text{tot}}[\rho] \), \( D[\rho] = \int \rho(r) \, r \, d^3r \), …

More difficult: spectroscopic information, gaps, ….
• Every observable quantity of a quantum system can be calculated from the density of the system ALONE (Hohenberg, Kohn, 1964)

• The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965)
HK 1-1 mapping for interacting particles

HK 1-1 mapping for non-interacting particles

\( v_{\text{ext}} [\rho] (r) \quad \rightarrow \quad \rho (r) \quad \rightarrow \quad v_s [\rho] (r) \)

Kohn-Sham Theorem

Let \( \rho_o (r) \) be the ground-state density of interacting electrons moving in the external potential \( v_o (r) \). Then there exists a local potential \( v_{s,o} (r) \) such that non-interacting particles exposed to \( v_{s,o} (r) \) have the ground-state density \( \rho_o (r) \), i.e.

\[
\left( -\frac{\nabla^2}{2} + v_{s,o} (r) \right) \phi_j (r) = \epsilon_j \phi_j (r), \quad \rho_o (r) = \sum_{j \text{ (with lowest } \epsilon_j)}^N \left| \phi_j (r) \right|^2
\]

proof: \( v_{s,o} (r) = v_s [\rho_o] (r) \)

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

Note: The KS equations do not follow from the variational principle!!
By construction, the HK mapping is well-defined for all those functions \( \rho(r) \) that are ground-state densities of some potential (so called V-representable functions \( \rho(r) \)).

**QUESTION:** Are all “reasonable” functions \( \rho(r) \) V-representable?


On a lattice (finite or infinite), any normalizable positive function \( \rho(r) \), that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable.

In other words: For any given \( \rho(r) \) (normalizable, positive, compatible with Pauli principle) there exists a potential, \( v_{\text{ext}}[\rho](r) \), yielding \( \rho(r) \) as interacting ground-state density, and there exists another potential, \( v_{s}[\rho](r) \), yielding \( \rho(r) \) as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given \( \rho(r) \) is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).
Basic 1-1 correspondence:

\[ \nu(rt) \leftrightarrow^{1-1} \rho(rt) \]

The time-dependent density determines uniquely
the time-dependent external potential and hence all
physical observables for fixed initial state.

KS theorem:

The time-dependent density of the interacting
system of interest can be calculated as density

\[ \rho(rt) = \sum_{j=1}^{N} \left| \varphi_j(rt) \right|^2 \]

of an auxiliary non-interacting (KS) system

\[ i\hbar \frac{\partial}{\partial t} \varphi_j(rt) = \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s[\rho](rt) \right) \varphi_j(rt) \]

with the local potential

\[ v_s[\rho(r't')](rt) = \nu(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}[\rho(r't')](rt) \]

Time-dependent density-functional formalism

Proof of basic 1-1 correspondence between $v(\mathbf{r}_t)$ and $\rho(\mathbf{r}_t)$

**Define maps**

\[ F : v(\mathbf{r}_t) \mapsto \Psi(t) \quad \tilde{F} : \Psi(t) \mapsto \rho(\mathbf{r}_t) \]

- **POTENTIALS** $v(\mathbf{r}_t)$
  - \( F \): solve t.d.Schrödinger equation with fixed $\Psi(t_0) = \Psi_o$

- **WAVE FUNCTIONS** $\Psi(t)$
  - $\tilde{F}$
  - $\rho(\mathbf{r}_t) = \langle \Psi(t) | \hat{\rho}(\mathbf{r}) | \Psi(t) \rangle$

- **DENSITIES** $\rho(\mathbf{r}_t)$
  - $\hat{\rho}(\mathbf{r}) = \sum_s \psi^+_s(\mathbf{r}) \psi_s(\mathbf{r})$

**FUNCTION** $G$

\[ G : v(\mathbf{r}_t) \mapsto \rho(\mathbf{r}_t) \]
THEOREM (time-dependent analogue of Hohenberg-Kohn theorem)

The map

\[ G : v(\vec{r}t) \mapsto \rho(\vec{r}t) \]

defined for all single-particle potentials \( v(\vec{r}t) \) which can be expanded into a Taylor series with respect to the time coordinate around \( t_0 \)

is invertible up to within an additive merely time-dependent function in the potential.
Proof:
to be shown:

\[ v(\vec{r}t) \neq \hat{v}'(\vec{r}t) + c(t) \quad \Rightarrow \quad \rho(\vec{r}t) \neq \rho'(\vec{r}t) \]

i.e. potential expandable into Taylor series

\[ \exists \ k \geq 0 : \ \frac{\partial^k}{\partial t^k} [v(\vec{r}t) - \hat{v}'(\vec{r}t)]_{t=t_0} \neq \text{constant} \]

step 1
\[ j(\vec{r}t) \neq j'(\vec{r}t) \]

step 2
\[ \rho(\vec{r}t) \neq \rho'(\vec{r}t) \]
The TDKS equations follow (like in the static case) from:

i. the basic 1-1 mapping for interacting and non-interacting particles

ii. the TD V-representability theorem (R. van Leeuwen, PRL 82, 3863 (1999)).

A TDDFT variational principle exists as well, but this is more tricky:
R. van Leeuwen
S. Mukamel
T. Gal
G. Vignale
Simplest possible approximation for $v_{xc} [\rho](\vec{r}t)$

Adiabatic Approximation:

$$v_{xc}^{\text{adiab}} (\vec{r}t) := v_{xc}^{\text{stat}} [n](r) \bigg|_{n=\rho(\vec{r}'t)}$$

where $v_{xc}^{\text{stat}} = xc$ potential of ground-state DFT
Adiabatic Approximation:

\[
V_{xc}^{\text{adiab}} (\vec{r} \, t) := V_{xc}^{\text{stat}} [n](r) \bigg|_{n=\rho(\vec{r}' \, t)}
\]

where \( V_{xc}^{\text{stat}} = xc \) potential of ground-state DFT

- Every approximate ground-state \( xc \) potential yields an adiabatic approximation to the time-dependent \( xc \) potential
- Deficiencies of approximate ground-state \( xc \) potentials are inherited by the corresponding adiabatic functionals

Example: \( v_{xc}^{\text{ALDA}} (\vec{r} \, t) := v_{xc}^{\text{hom}} (n) \bigg|_{n=\rho(\vec{r} \, t)} \)

has the wrong asymptotic form for large \( r \)
Two sources of troubles:

- deficiencies of ground-state xc functional
- adiabatic approximation
Two sources of troubles:

- deficiencies of ground-state xc functional
- adiabatic approximation

Which problem is more severe?

Investigate the best possible adiabatic approximation, i.e. the one that follows from the exact ground-state xc potential
• Solve 1D model for He atom in strong laser fields (numerically) exactly. This yields exact TD density $\rho(r,t)$.

• Inversion of one-particle TDSE yields exact TDKS potential. Then, subtracting the laser field and the TD-Hartree term, yields the exact TD xc potential.

• Inversion of one-particle ground-state SE yields the exact static KS potential, $v_{KS-static}[\rho(t)]$, that gives (for each separate $t$) $\rho(r,t)$ as ground-state density.

• Inversion of the many-particle ground-state SE yields the static external potential, $v_{ext-static}[\rho(t)]$, that gives (for each separate $t$) $\rho(r,t)$ as interacting ground-state density.

• Compare the exact TD xc potential of step 1 with the exact adiabatic approximation which is obtained by subtraction:

$$v_{xc-exact-adiab}(t) = v_{KS-static}[\rho(t)] - v_{H}[\rho(t)] - v_{ext-static}[\rho(t)]$$
E(t) ramped over 27 a.u. (0.65 fs) to the value $E=0.14$ a.u. and then kept constant

4-cycle pulse with $\lambda = 780$ nm, $I_1 = 4 \times 10^{14}$ W/cm$^2$, $I_2 = 7 \times 10^{14}$ W/cm$^2$

LINEAR RESPONSE THEORY

\( t = t_0 : \) Interacting system in ground state of potential \( v_0(r) \) with density \( \rho_0(r) \)

\( t > t_0 : \) Switch on perturbation \( v_1(r, t) \) (with \( v_1(r, t_0) = 0 \)).

Density: \( \rho(r, t) = \rho_0(r) + \delta \rho(r, t) \)

Consider functional \( \rho[v](r, t) \) defined by solution of interacting TDSE

Functional Taylor expansion of \( \rho[v] \) around \( v_0 \):

\[
\rho[v](r, t) = \rho[v_0](r, t) + \int \frac{\delta \rho[v]}{\delta v} \bigg|_{v_0} v_1(r', t') \, d^3r'dt'
\]

\[
+ \frac{1}{2} \int\int \frac{\delta^2 \rho[v]}{\delta v(r') \delta v(r''')} \bigg|_{v_0} v_1(r', t') v_1(r'', t'') \, d^3r'd^3r''dt'dt''
\]

\[\vdots\]
\( \rho_1(r,t) = \text{linear density response of interacting system} \)

\[
\chi(rt, r't') := \frac{\delta \rho[v](rt)}{\delta v(r't')} \bigg|_{v_0} = \text{density-density response function of interacting system}
\]

Analogous function \( \rho_s[v_s](r t) \) for non-interacting system

\[
\rho_s[v_s](rt) = \rho_s[v_{s,0} + v_{s,1}](rt) = \rho_s[v_{s,0}](rt) + \int \frac{\delta \rho_s[v_s](rt)}{\delta v_s(r't')} \bigg|_{v_{s,0}} v_{s,1}(r't') \, d^3r'dt' + \ldots
\]

\[
\chi_s(rt, r't') := \frac{\delta \rho_s[v_s](rt)}{\delta v_s(r't')} \bigg|_{v_{s,0}} = \text{density-density response function of non-interacting system}
\]
Standard linear response formalism

\[ H(t_0) = \text{full static Hamiltonian at } t_0 \]

\[ H(t_0)|m\rangle = E_m|m\rangle \quad \text{← exact many-body eigenfunctions and energies of system} \]

full response function

\[ \chi(r, r'; \omega) = \lim_{\eta \to 0^+} \sum_m \left( \frac{\langle 0 | \hat{\rho}(r) | m \rangle \langle m | \hat{\rho}(r) | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{\rho}(r') | m \rangle \langle m | \hat{\rho}(r') | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right) \]

\[ \Rightarrow \text{The exact linear density response} \]

\[ \rho_1(\omega) = \chi(\omega) v_1 \]

has poles at the exact excitation energies \( \Omega = E_m - E_0 \)
**GOAL:** Find a way to calculate $\rho_1(r\ t)$ without explicitly evaluating $\chi(r\ t,r't')$ of the interacting system.

**starting point:** Definition of xc potential

$$v_{xc}[\rho](rt) := v_S[\rho](rt) - v_{ext}[\rho](rt) - v_H[\rho](rt)$$

**Notes:**

- $v_{xc}$ is well-defined through non-interacting / interacting 1-1 mapping.
- $v_S[\rho]$ depends on initial determinant $\Phi_0$.
- $v_{ext}[\rho]$ depends on initial many-body state $\Psi_0$.

$\Rightarrow$ **In general,** $v_{xc} = v_{xc}[\rho, \Phi_0, \Psi_0]$

only if system is initially in ground-state then, via HK, $\Phi_0$ and $\Psi_0$ are determined by $\rho_0$ and $v_{xc}$ depends on $\rho$ alone.
\[
\left. \frac{\delta V_{xc}[\rho](rt)}{\delta \rho(r't')} \right|_{\rho_0} = \left. \frac{\delta V_S[\rho](rt)}{\delta \rho(r't')} \right|_{\rho_0} - \left. \frac{\delta V_{ext}[\rho](rt)}{\delta \rho(r't')} \right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{|r-r'|}
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{|r-r'|}
\]

\[
\delta v_{xc}(rt, r't')
\]

\[
\delta v_{S}(rt, r't')
\]

\[
\delta v_{ext}(rt, r't')
\]

\[
\delta (t-t')
\]

\[
f_{xc} + V_{ee} = \chi^{-1} - \chi^{-1}
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{|r-r'|}
\]

\[
\chi_S^{-1}(rt, r't') \quad \chi^{-1}(rt, r't') \quad W_C(rt, r't')
\]

\[
\chi_S \cdot f_{xc} + V_{ee} = \chi_S^{-1} - \chi^{-1} \cdot \chi
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_{S}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{r-r'}
\]

\[
\chi_S \cdot \left( f_{xc} + V_{ee} \right) \chi = \chi - \chi_S
\]
\[ \chi = \chi_S + \chi_S \left( V_{ee} + f_{xc} \right) \chi \]

Act with this operator equation on arbitrary \( v_1(r, t) \) and use \( \chi v_1 = \rho_1 \):

\[
\rho_1 (r, t) = \int d^3r' dt' \chi_S (r, r') \left[ v_1 (r, t) + \int d^3r'' dt'' \left\{ V_{ee} (r', r''') + f_{xc} (r', r'''') \right\} \rho_1 (r'''') \right]
\]

- Exact integral equation for \( \rho_1(r, t) \), to be solved iteratively
- Need approximation for \( f_{xc} (r', r''') \) (either for \( f_{xc} \) directly or for \( v_{xc} \))

\[
\frac{\delta v_{xc} [\rho](r', r''')}{\delta \rho (r''')} \bigg|_{\rho_0}
\]
In the adiabatic approximation, the xc potential $v_{xc}(t)$ at time $t$ only depends on the density $\rho(t)$ at the very same point in time.

**Adiabatic approximation**

$\mathbf{v}_{\text{adiab}}^{\text{xc}}[\rho](rt) := \mathbf{v}_{\text{xc}}^{\text{static DFT}}[\rho(t)](rt)$

\[ e.g. \text{ adiabatic LDA: } \mathbf{v}_{\text{xc}}^{\text{ALDA}}(rt) := \mathbf{v}_{\text{xc}}^{\text{LDA}}(\rho(rt)) = -\alpha \rho(rt)^{1/3} + \cdots \]

\[ \Rightarrow f_{\text{xc}}^{\text{ALDA}}(rt, r't') = \left. \frac{\delta v_{\text{xc}}^{\text{ALDA}}(rt)}{\delta \rho(r't')} \right|_{\rho_0} = \delta(r-r') \delta(t-t') \left. \frac{\partial v_{\text{xc}}^{\text{ALDA}}}{\partial \rho(r)} \right|_{\rho_0(r)} \]

\[ = \delta(r-r') \delta(t-t') \left. \frac{\partial^2 e_{\text{xc}}^{\text{hom}}}{\partial n^2} \right|_{\rho_0(r)} \]
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.

Photo-absorption in weak lasers

No absorption if $\omega < \text{lowest excitation energy}$
Discrete excitation energies from TDDFT

exact representation of linear density response:

\[
\rho_1(\omega) = \hat{\chi}_S(\omega) (v_1(\omega) + \hat{V}_{ee}\rho_1(\omega) + \hat{f}_{xc}(\omega)\rho_1(\omega))
\]

“\(^\wedge\)” denotes integral operators, i.e.

\[
\hat{f}_{xc}\rho_1 = \int f_{xc}(\vec{r}, \vec{r}')\rho_1(\vec{r}')d^3r'
\]

where

\[
\hat{\chi}_S(\vec{r}, \vec{r}'; \omega) = \sum_{j,k} \frac{M_{jk}(\vec{r}, \vec{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}
\]

with

\[
M_{jk}(\vec{r}, \vec{r}') = (f_k - f_j)\phi_j(\vec{r})\phi^*_j(\vec{r}')\phi_k(\vec{r}')\phi^*_k(\vec{r})
\]

\[
f_m = \begin{cases} 
1 & \text{if } \phi_m \text{ is occupied in KS ground state} \\
0 & \text{if } \phi_m \text{ is unoccupied in KS ground state} 
\end{cases}
\]

\[
\epsilon_j - \epsilon_k \quad \text{KS excitation energy}
\]
\[
\left( \hat{1} - \hat{\chi}_S (\omega) \left[ \hat{V}_{ee} + \hat{f}_{xc} (\omega) \right] \right) \rho_1 (\omega) = \hat{\chi}_S (\omega) v_1 (\omega)
\]

\[
\rho_1 (\omega) \to \infty \text{ for } \omega \to \Omega \text{ (exact excitation energy) but right-hand side remains finite for } \omega \to \Omega
\]

hence
\[
\left( \hat{1} - \hat{\chi}_S (\omega) \left[ \hat{V}_{ee} + \hat{f}_{xc} (\omega) \right] \right) \xi (\omega) = \lambda (\omega) \xi (\omega)
\]

\[
\lambda (\omega) \to 0 \text{ for } \omega \to \Omega
\]

This condition rigorously determines the exact excitation energies, i.e.,
\[
\left( \hat{1} - \hat{\chi}_S (\Omega) \left[ \hat{V}_{ee} + \hat{f}_{xc} (\Omega) \right] \right) \xi (\Omega) = 0
\]
This leads to the (non-linear) eigenvalue equation

\[ \sum_{q'} \left( M_{qq'}(\Omega) + \omega_q \delta_{qq'} \right) \beta_{q'} = \Omega \beta_q \]

\[ M_{qq'} = \alpha_{q'} \int d^3r \int d^3r' \Phi_q(r) \left( \frac{1}{|r-r'|} + f_{xc}(r, r', \Omega) \right) \Phi_{q'}(r') \]

\[ q = (j, a) \text{ double index} \]

\[ \alpha_q = f_a - f_j \]

\[ \omega_q = \varepsilon_a - \varepsilon_j \]

Equivalent to Casida equations if:
- \( \omega \)-dependence of \( f_{xc} \) is neglected
- orbitals are real-valued
- pure density-response is considered in Casida eqs.
<table>
<thead>
<tr>
<th>Atom</th>
<th>Experimental Excitation Energies $^{1}S\rightarrow^{1}P$ (in Ry)</th>
<th>KS energy differences $\Delta \epsilon_{KS}$ (Ry)</th>
<th>$\Delta \epsilon_{KS} + K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.388</td>
<td>0.259</td>
<td>0.391</td>
</tr>
<tr>
<td>Mg</td>
<td>0.319</td>
<td>0.234</td>
<td>0.327</td>
</tr>
<tr>
<td>Ca</td>
<td>0.216</td>
<td>0.157</td>
<td>0.234</td>
</tr>
<tr>
<td>Zn</td>
<td>0.426</td>
<td>0.315</td>
<td>0.423</td>
</tr>
<tr>
<td>Sr</td>
<td>0.198</td>
<td>0.141</td>
<td>0.210</td>
</tr>
<tr>
<td>Cd</td>
<td>0.398</td>
<td>0.269</td>
<td>0.391</td>
</tr>
</tbody>
</table>


$$\Delta E = \Delta \epsilon_{KS} + K$$

$$K = \int d^3r \int d^3r' \varphi_j (r) \varphi_j^* (r') \varphi_k (r') \varphi_k^* (r) \left( \frac{1}{|r-r'|} + f_{xc} (r, r') \right)$$
## Excitation energies of CO molecule

<table>
<thead>
<tr>
<th>State</th>
<th>$\Omega_{\text{expt}}$</th>
<th>KS-transition</th>
<th>$\Delta\varepsilon_{\text{KS}}$</th>
<th>$\Delta\varepsilon_{\text{KS} + K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3127</td>
<td>$5\Sigma \rightarrow 2\Pi$</td>
<td>0.2523</td>
<td>0.3267</td>
</tr>
<tr>
<td>a</td>
<td>0.2323</td>
<td>$3\Pi$</td>
<td></td>
<td>0.2238</td>
</tr>
<tr>
<td>I</td>
<td>0.3631</td>
<td>$1\Sigma \rightarrow 2\Pi$</td>
<td>0.3626</td>
<td>0.3626</td>
</tr>
<tr>
<td>D</td>
<td>0.3759</td>
<td>$1\Delta$</td>
<td></td>
<td>0.3812</td>
</tr>
<tr>
<td>a'</td>
<td>0.3127</td>
<td>$3\Sigma^+$</td>
<td></td>
<td>0.3181</td>
</tr>
<tr>
<td>e</td>
<td>0.3631</td>
<td>$3\Sigma^-$</td>
<td></td>
<td>0.3626</td>
</tr>
<tr>
<td>d</td>
<td>0.3440</td>
<td>$3\Delta$</td>
<td></td>
<td>0.3404</td>
</tr>
</tbody>
</table>


approximations made: $v_{xc}^{LDA}$ and $f_{xc}^{ALDA}$
Quantum defects in Helium

\[ E_n = -\frac{1}{2(n - \mu_n)^2} \text{ [a.u.]} \]

3P Series

Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye, the errors of the discrete excitation energies were connected with lines.

Failures of ALDA in the linear response regime

• $\text{H}_2$ dissociation is incorrect:

$$E\left(1\Sigma_u^+\right) - E\left(1\Sigma_g^+\right) \xrightarrow{R \to \infty} 0 \quad \text{(in ALDA)}$$

(see: Gritsenko, van Gisbergen, Görling, Baerends, JCP 113, 8478 (2000))

• response of long chains strongly overestimated

(see: Champagne et al., JCP 109, 10489 (1998) and 110, 11664 (1999))

• charge-transfer excitations not properly described

(see: Dreuw et al., JCP 119, 2943 (2003))

• in the optical spectrum of periodic solids, there are two problems:
  --absorption edge is wrong (LDA KS gap)
  --excitons are missing
Solid Argon

**OBSERVATION:**
In the long-wavelength-limit (q = 0), relevant for optical absorption, ALDA is not reliable. In particular, excitonic peaks are completely missing. Results are very close to RPA.

**EXPLANATION:**
In the TDDFT response equation, the bare Coulomb interaction and the xc kernel only appear as sum \((V_{ee} + f_{xc})\). For \(q \to 0\), \(V_{ee}\) diverges like \(1/q^2\), while \(f_{xc}\) in ALDA goes to a constant. Hence results are close to \(f_{xc} = 0\) (RPA) in the \(q \to 0\) limit.

**CONCLUSION:**
exact property \(f_{xc}^{\text{exact}} \xrightarrow{q \to 0} 1/q^2\)
Approximations for \(f_{xc}\) are needed which, for \(q \to 0\), correctly diverge like \(1/q^2\). Such approximations can be derived from many-body perturbation theory (see, e.g., L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)).
Excitons in TDDFT
TDDFT response equation (a matrix equation)

\[
\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + \chi_S(\mathbf{q}, \omega) \nu(\mathbf{q}) \left[ 1 - (\nu(\mathbf{q}) + f_{xc}(\mathbf{q}, \omega)) \chi_S(\mathbf{q}, \omega) \right]^{-1}
\]

exact equation

\[
f_{xc}(\mathbf{r}, \mathbf{r}', t - t') \equiv \delta\nu_{xc}(\mathbf{r}, t)/\delta\rho(\mathbf{r}', t') \quad \text{xc kernel}
\]

\[
\chi_S(\mathbf{q}, \omega) \quad \text{Kohn-Sham response function}
\]

RPA corresponds to: \( f_{xc} \equiv 0 \)

\[
\varepsilon_{\text{RPA}}^{-1}(\mathbf{q}, \omega) = 1 + \chi_S(\mathbf{q}, \omega) \nu(\mathbf{q}) \left[ 1 - \nu(\mathbf{q}) \chi_S(\mathbf{q}, \omega) \right]^{-1}
\]
Bootstrap kernel (Sharma, Dewhurst, Sanna, EKUG, PRL 107, 186401 (2011))

\[
f_{xc}^{\text{boot}}(\mathbf{q}, \omega) = -\frac{\varepsilon^{-1}(\mathbf{q}, \omega = 0) \nu(\mathbf{q})}{\varepsilon_{\text{RPA}}^{00}(\mathbf{q}, \omega = 0) - 1} = \frac{\varepsilon^{-1}(\mathbf{q}, \omega = 0)}{\chi_{S}^{00}(\mathbf{q}, \omega = 0)}
\]

\[
f_{xc}^{\text{appr}}(\mathbf{q}, \omega) = \frac{1}{\chi_{S}(\mathbf{q}, \omega = 0)} - \frac{1}{\chi_{0}(\mathbf{q}, \omega = 0)} + f_{xc}^{\text{boot}}(\mathbf{q}, \omega)
\]

\[
\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + \chi_{S}(\mathbf{q}, \omega) \nu(\mathbf{q}) \left[ 1 - \left( \nu(\mathbf{q}) + f_{xc}^{\text{appr}}(\mathbf{q}, \omega) \right) \chi_{S}(\mathbf{q}, \omega) \right]^{-1}
\]

where \(\chi_{0}\) is a single-particle response function that has the right gap, e.g. \(G_{0}W_{0}\), LDA+U, LDA+Scissors, Tran-Blaha functional, …
Charge transfer excitations and the discontinuity of $f_{xc}$
charge-transfer excitation

\[ \Omega_{\text{CT}} \approx \text{IP}^{(A)} - \text{EA}^{(B)} - \int d^3r \int d^3r' \frac{\varphi_A(r)^2 \varphi_B(r')^2}{|r - r'|} \]

**CT excitation energy**

**Infinite R**

\[ \text{IP}^{(A)} = - \varepsilon_{\text{HOMO}}^{(A)} \]

\[ \text{EA}^{(B)} = - \varepsilon_{\text{LUMO}}^{(B)} - \Delta_{\text{xc}}^{(B)} = - \varepsilon_{\text{MOL}}^{(B)} \]

**Finite (but large) R**

\[ \text{IP}^{(A)} = - \varepsilon_{\text{MOL}}^{(A)} \]

\[ \text{EA}^{(B)} = - \varepsilon_{\text{MOL}}^{(B)} \]

\[ \Omega_{\text{CT}} \approx \varepsilon_{\text{MOL}}^{(B)} - \varepsilon_{\text{MOL}}^{(A)} - \int d^3r \int d^3r' \frac{\varphi_A(r)^2 \varphi_B(r')^2}{|r - r'|} \]
\[ \Omega_{CT} \approx \varepsilon^{(B)}_{\text{MOL}} - \varepsilon^{(A)}_{\text{MOL}} - \int d^3r \int d^3r' \frac{\left| \varphi_A(r) \right|^2 \left| \varphi_B(r') \right|^2}{|r - r'|} \approx 1/R \]
\[ \Omega_{\text{CT}} \approx \varepsilon_{\text{MOL}}^{(B)} - \varepsilon_{\text{MOL}}^{(A)} - \int d^3r \int d^3r' \frac{\varphi_A(r)^2 \varphi_B(r')^2}{|r - r'|} \]

\[ \sim 1/R \]

**In TDDFT (single-pole approximation)**

\[ \Omega_{\text{CT}} \approx \varepsilon_{\text{MOL}}^{(B)} - \varepsilon_{\text{MOL}}^{(A)} - \int d^3r \int d^3r' \varphi_A^*(r')\varphi_B(r')f_{xc}(r, r', \Omega_{\text{CT}})\varphi_A(r)\varphi_B^*(r) \]
\[ \Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3 r \int d^3 r' \frac{\varphi_A(r)^2 \varphi_B(r')^2}{|r - r'|} \]

\[ \sim 1/R \]

In TDDFT (single-pole approximation)

\[ \Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3 r \int d^3 r' \varphi_A^*(r')\varphi_B(r') f_{xc}(r, r', \Omega_{CT}) \varphi_A(r)\varphi_B^*(r) \]

Exponentially small

Exponentially small
\[ \Omega_{\text{CT}} \approx \varepsilon^{(B)}_{\text{MOL}} - \varepsilon^{(A)}_{\text{MOL}} - \int d^3 r \int d^3 r' \frac{\mid \varphi_A(r) \mid^2 \mid \varphi_B(r') \mid^2}{\mid r - r' \mid} \]

\[ \approx 1/R \]

**In TDDFT (single-pole approximation)**

\[ \Omega_{\text{CT}} \approx \varepsilon^{(B)}_{\text{MOL}} - \varepsilon^{(A)}_{\text{MOL}} - \int d^3 r \int d^3 r' \varphi^*_A(r')\varphi_B(r') f_{\text{xc}}(r, r', \Omega_{\text{CT}}) \varphi_A(r)\varphi^*_B(r) \]

Exponentially small \hspace{1cm} Exponentially small

**CONCLUSIONS:** To describe CT excitations correctly

- \( v_{\text{xc}} \) must have proper derivative discontinuities
- \( f_{\text{xc}}(r, r') \) must increase exponentially as function of \( r \) and of \( r' \) for \( \omega \rightarrow \Omega_{\text{CT}} \)
Discontinuity of $v_{xc}(r)$:

$$v_{xc}^+(r) = v_{xc}^-(r) + \Delta_{xc}$$

$\Delta_{xc}$ is constant throughout space

Discontinuity of $f_{xc}(r,r')$:

$$f_{xc}^+(r, r') = f_{xc}^-(r, r') + g_{xc}(r) + g_{xc}(r')$$

M. Hellgren, EKUG, PRA 85, 022514 (2012)
This exponentially increasing behaviour is achieved by the discontinuity:

\[
g_{xc}(r) \sim \frac{\left| \phi_L(r) \right|}{n(r)} \sim e^{-2(\sqrt{2A_s} - \sqrt{1})r} \quad r \to \infty
\]
He-Be neutral diatomic in 1D

\[ F_{HL}(x, \omega) = \int dx' f_x(x, x', \omega) \Phi_{HL}(x') \]

M. Hellgren, EKUG, PRA 85, 022514 (2012)
$\omega_{CT} = \omega_q + 2 \langle q | v + f_x (\omega_q) | q \rangle \rightarrow \omega_q + \Delta_x - 1/R$

M. Hellgren, EKUG, PRA 85, 022514 (2012)
Thanks!