Time-dependent density functional theory

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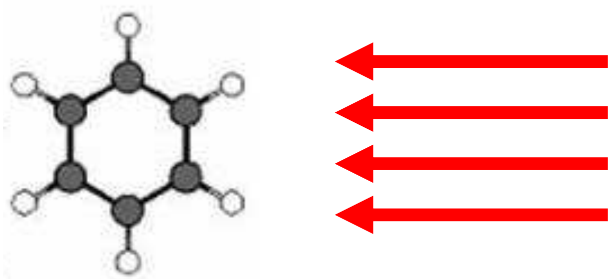
What do we want to describe?

System in laser field:
Generic situation



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

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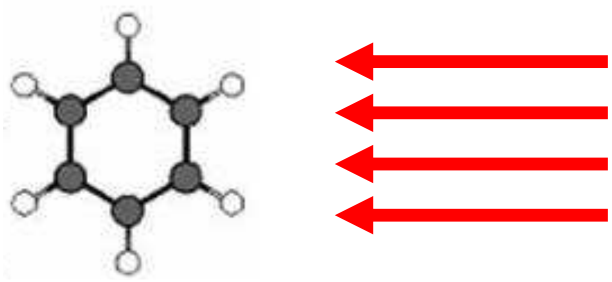

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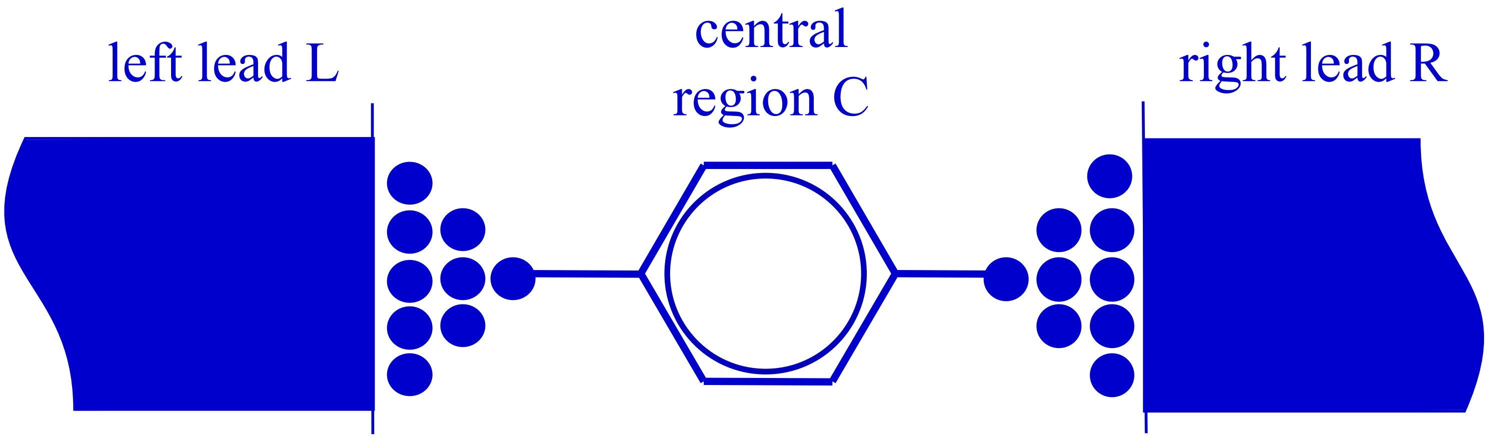
Electronic transport: Generic situation



Bias between L and R is turned on: U(t) ⟶ V

This Hamiltonian involves two approximations:

- Nuclei treated as clamped or moving on classical trajectories
- Photons treated as classical electromagnetic fields

Why don’t we just solve the many-body Schrödinger equation

Example: Oxygen atom (8 electrons)

$\Psi\left(\vec{r}_1, \cdots, \vec{r}_8\right)$ depends on 24 coordinates

rough table of the wavefunction

10 entries per coordinate: ⇒ 10^{24} entries

1 byte per entry: ⇒ 10^{24} bytes

5×10^{9} bytes per DVD: ⇒ 2×10^{14} DVDs

10 g per DVD: ⇒ 2×10^{15} g of DVDs

= 2×10^{9} t of DVDs

Two fundamentally different classes of ab-initio approaches:

- **Wave function approaches**
  - Configuration interaction (also stochastic CI)
  - Tensor networks
- **“Functional Theories”**

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- **Wave function approaches**

  -- Configuration interaction
  (also stochastic CI)
  -- Tensor networks

- **“Functional Theories”**

  **Write total energy as functional
  of a simpler quantity and minimize**

“Functional Theories”

MBPT	**RDMFT**	**DFT**
$G(r, r', t - t')$	$\gamma(r, r') = G(r, r', 0^{+})$	$\rho(r) = \gamma(r, r)$

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$\Phi_{xc}[G]$	$E_{xc}[\gamma]$	$E_{xc}[\varrho]$
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numerically		
heavy	moderate	light

ESSENCE OF DENSITY-FUNTIONAL THEORY

- **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**

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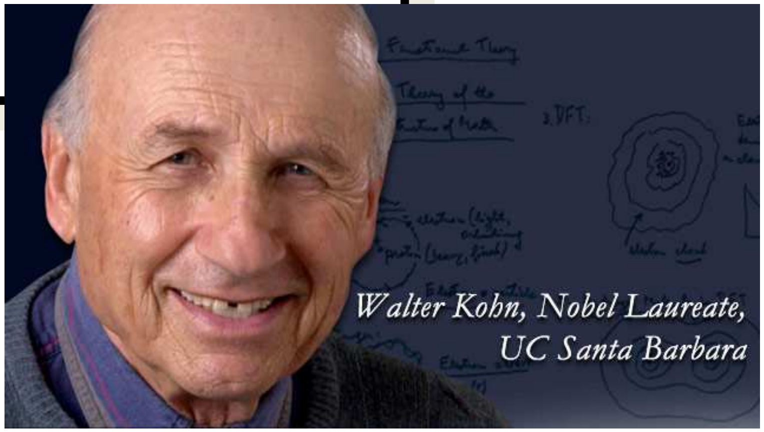
Hohenberg-Kohn theorem (1964)
Kohn-Sham theorem (1965)
(for the ground state)


Walter Kohn, Nobel Laureate,
UC Santa Barbara

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

Strong laser ($v_{laser}(t) \geq v_{en}$) :

Non-perturbative solution of full TDSE required

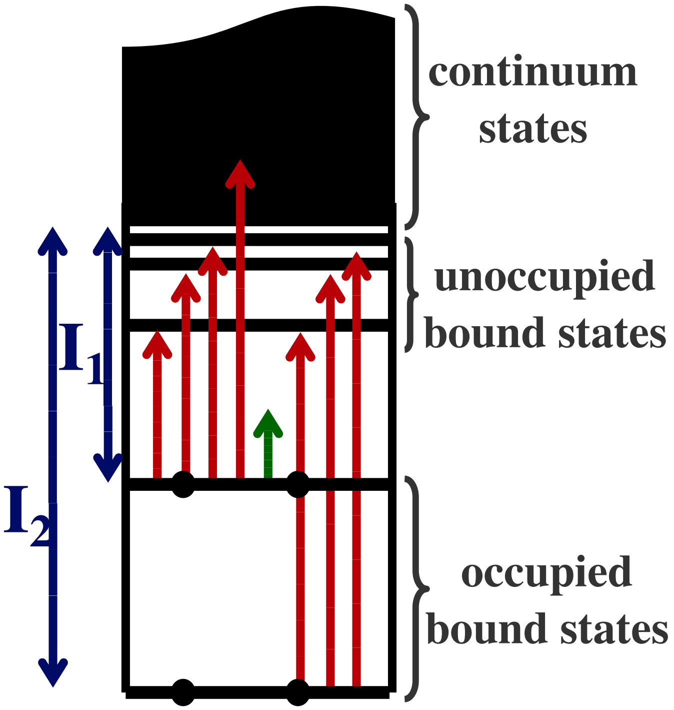
Weak laser ($v_{laser}(t) << v_{en}$) :

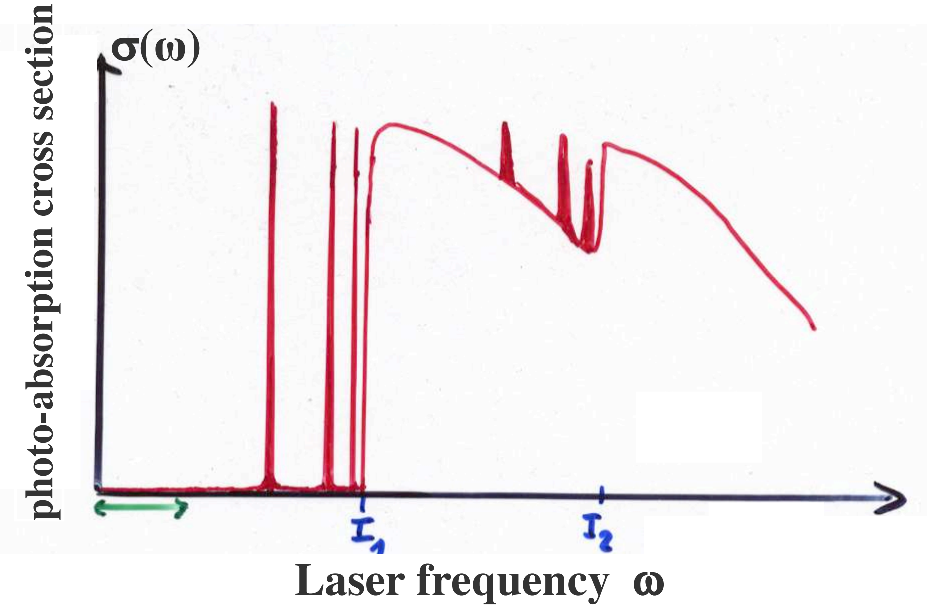
Calculate 1. **Linear density response** $\rho_1(\vec{r}\ t)$

2. **Dynamical polarizability** $\alpha(\omega) = -\frac{e}{E} \int z\, \rho_1(\vec{r}, \omega) d^3r$

3. **Photo-absorption cross section** $\sigma(\omega) = -\frac{4\pi\omega}{c} \mathrm{Im}\,\alpha$

Photo-absorption in weak lasers





OUTLINE

- **Basic theorems of TDDFT**

- **TDDFT in the linear response regime:**
  - -- Dyson equation for the reponse function
  - -- Photo-absorption in molecules
  - -- Photo-absorption in solids

- **Beyond the linear regime:**
  - -- Transport through molecular junctions
  - -- Laser-driven spin dynamics in solids
  - -- Combination of TDDFT with Optimal Control Theory

Basic theorems of TDDFT

(E. Runge, E.K.U.G., PRL 52, 997 (1984))

1-1 correspondence (TD analogue of Hohenberg-Kohn theorem):

$$v(rt) \xleftrightarrow{1\text{-}1} \rho(rt)$$

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

TDKS 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

$$v_S\left[\rho(r't')\right](rt) = v(rt) + \int d^3r' \frac{\rho(r't)}{|r - r'|} + v_{xc}\left[\rho(r't')\right](rt)$$

Basic theorems of TDDFT

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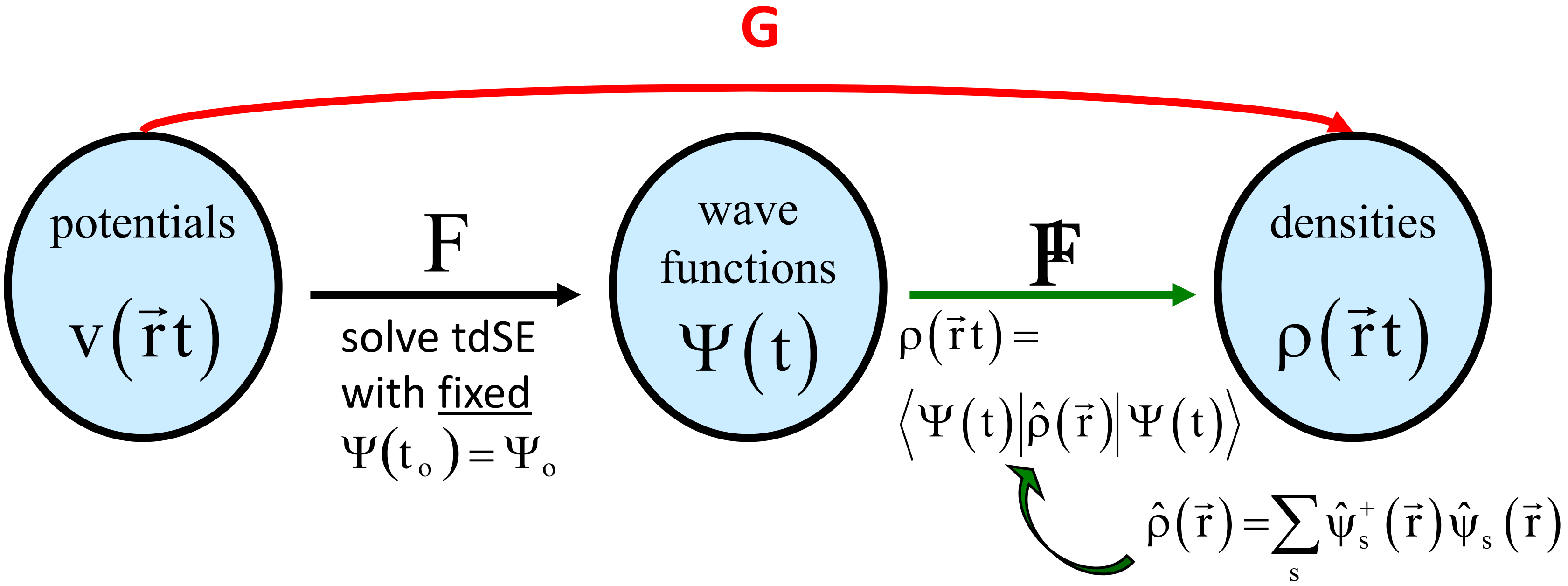
with the local potential

$$v_S\left[\rho(\mathbf{r}'t')\right](\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}\left[\rho(\mathbf{r}'t')\right](\mathbf{r}t)$$

Proof of the 1-1 correspondence between $\mathbf{v}(\vec{\mathbf{r}}\,\mathbf{t})$ and $\boldsymbol{\rho}(\vec{\mathbf{r}}\,\mathbf{t})$

define maps $F: \; v(\vec{r}t) \mapsto \Psi(t)$ $\tilde{F}: \; \Psi(t) \mapsto \rho(\vec{r}t)$



G

potentials $v(\vec{r}t)$

F

solve tdSE with fixed $\Psi(t_o) = \Psi_o$

wave functions $\Psi(t)$

$\tilde{F}$

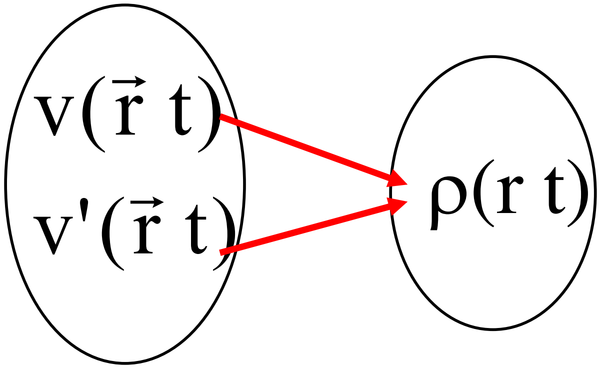
$\rho(\vec{r}t) = \langle \Psi(t) | \hat{\rho}(\vec{r}) | \Psi(t) \rangle$

$\hat{\rho}(\vec{r}) = \sum_s \hat{\psi}_s^+(\vec{r})\hat{\psi}_s(\vec{r})$

densities $\rho(\vec{r}t)$

$$G: \; v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

to be shown that



$$\begin{tikzcd} v(\vec{r}\; t) \arrow[dr] & \\ & \rho(r\; t) \\ v'(\vec{r}\; t) \arrow[ur] & \end{tikzcd}$$

is impossible

i.e. $\mathbf{v(\vec{r}\; t) \neq v'(\vec{r}\; t) + c(t) \;\Rightarrow\; \rho(\vec{r}\; t) \neq \rho'(\vec{r}\; t)}$

proof (basic idea):

$$\begin{tikzcd} v(\vec{r}\; t) \arrow[r] & \vec{j}(\vec{r}\; t) \arrow[r] & \rho(\vec{r}\; t) \\ v'(\vec{r}\; t) \arrow[r] & \vec{j}'(\vec{r}\; t) \arrow[r] & \rho'(\vec{r}\; t) \end{tikzcd}$$

use

$$i\frac{\partial \vec{j}(\vec{r},t)}{\partial t} = \left\langle \Psi(t) \middle| \left[\hat{j}(\vec{r}) \, , \, \hat{H}(t) \right] \middle| \Psi(t) \right\rangle$$

equation of motion for $\vec{j}$

and

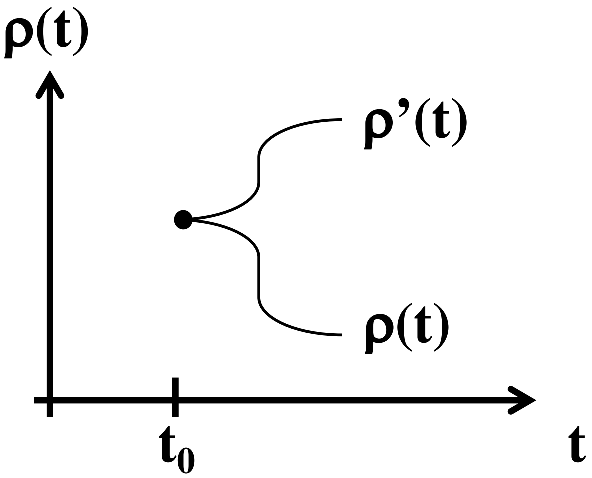
$$\frac{\partial \rho(\vec{r},t)}{\partial t} = -\operatorname{div} j(\vec{r},t)$$

continuity equation

to show that there exists an integer k>0 such that

$$\left.\frac{\partial^k \rho}{\partial t^k}\right|_{t_0} \neq \left.\frac{\partial^k \rho'}{\partial t^k}\right|_{t_0}$$

⇒ ρ and ρ' will become different from each other infinitesimally later than t_0



Simplest possible approximation for $v_{xc}[\rho](\vec{r}t)$

Adiabatic Local Density Approximation (ALDA)

$$v_{xc}^{ALDA}(\vec{r}\,t) := v_{xc,stat}^{hom}(n)\Big|_{n=\rho(\vec{r}\,t)}$$

$v_{xc,stat}^{hom}$ **= xc potential of static homogeneous e-gas**

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Any approximate ground-state-DFT xc functional can be used to generate an adiabatic approximation for TDDFT

$$v_{xc}^{adiab}(\vec{r}\;t) := \;\; v_{xc,GS}^{approx}[n]\Big|_{n=\rho(\vec{r}\;t)}$$

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_o**:**

$$
\begin{aligned}
\rho[v](r\,t) &= \rho[v_0 + v_1](r\,t) \\
&= \rho[v_0](r\,t) && \longrightarrow \rho_o(r) \\
&\quad + \int \left.\frac{\delta\rho[v](r\,t)}{\delta v(r'\,t')}\right|_{v_0} v_1(r'\,t')\,d^3r'\,dt' && \longrightarrow \rho_1(r\,t) \\
&\quad + \frac{1}{2}\int\int \left.\frac{\delta^2\rho[v](r\,t)}{\delta v(r'\,t')\,\delta v(r''\,t'')}\right|_{v_0} v_1(r',t')\,v_1(r'',t'')\,d^3r'\,d^3r''\,dt'\,dt'' && \longrightarrow \rho_2(r\,t) \\
&\quad \vdots
\end{aligned}
$$

$\rho_1(r,t)$ = linear density response of interacting system

$$\chi(r\,t, r'\,t') := \left.\frac{\delta\rho[v](r\,t)}{\delta v(r'\,t')}\right|_{v_0}$$ **= density-density response function of interacting system**

Lehmann representation of the full response function

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

with the exact many-body eigenfunctions and energies of the initial unperturbed interacting system Hamiltnian $H(t_0)|m\rangle = E_m|m\rangle$

⇒ The exact linear density response

$$\rho_1(\omega) = \chi(\omega)\, v_1$$

has poles at the exact excitation energies $\Omega = E_m - E_0$

Analogous functional $\rho_s[v_s](r\,t)$ for non-interacting system

$$\rho_S[v_S](r\,t) = \rho_S[v_{S,0} + v_{S,1}](r\,t) = \rho_S[v_{S,0}](r\,t) + \int \left.\frac{\delta\rho_S[v_S](r\,t)}{\delta v_S(r'\,t')}\right|_{v_{S,0}} v_{S,1}(r'\,t')\, d^3r'\,dt' + \cdots$$

$$\chi_S(r\,t, r'\,t') := \left.\frac{\delta\rho_S[v_S](r\,t)}{\delta v_S(r'\,t')}\right|_{v_{S,0}}$$ = **density-density response function of non-interacting system**

χ_S (r,r',ω) has also poles as function of ω, but at the non-interacting single-particle (KS) excitation energies.

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**

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

v_{xc} is well-defined through the non-interacting and the interacting 1-1 mapping.

$$\begin{tikzcd}[column sep=huge]
\mathbf{v}_{ext}[\boldsymbol{\rho}](\mathbf{r},\mathbf{t}) \arrow[r, leftrightarrow, "\text{1-1 mapping for interacting particles}"] & \boldsymbol{\rho}(\mathbf{r},\mathbf{t}) \arrow[r, leftrightarrow, "\text{1-1 mapping for non-interacting particles}"] & \mathbf{v}_s[\boldsymbol{\rho}](\mathbf{r},\mathbf{t})
\end{tikzcd}$$

$$\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0} = \left.\frac{\delta v_{S}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0} - \left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}$$

$$\underset{\overset{\uparrow}{f_{xc}(r\,t,r'\,t')}}{\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}}} = \underset{\overset{\uparrow}{\chi_S^{-1}(r\,t,r'\,t')}}{\left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}}} - \underset{\overset{\uparrow}{\chi^{-1}(r\,t,r'\,t')}}{\left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}}} - \underset{\overset{\uparrow}{W_C(r\,t,r'\,t')}}{\frac{\delta(t-t')}{|r-r'|}}$$

$$\begin{array}{ccccccc}
\left.\dfrac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}} & = & \left.\dfrac{\delta v_S[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}} & - & \left.\dfrac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\boldsymbol{\rho_0}} & - & \dfrac{\delta(t-t')}{|r-r'|} \\
\uparrow & & \uparrow & & \uparrow & & \uparrow \\
f_{xc}(r\,t, r'\,t') & & \chi_S^{-1}(r\,t, r'\,t') & & \chi^{-1}(r\,t, r'\,t') & & W_C(r\,t, r'\,t')
\end{array}$$

$$f_{xc} + W_C = \chi_S^{-1} - \chi^{-1}$$

$$\underset{\displaystyle f_{xc}(r\,t, r'\,t')}{\underset{\uparrow}{\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}}} = \underset{\displaystyle \chi_S^{-1}(r\,t, r'\,t')}{\underset{\uparrow}{\left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}}} - \underset{\displaystyle \chi^{-1}(r\,t, r'\,t')}{\underset{\uparrow}{\left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}}} - \underset{\displaystyle W_C(r\,t, r'\,t')}{\underset{\uparrow}{\frac{\delta(t-t')}{|r-r'|}}}$$

$$\chi_S \bullet \left| f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \right| \bullet \chi$$

$$\underset{\underset{f_{xc}(r\,t, r'\,t')}{\uparrow}}{\left.\frac{\delta v_{xc}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}} = \underset{\underset{\chi_S^{-1}(r\,t, r'\,t')}{\uparrow}}{\left.\frac{\delta v_S[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}} - \underset{\underset{\chi^{-1}(r\,t, r'\,t')}{\uparrow}}{\left.\frac{\delta v_{ext}[\rho](r\,t)}{\delta\rho(r'\,t')}\right|_{\rho_0}} - \underset{\underset{W_C(r\,t, r'\,t')}{\uparrow}}{\frac{\delta(t-t')}{|r-r'|}}$$

$$\chi_S \bullet \left| f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \right| \bullet \chi$$

$$\chi_S \left(f_{xc} + W_C \right) \chi = \chi - \chi_S$$

$$\chi = \chi_S + \chi_S \left(W_{ee} + f_{xc} \right) \chi$$

Act with this operator equation on arbitrary $\mathbf{v_1(r\ t)}$ and use $\boldsymbol{\chi}\ \mathbf{v_1 = \rho_1}$:

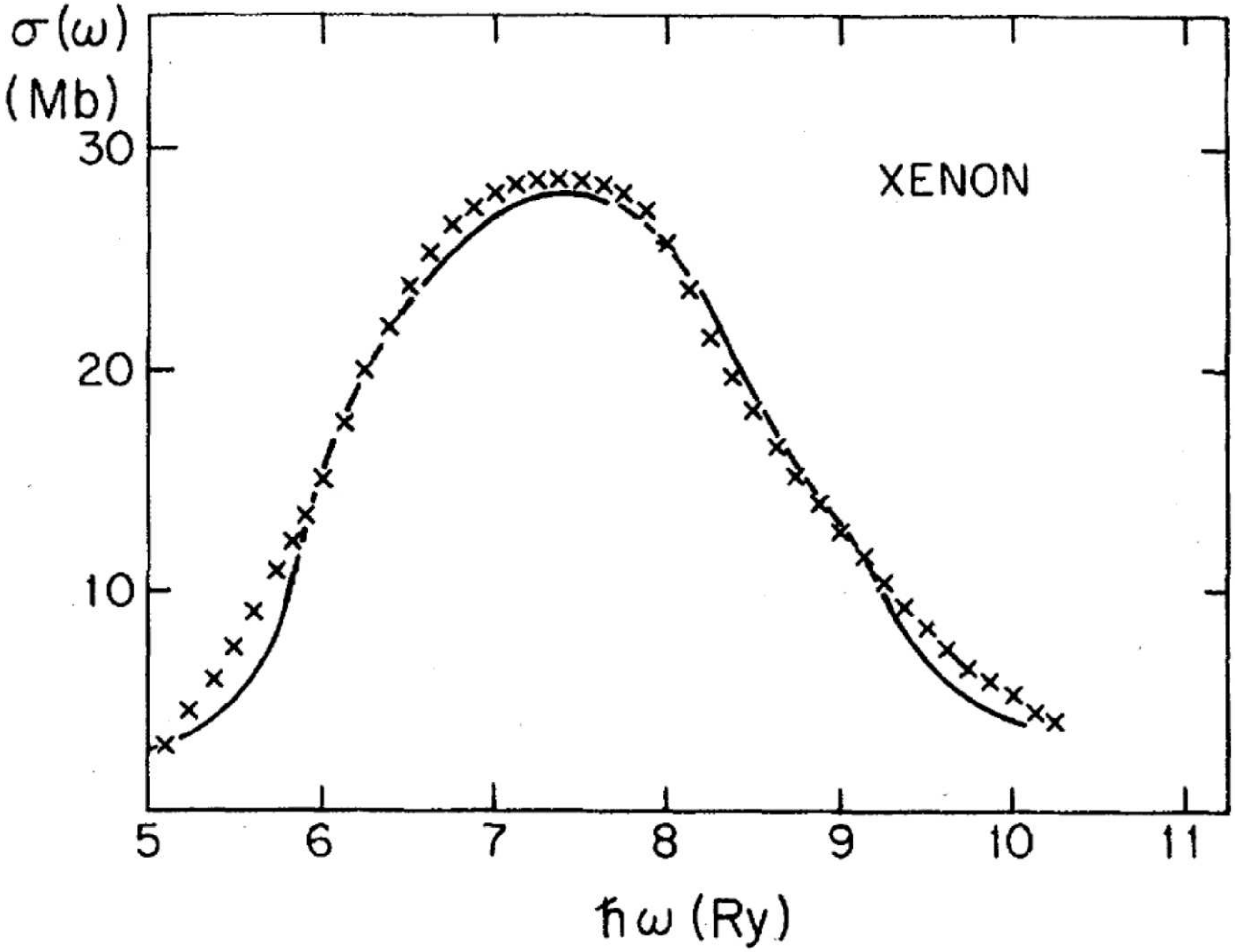
$$\boxed{\boldsymbol{\rho}_1 (\mathbf{r\ t}) = \int \mathbf{d^3r'dt'}\chi_S (\mathbf{r\ t,r't'}) \left[\mathbf{v}_1 (\mathbf{r\ t}) + \int \mathbf{d^3r''dt''} \left\{ \mathbf{W}_{ee} (\mathbf{r't',r''t''}) + \mathbf{f}_{xc} (\mathbf{r't',r''t''}) \right\} \boldsymbol{\rho}_1 (\mathbf{r''t''}) \right]}$$

- Exact integral equation for $\rho_1(r\ t)$, to be solved iteratively

- Need approximation for $f_{xc}\left(r'\,t', r''\,t''\right) = \left.\dfrac{\delta v_{xc}[\rho](r'\,t')}{\delta\rho(r''\,t'')}\right|_{\rho_0}$

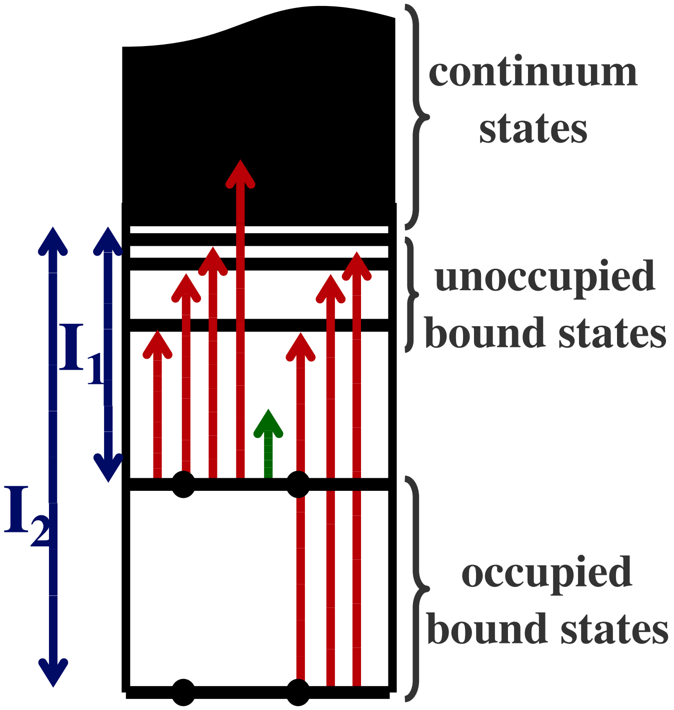
  (either for f_{xc} directly or for v_{xc})

Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.



Solid line: self-consistent time-dependent KS calculation [A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980)]; crosses: experimental data [R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. 188, 1375 (1969)].

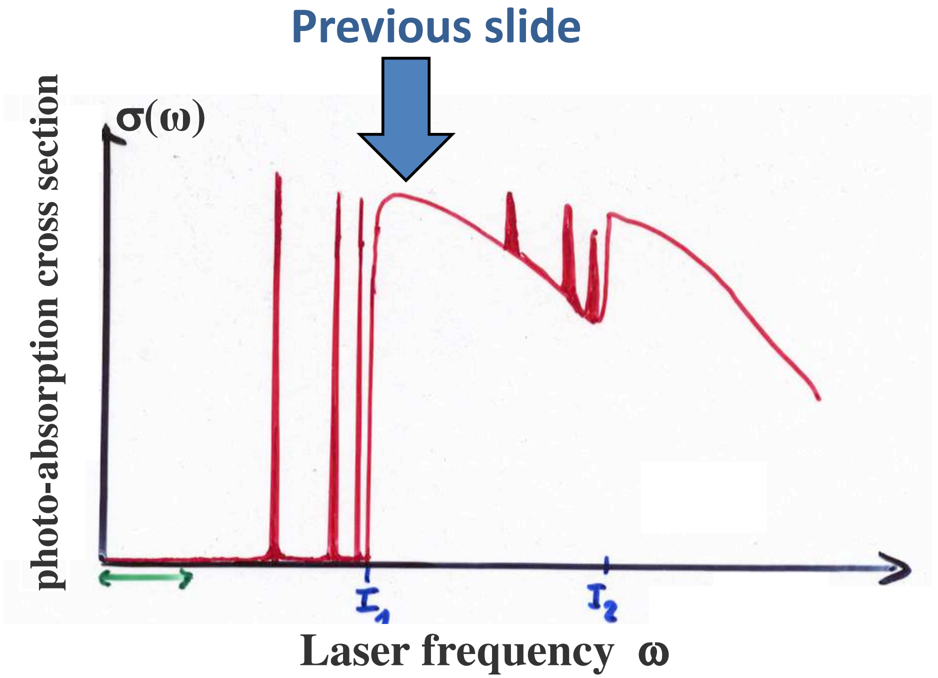
Photo-absorption in weak lasers



continuum states

unoccupied bound states

occupied bound states


Previous slide

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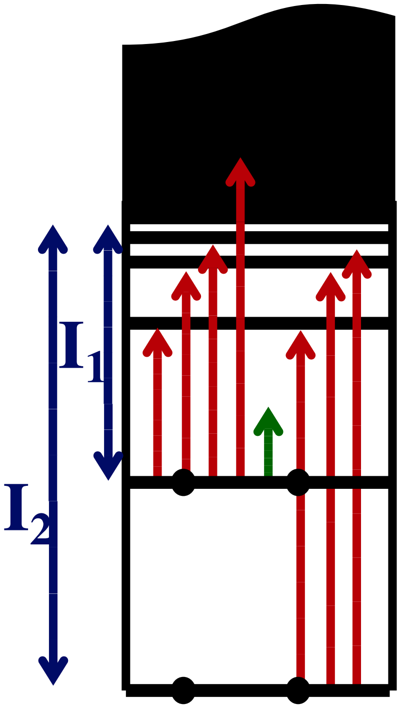

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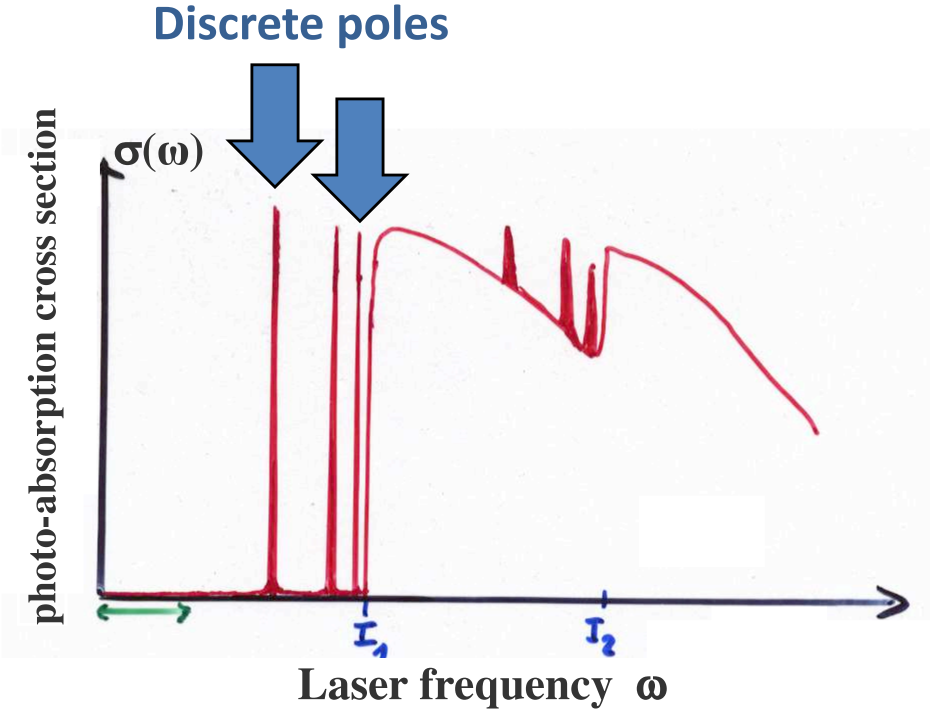

Looking at those frequencies, Ω, for which $\varrho_1(\omega)$ has poles, leads to a (non-linear) eigenvalue equation

M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)
T. Grabo, M. Petersilka, EKUG, J. Mol. Struc. (Theochem) 501, 353 (2000)
M.E. Casida, Recent Advances in Density Functional Methods I, 155 (1996)

$$\boxed{\sum_{q'} \left(A_{qq'}(\Omega) + \omega_q \delta_{qq'} \right) \beta_{q'} = \Omega \beta_q}$$

where

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

$q = (j, a)$ double index $\qquad \alpha_q = f_a - f_j$

$\Phi_q(r) = \varphi_a^*(r) \varphi_j(r) \qquad \omega_q = \varepsilon_a - \varepsilon_j$

Atom	Experimental Excitation Energies $^1S \rightarrow {}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	TDDFT
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

Excitation energies of CO molecule [mH]

State	$\Omega_{\text{expt KS}}$	KS-transition	$\Delta\epsilon_{\text{KS}}$	TDDFT
A $^1\Pi$	312.7	$5\sigma \rightarrow 2\pi$	252.3	310.2
a $^3\Pi$	232.3			221.4
I $^1\Sigma^-$	363.1	$1\pi \rightarrow 2\pi$	362.6	362.6
e $^3\Sigma^-$	363.1			362.6
a’ $^3\Sigma^+$	312.7			314.9
D $^1\Delta$	375.9			380.7
d $^3\Delta$	344.0			339.6

Molecular excitation energies from time-dependent density-functional theory
T Grabo, M Petersilka, EKU Gross, J Mol Struc-Theochem 501, 353 (2000).

Failures of ALDA in the linear response regime

- **H_2 dissociation is incorrect:**

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(see: Gritsenko, van Gisbergen, Görling, Baerends, J. Chem. Phys. 113, 8478 (2000))

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These difficulties have largely been solved by xc functionals more advanced than ALDA