

Time-dependent density functional theory

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DAY 1

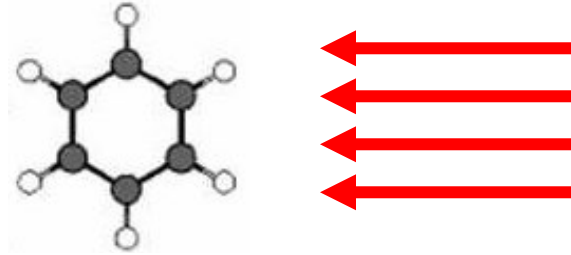
- Basic theorems of TDDFT
- TDDFT in the linear response regime:
 - Dyson-like equation for the response function
 - Calculation of photo-absorption spectra

DAY 2

- TDDFT beyond the linear regime:
 - Ultrafast laser-driven spin dynamics
 - xc functional for non-collinear magnetism

What do we want to describe?

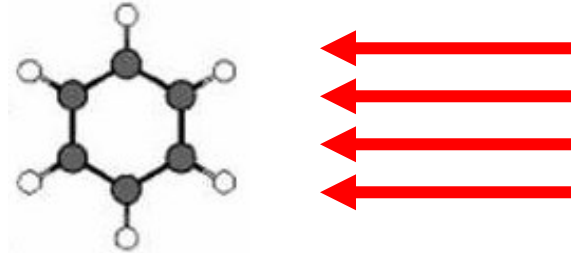
System in laser field:
Generic situation



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

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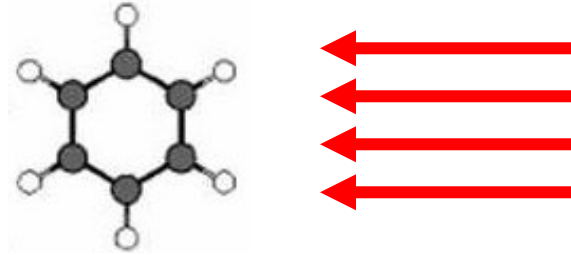
System in laser field:
Generic situation



$$\hat{H}(t) = \hat{T}_e + \hat{T}_n + \hat{W}_{ee} + \hat{W}_{nn} + \underbrace{\sum_{j,\alpha} -\frac{Z_\alpha e^2}{|\mathbf{r}_j - \mathbf{R}_\alpha|} + \vec{r}_j \cdot \vec{E}(t) \cdot \sin \omega t}_{\hat{V}_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)}$$

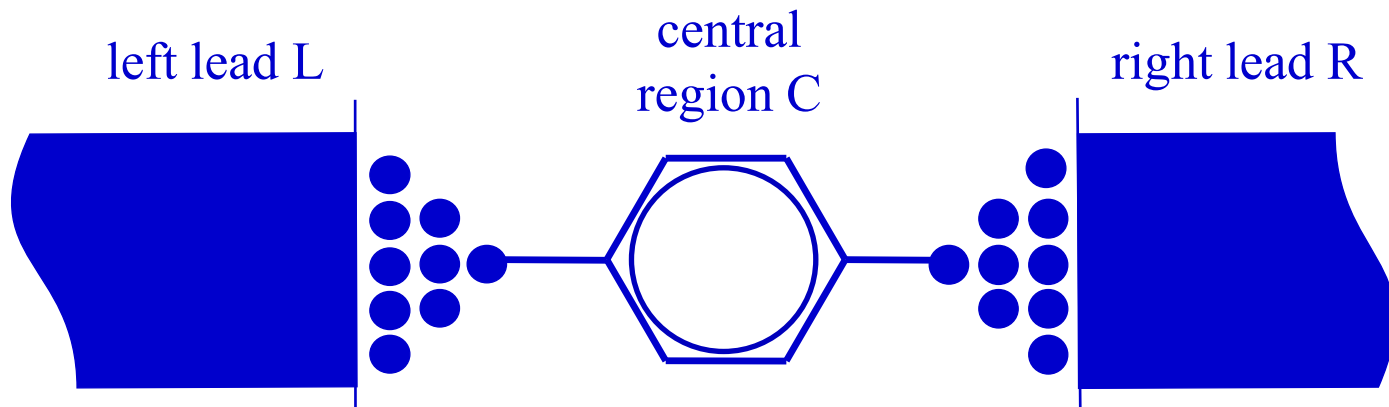
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Generic situation



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Electronic transport: Generic situation



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

Why don't we just solve the many-particle SE?

Example: Aluminium atom (13 electrons)

$\Psi(\vec{r}_1, \dots, \vec{r}_{13})$ depends on 39 coordinates

rough table of the wavefunction

10 entries per coordinate: $\Rightarrow 10^{39}$ entries

1 byte per entry: $\Rightarrow 10^{39}$ bytes

10^{12} bytes per SSD: $\Rightarrow 10^{27}$ SSDs

20 g per SSD: $\Rightarrow 2 \times 10^{28}$ g SSDs (4x earth)

For Ti atom the required mass of SSDs exceeds mass of the universe

ESSENCE OF DENSITY-FUNCTIONAL 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

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

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

Non-perturbative solution of full TDSE required

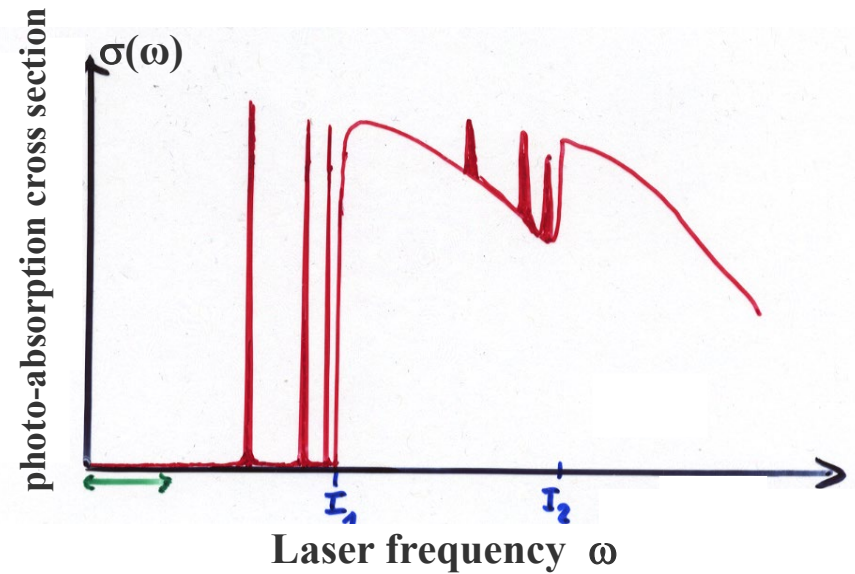
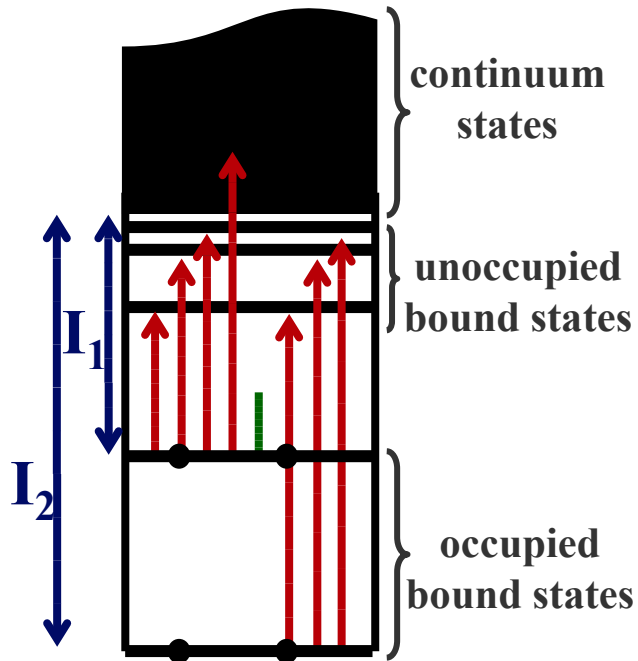
Weak laser ($v_{\text{laser}}(\mathbf{t}) \ll v_{\text{en}}$) :

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

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

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

Photo-absorption in weak lasers



Basic theorems of TDDFT

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

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

$v(\mathbf{r}t) \xleftrightarrow{1-1} \rho(\mathbf{r}t)$ 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

$$\rho(\mathbf{r}t) = \sum_{j=1}^N \left| \varphi_j(\mathbf{r}t) \right|^2$$

of an auxiliary non-interacting (KS) system

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

with the local potential

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

Basic theorems of TDDFT

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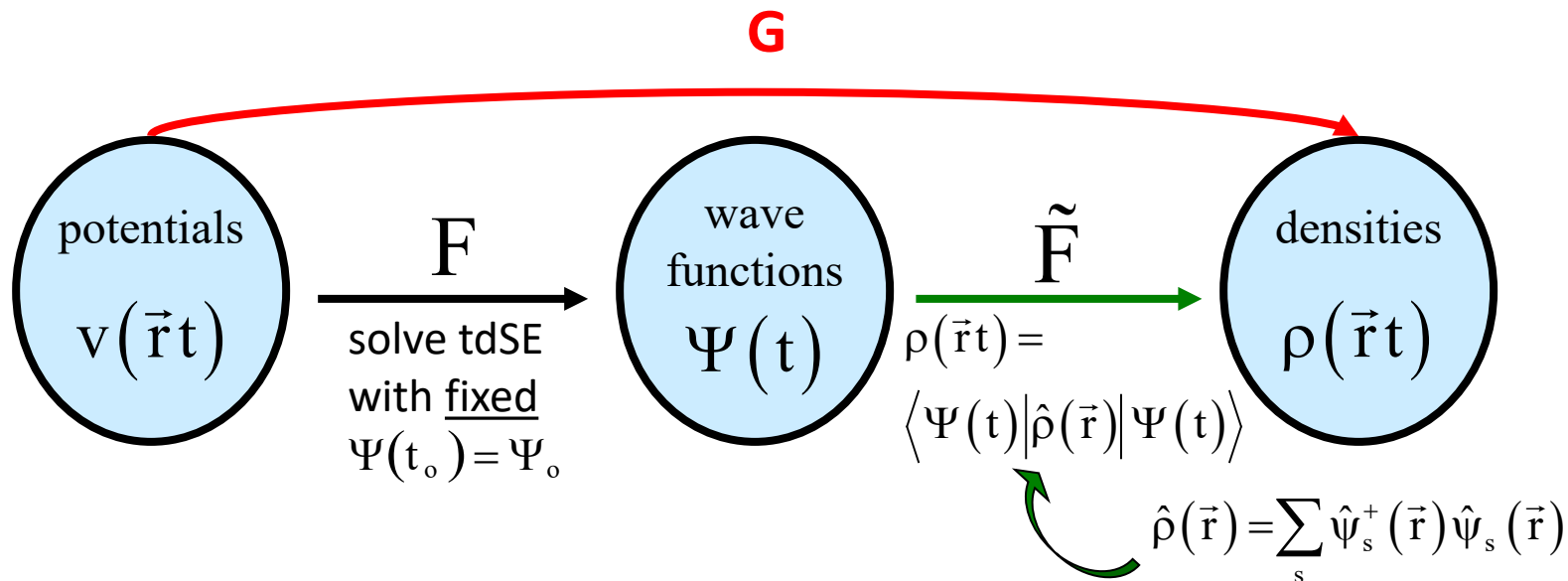
$$v_s[\rho(\mathbf{r}'t')](\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[\rho(\mathbf{r}'t')](\mathbf{r}t)$$

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

define maps

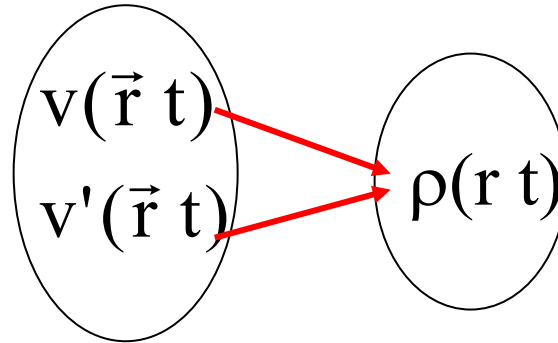
$$F: v(\vec{r}t) \mapsto \Psi(t)$$

$$\tilde{F}: \Psi(t) \mapsto \rho(\vec{r}t)$$



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

to be shown that



is impossible

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

proof (basic idea):

$$\begin{array}{l} v(\vec{r}, t) \xrightarrow{\text{red}} \vec{j}(\vec{r}, t) \xrightarrow{\text{green}} \rho(\vec{r}, t) \\ v'(\vec{r}, t) \xrightarrow{\text{red}} \vec{j}'(\vec{r}, t) \xrightarrow{\text{green}} \rho'(\vec{r}, t) \end{array}$$

use

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

equation of motion for \vec{j}

and

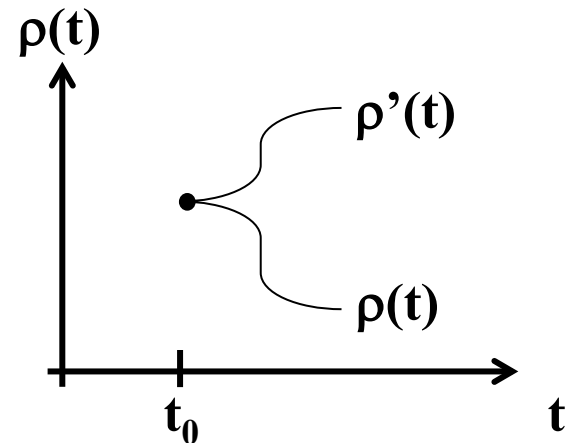
$$\frac{\partial \rho(\vec{r}, t)}{\partial t} = -\text{div } \vec{j}(\vec{r}, t)$$

continuity equation

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

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

$\Rightarrow \rho$ 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)

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

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

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

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

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

LINEAR RESPONSE THEORY

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

$t > t_0$: Switch on perturbation $\mathbf{v}_1(\mathbf{r}, t)$ (with $\mathbf{v}_1(\mathbf{r}, t_0) = 0$).

Density: $\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t)$

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

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

$$\begin{aligned}
 \rho[v](\mathbf{r}, t) &= \rho[v_0 + \mathbf{v}_1](\mathbf{r}, t) \\
 &= \rho[v_0](\mathbf{r}, t) && \longrightarrow \rho_0(\mathbf{r}) \\
 &\quad + \int \frac{\delta\rho[v](\mathbf{r}, t)}{\delta v(\mathbf{r}', t')} \Big|_{v_0} \mathbf{v}_1(\mathbf{r}', t') d^3r' dt' && \longrightarrow \rho_1(\mathbf{r}, t) \\
 &\quad + \frac{1}{2} \iint \frac{\delta^2\rho[v](\mathbf{r}, t)}{\delta v(\mathbf{r}', t')\delta v(\mathbf{r}'', t'')} \Big|_{v_0} \mathbf{v}_1(\mathbf{r}', t')\mathbf{v}_1(\mathbf{r}'', t'') d^3r' d^3r'' dt' dt'' && \longrightarrow \rho_2(\mathbf{r}, t) \\
 &\quad \vdots
 \end{aligned}$$

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

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

Lehmann representation of the full response function

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

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

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

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

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

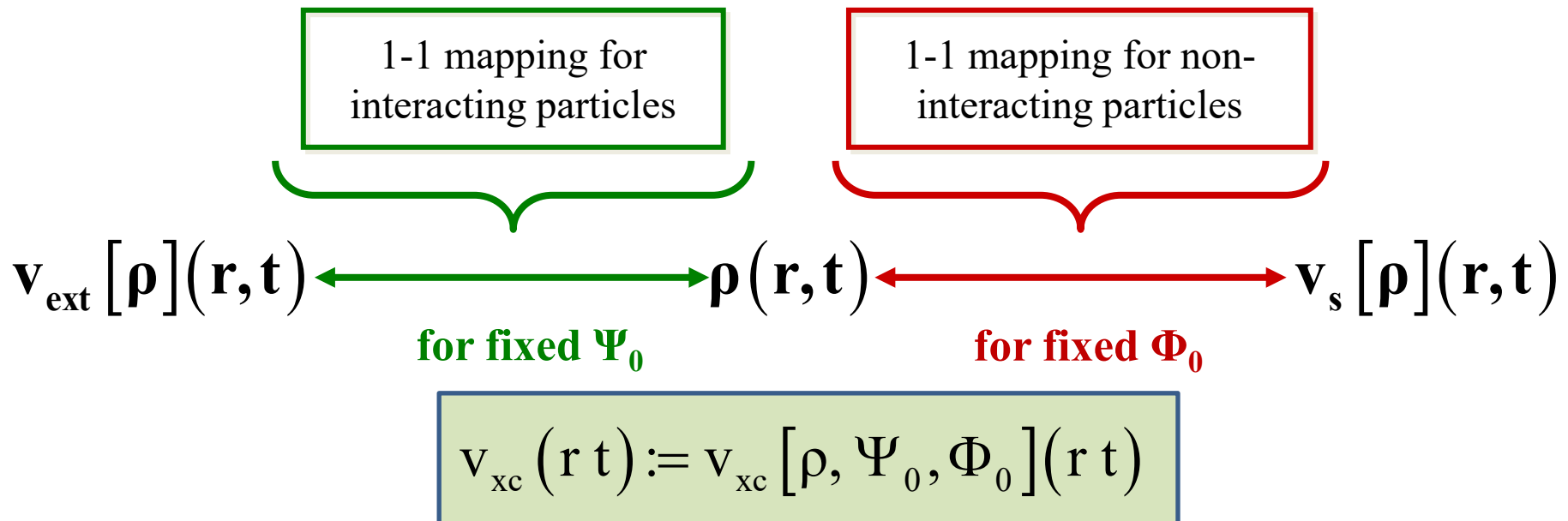
$\chi_s(r, r', \omega)$ has also poles as function of ω , but at the non-interacting single-particle (KS) excitation energies.

GOAL: Find a way to calculate $\rho_1(\mathbf{r}, t)$ without explicitly evaluating $\chi(\mathbf{r}, t, \mathbf{r}', t')$ of the interacting system

starting point: Definition of xc potential

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

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



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

$$\begin{aligned}
\left. \frac{\delta v_{\text{xc}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} &= \left. \frac{\delta v_{\text{S}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} - \left. \frac{\delta v_{\text{ext}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} - \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad \uparrow \qquad \qquad \qquad \uparrow \qquad \qquad \qquad \uparrow \qquad \qquad \qquad \uparrow \\
&\quad \mathbf{f}_{\text{xc}}(\mathbf{r}, t, \mathbf{r}', t') \qquad \chi_{\text{S}}^{-1}(\mathbf{r}, t, \mathbf{r}', t') \qquad \chi^{-1}(\mathbf{r}, t, \mathbf{r}', t') \qquad \mathbf{W}_{\text{C}}(\mathbf{r}, t, \mathbf{r}', t')
\end{aligned}$$

$$\begin{aligned}
\left. \frac{\delta v_{\text{xc}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} &= \left. \frac{\delta v_{\text{S}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} - \left. \frac{\delta v_{\text{ext}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} - \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} \\
\uparrow & \qquad \qquad \qquad \uparrow & \qquad \qquad \qquad \uparrow & \qquad \qquad \qquad \uparrow \\
\mathbf{f}_{\text{xc}}(\mathbf{r}, t, \mathbf{r}', t') & \qquad \chi_{\text{S}}^{-1}(\mathbf{r}, t, \mathbf{r}', t') & \qquad \chi^{-1}(\mathbf{r}, t, \mathbf{r}', t') & \qquad \mathbf{W}_{\text{C}}(\mathbf{r}, t, \mathbf{r}', t')
\end{aligned}$$

$$\mathbf{f}_{\text{xc}} + \mathbf{W}_{\text{C}} = \chi_{\text{S}}^{-1} - \chi^{-1}$$

$$\begin{array}{cccc}
\left. \frac{\delta v_{\text{xc}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & = & \left. \frac{\delta v_{\text{S}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & - & \left. \frac{\delta v_{\text{ext}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & - & \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} \\
\uparrow & & \uparrow & & \uparrow & & \uparrow \\
\mathbf{f}_{\text{xc}}(\mathbf{r}, t, \mathbf{r}', t') & & \chi_{\text{S}}^{-1}(\mathbf{r}, t, \mathbf{r}', t') & & \chi^{-1}(\mathbf{r}, t, \mathbf{r}', t') & & \mathbf{W}_{\text{C}}(\mathbf{r}, t, \mathbf{r}', t')
\end{array}$$

$$\chi_{\text{S}} \cdot \left| \mathbf{f}_{\text{xc}} + \mathbf{W}_{\text{C}} = \chi_{\text{S}}^{-1} - \chi^{-1} \right| \cdot \chi$$

$$\begin{array}{cccc}
\left. \frac{\delta v_{xc}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & = & \left. \frac{\delta v_s[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & - & \left. \frac{\delta v_{ext}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} & - & \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} \\
\uparrow & & \uparrow & & \uparrow & & \uparrow \\
\mathbf{f}_{xc}(\mathbf{r}, t, \mathbf{r}', t') & & \chi_S^{-1}(\mathbf{r}, t, \mathbf{r}', t') & & \chi^{-1}(\mathbf{r}, t, \mathbf{r}', t') & & \mathbf{W}_C(\mathbf{r}, t, \mathbf{r}', t')
\end{array}$$

$$\chi_S \cdot \left| \mathbf{f}_{xc} + \mathbf{W}_C = \chi_S^{-1} - \chi^{-1} \right| \cdot \chi$$

$$\chi_S (\mathbf{f}_{xc} + \mathbf{W}_C) \chi = \chi - \chi_S$$

$$\chi = \chi_S + \chi_S \left(\mathbf{W}_{ee} + \mathbf{f}_{xc} \right) \chi$$

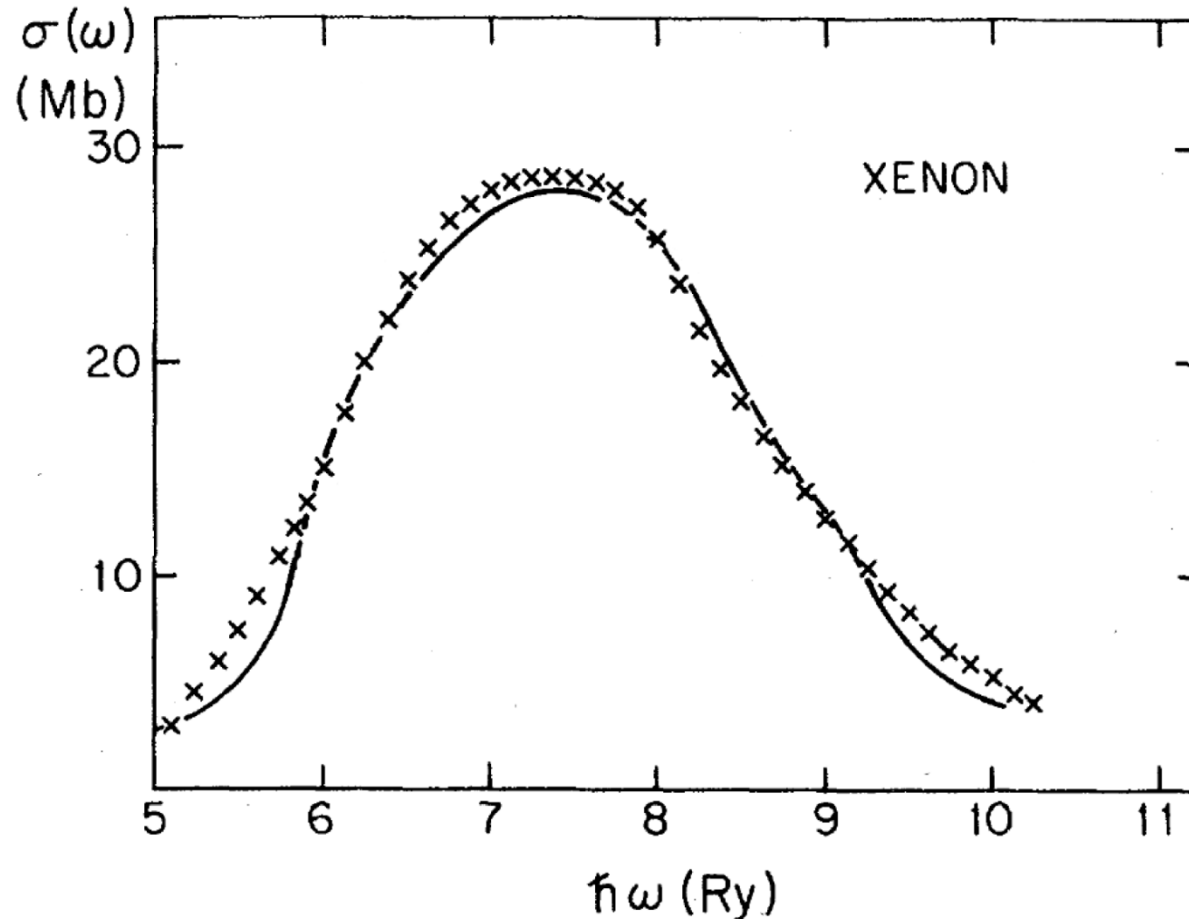
Act with this operator equation on arbitrary $\mathbf{v}_1(\mathbf{r}, t)$ and use $\chi \mathbf{v}_1 = \rho_1$:

$$\rho_1(\mathbf{r}, t) = \int d^3\mathbf{r}' dt' \chi_S(\mathbf{r}, t, \mathbf{r}', t') \left[\mathbf{v}_1(\mathbf{r}, t) + \int d^3\mathbf{r}'' dt'' \{ \mathbf{W}_{ee}(\mathbf{r}', t', \mathbf{r}'', t'') + \mathbf{f}_{xc}(\mathbf{r}', t', \mathbf{r}'', t'') \} \rho_1(\mathbf{r}'', t'') \right]$$

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

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

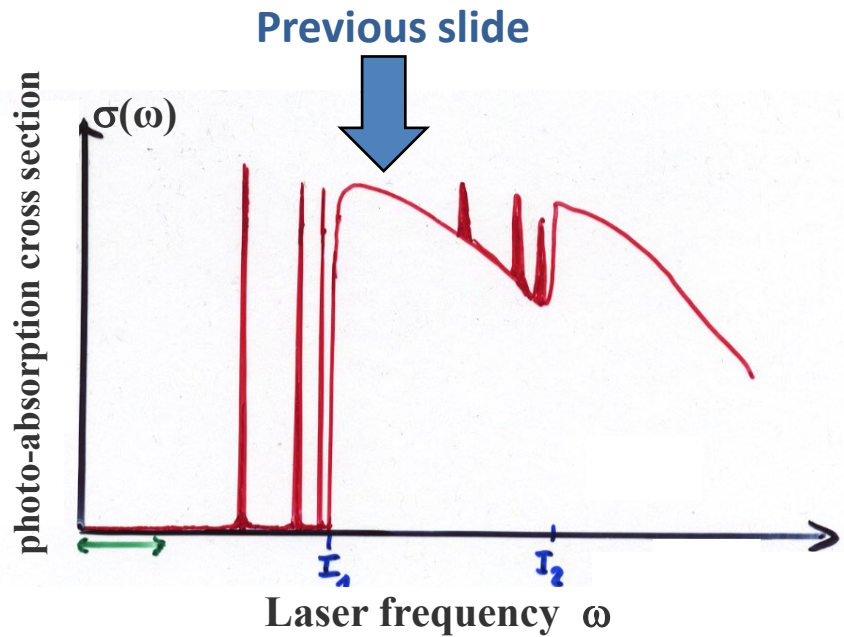
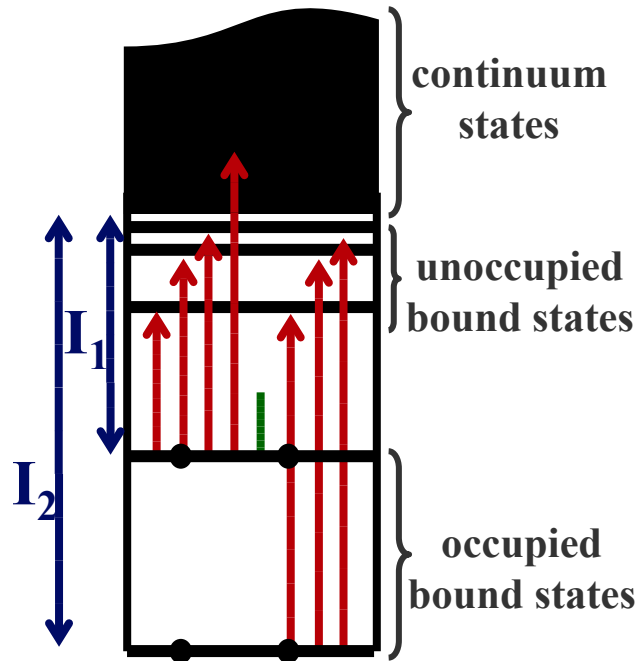
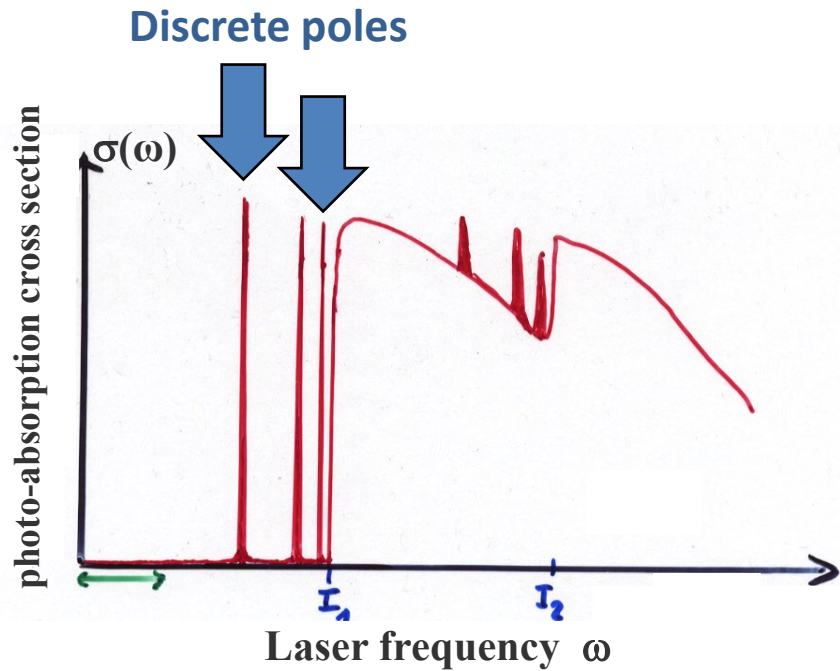
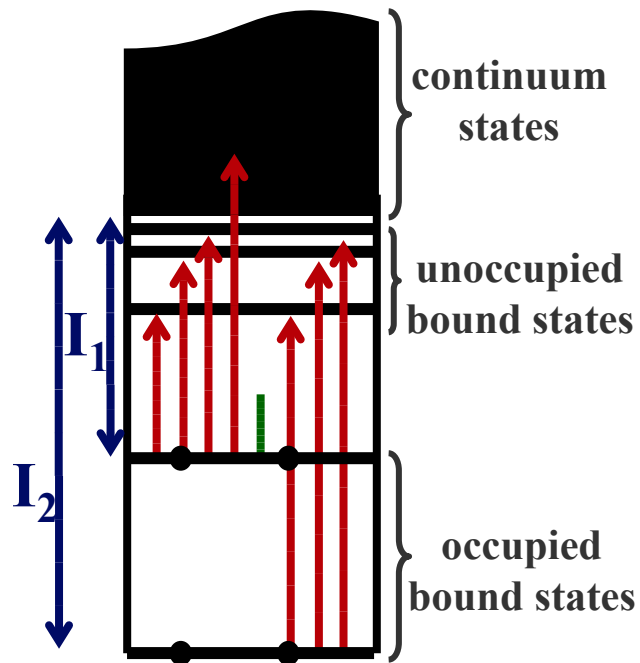


Photo-absorption in weak lasers



Looking at those frequencies, Ω , for which $\rho_1(\omega)$ 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)

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

where

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

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

$$\alpha_q = f_a - f_j$$

$$\Phi_q(\mathbf{r}) = \varphi_a^*(\mathbf{r}) \varphi_j(\mathbf{r})$$

$$\omega_q = \varepsilon_a - \varepsilon_j$$

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, EKV Gross, J Mol Struct-Theochem 501, 353 (2000).**

Failures of ALDA in the linear response regime

- **H₂ dissociation is incorrect:**

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

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

- **response of long chains strongly overestimated**

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

- **in periodic solids, $f_{xc}^{ALDA}(q, \omega, \rho) = c(\rho)$ whereas,**

for insulators, $f_{xc}^{exact} \xrightarrow{q \rightarrow 0} 1/q^2$ divergent.

- **charge-transfer excitations not properly described**

(see: Dreuw et al., J. Chem. Phys. 119, 2943 (2003))

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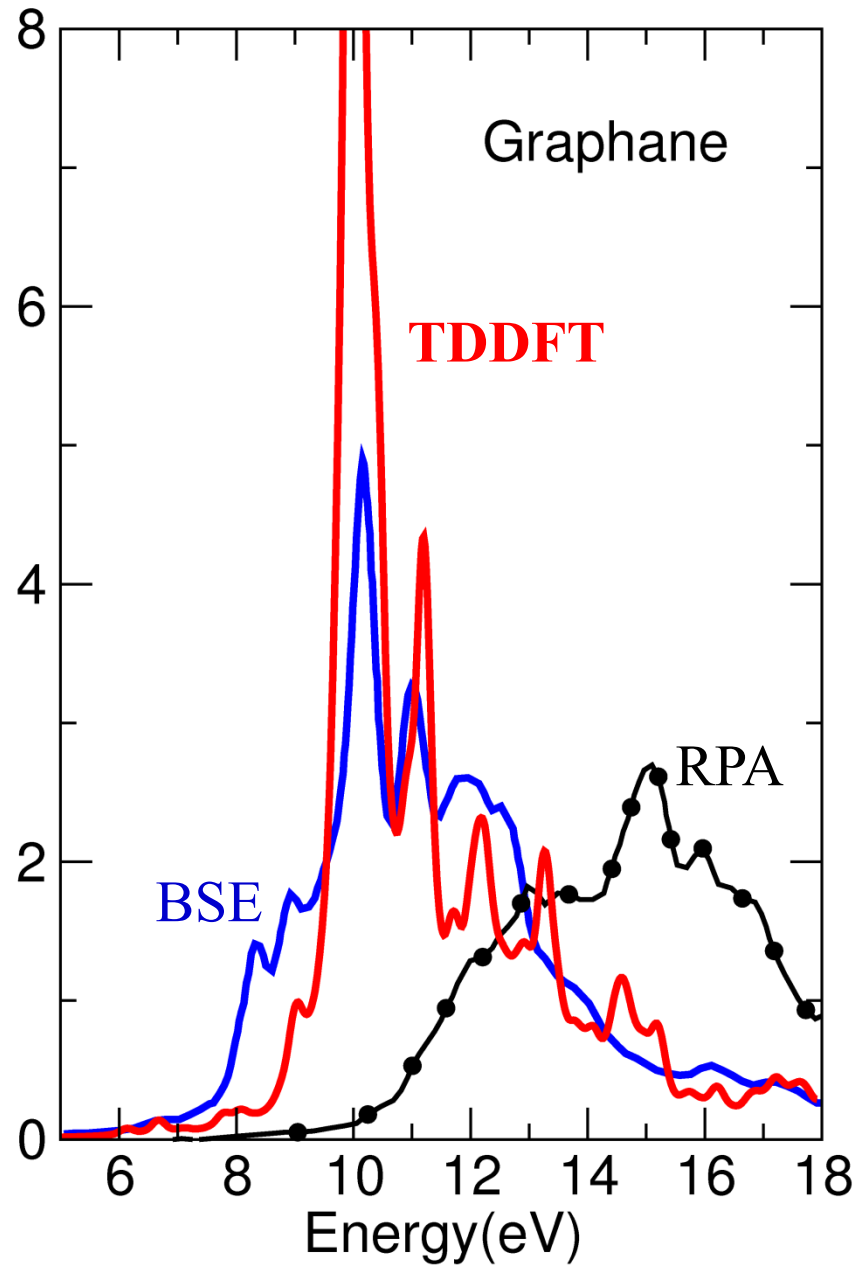
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(see: Dreuw et al., J. Chem. Phys. 119, 2943 (2003))

These difficulties have largely been solved by xc functionals more advanced than ALDA. But no single functional cures all problems!

Linear-response TDDFT is now being used to predict and to interpret experimental optical spectra in essentially all corners of physics and chemistry.

Some examples:

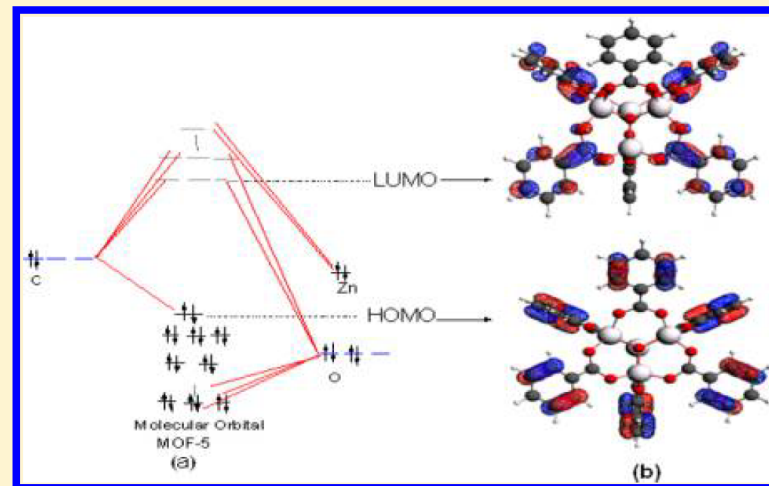


Luminescent Properties of Metal–Organic Framework MOF-5: Relativistic Time-Dependent Density Functional Theory Investigations

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ABSTRACT: The electronically excited state and luminescence property of metal–organic framework MOF-5 were investigated using relativistic density functional theory (DFT) and time-dependent DFT (TDDFT). The geometry, IR spectra, and UV–vis spectra of MOF-5 in the ground state were calculated using relativistic DFT, leading to good agreement between the experimental and theoretical results. The frontier molecular orbitals and electronic configuration indicated that the luminescence mechanism in MOF-5 follows ligand-to-ligand charge transfer (LLCT), namely, $\pi^* \rightarrow \pi$, rather than emission with the ZnO quantum dot (QD) proposed by Bordiga et al. The geometry and IR spectra of MOF-5 in the electronically excited state have been calculated using the relativistic TDDFT and compared with those for the ground state. The comparison reveals that the Zn_4O_{13} QD is rigid, whereas the ligands BDC^{2-} are nonrigid. In addition, the calculated emission band of MOF-5 is in good agreement with the experimental result and is similar to that of the ligand H_2BDC . The combined results confirmed that the luminescence mechanism for MOF-5 should be LLCT with little mixing of the ligand-to-metal charge transfer. The reason for the MOF-5 luminescence is explained by the excellent coplanarity between the six-membered ring consisting of zinc, oxygen, carbon, and the benzene ring.



A NANOPLASMONIC SWITCH BASED ON MOLECULAR MACHINES

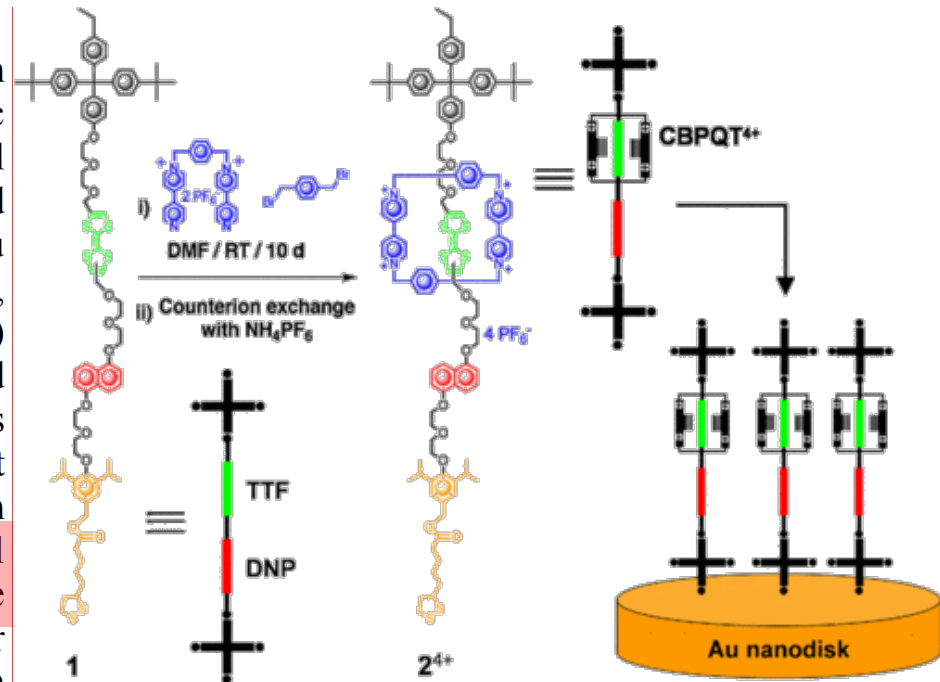
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ABSTRACT

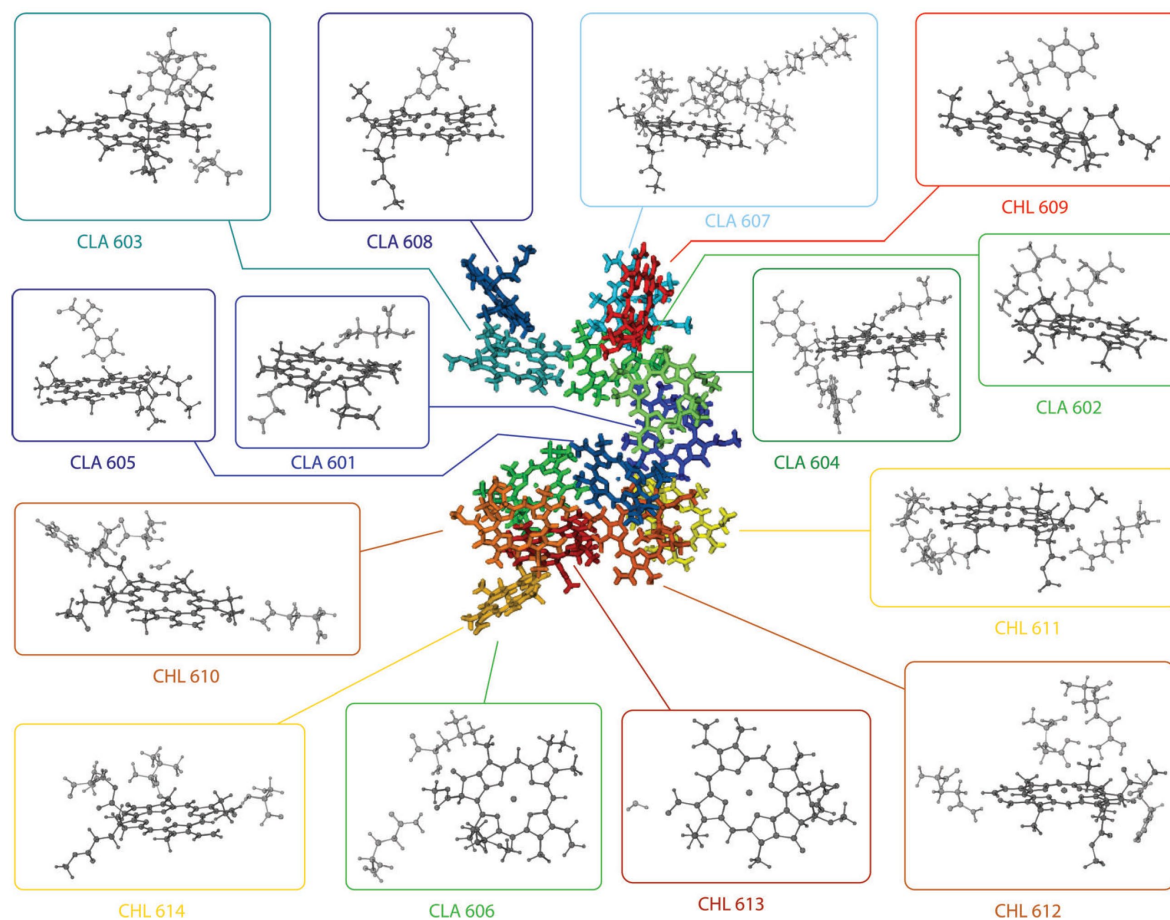
We aim to develop a molecular-machine-driven nanoplasmonic switch for its use in future nanophotonic integrated circuits (ICs) that have applications in optical communication, information processing, biological and chemical sensing. Experimental data show that an Au nanodisk array, coated with rotaxane molecular machines, switches its localized surface plasmon resonances (LSPR) reversibly when it is exposed to chemical oxidants and reductants. Conversely, bare Au nanodisks and disks coated with mechanically inert control compounds, do not display the same switching behavior. Along with calculations based on time-dependent density functional theory (TDDFT), these observations suggest that the nanoscale movements within surface-bound “molecular machines” can be used as the active components in plasmonic devices.

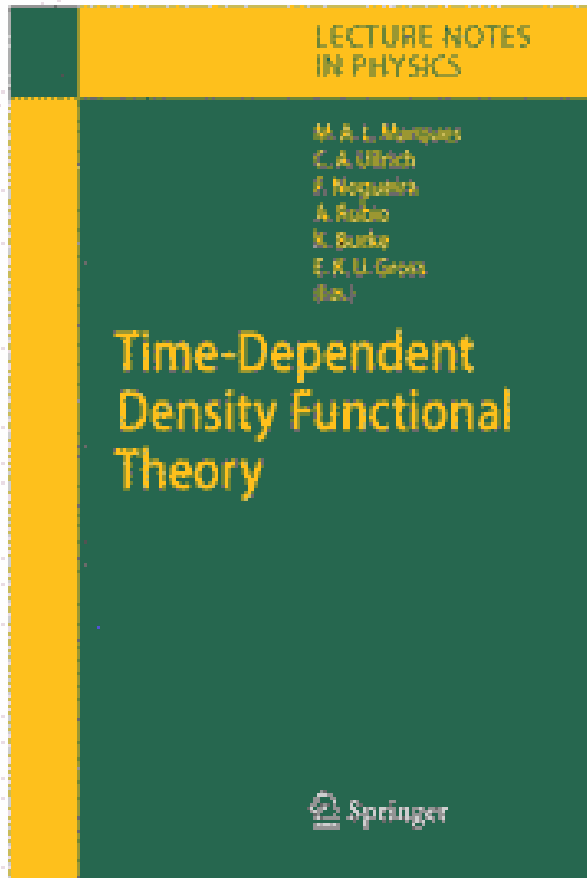


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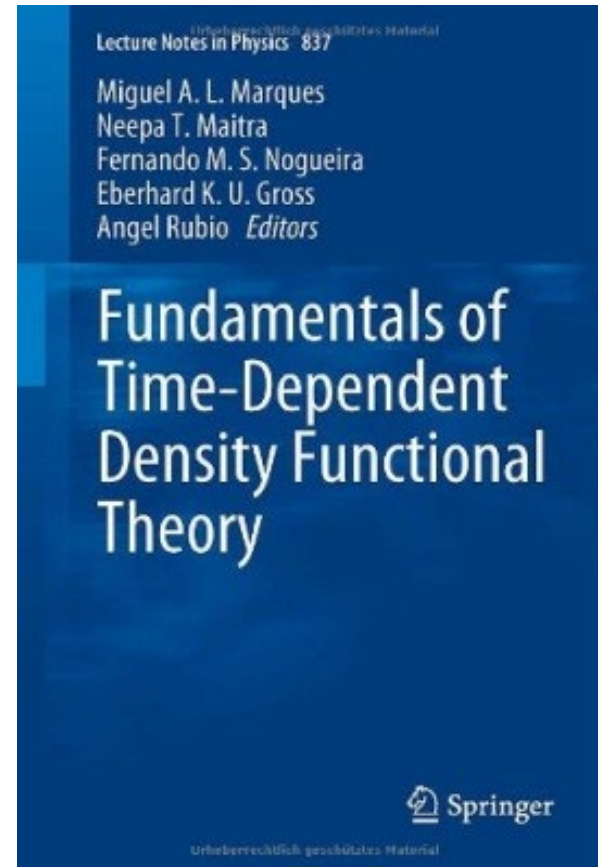
First-principles calculation of electronic spectra of light-harvesting complex II†

Carolin König and Johannes Neugebauer*





Lecture Notes in Physics 706
(Springer, 2006)



Lecture Notes in Physics 837
(Springer, 2012)