

Tutorial on TDDFT: Part 2



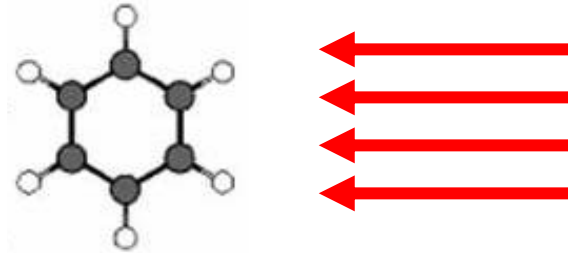
E. K. U. GROSS

Freie Universität Berlin

www: <http://users.physik.fu-berlin.de/~ag-gross>

What do we want to describe?

Generic situation:
Molecule in laser field



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

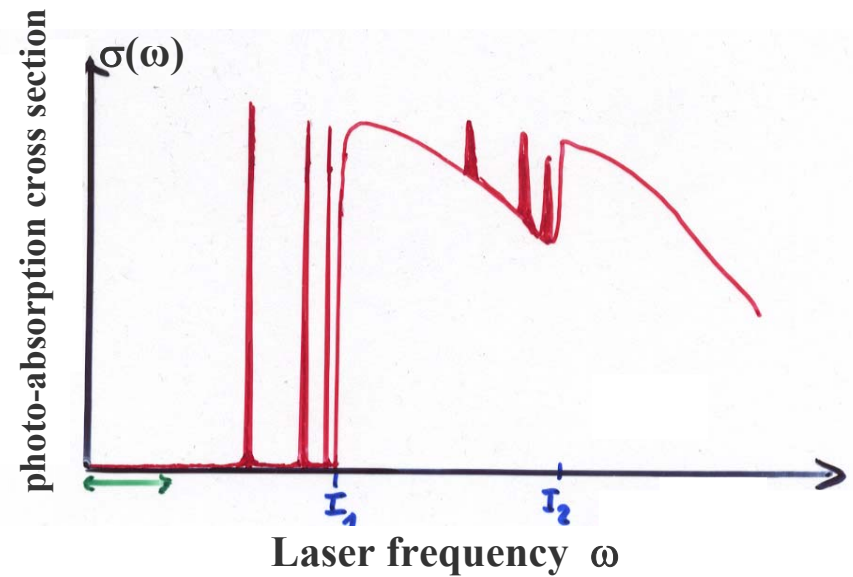
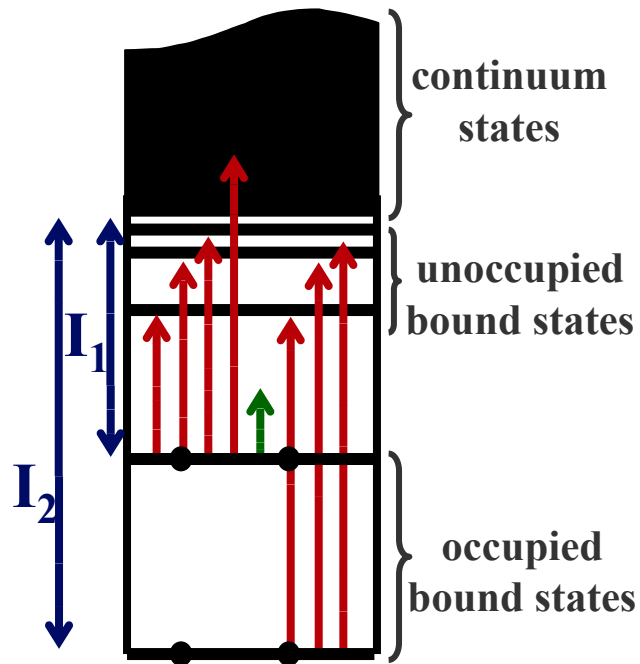
Strong laser ($v_{\text{laser}}(\mathbf{t}) \geq v_{\text{en}}$):

Non-perturbative solution of full TDSE required

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

- Calculate
1. Linear density response $\rho_1(\mathbf{r}, \mathbf{t})$ \rightarrow
 2. Dynamical polarizability $\alpha(\omega) = -\frac{e}{E} \int z \rho_1(\vec{r}, \omega) d^3 r$
 3. Photo-absorption cross section $\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im} \alpha$

Photo-absorption in weak lasers



No absorption if $\omega <$ lowest excitation energy

Time-dependent density-functional formalism

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

Basic 1-1 correspondence:

$v(\mathbf{r}, t) \xleftrightarrow{1-1} \rho(\mathbf{r}, t)$ The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables for fixed initial state.

KS theorem:

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

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

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

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

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**

**Approximation with correct asymptotic $-1/r$ behavior:
time-dependent optimized effective potential (TDOEP)**

C. A. Ullrich, U. Gossmann, E.K.U.G., PRL 74, 872 (1995)

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 :

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

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

$$\chi(\mathbf{r},t, \mathbf{r}',t') := \left. \frac{\delta\rho[\mathbf{v}](\mathbf{r},t)}{\delta\mathbf{v}(\mathbf{r}',t')} \right|_{\mathbf{v}_0} = \text{density-density response function of interacting system}$$


Analogous function $\rho_s[\mathbf{v}_s](\mathbf{r},t)$ for non-interacting system

$$\rho_s[\mathbf{v}_s](\mathbf{r},t) = \rho_s[\mathbf{v}_{s,0} + \mathbf{v}_{s,1}](\mathbf{r},t) = \rho_s[\mathbf{v}_{s,0}](\mathbf{r},t) + \int \left. \frac{\delta\rho_s[\mathbf{v}_s](\mathbf{r},t)}{\delta\mathbf{v}_s(\mathbf{r}',t')} \right|_{\mathbf{v}_{s,0}} \mathbf{v}_{s,1}(\mathbf{r}',t') d^3r' dt' + \dots$$

$$\chi_s(\mathbf{r},t, \mathbf{r}',t') := \left. \frac{\delta\rho_s[\mathbf{v}_s](\mathbf{r},t)}{\delta\mathbf{v}_s(\mathbf{r}',t')} \right|_{\mathbf{v}_{s,0}} = \text{density-density response function of non-interacting system}$$

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

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


Notes:

- v_{xc} is well-defined through non-interacting/ interacting 1-1 mapping.
- $v_S[\rho]$ depends on initial determinant Φ_0 .
- $v_{\text{ext}}[\rho]$ depends on initial many-body state Ψ_0 .

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

only if system is initially in ground-state then, via HK, Φ_0 and Ψ_0 are determined by ρ_0 and v_{xc} depends on ρ alone.

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

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

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

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

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

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

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

$$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ \mathbf{f}_{xc}(\mathbf{r}, t, \mathbf{r}', t') & \chi_S^{-1}(\mathbf{r}, t, \mathbf{r}', t') & \chi^{-1}(\mathbf{r}, t, \mathbf{r}', t') & \mathbf{W}_C(\mathbf{r}, t, \mathbf{r}', t') \end{array}$$

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

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

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

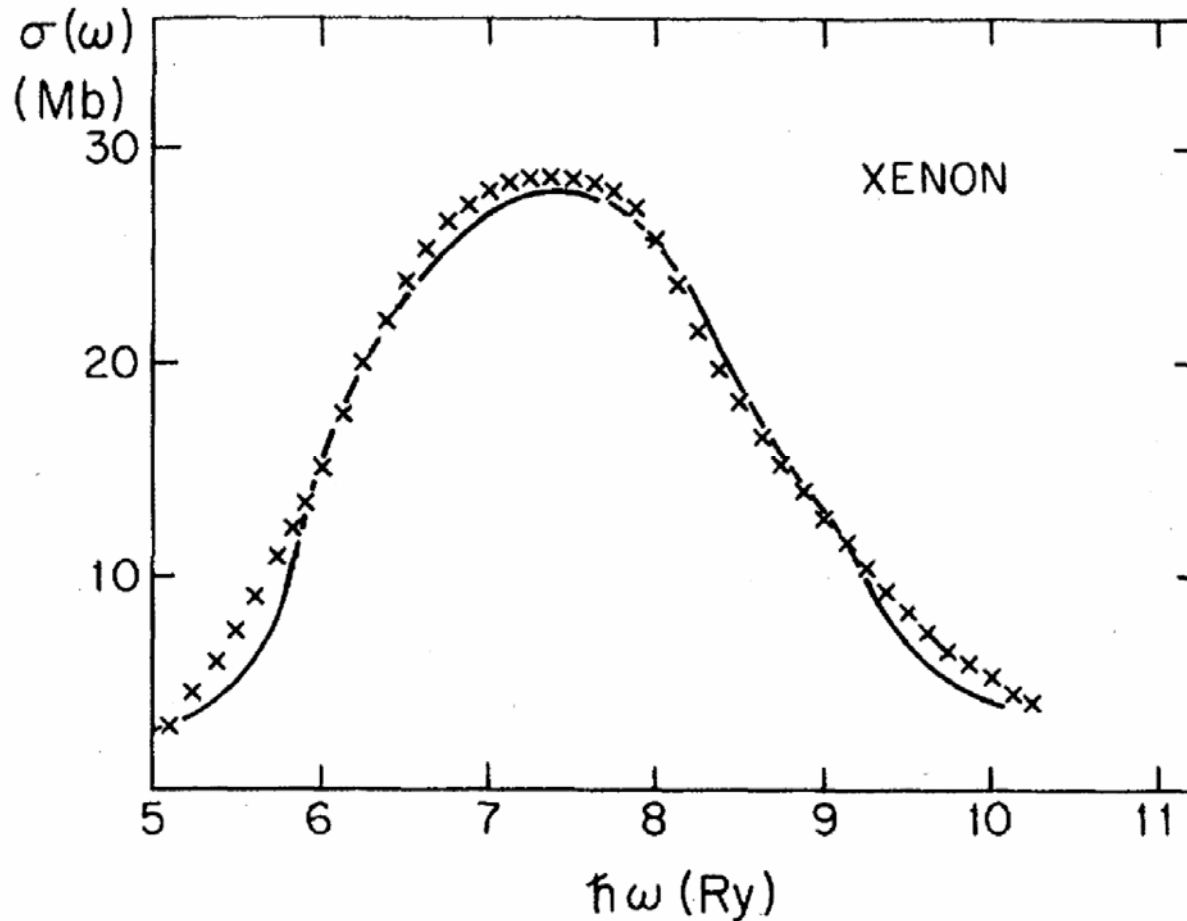
Act with this operator equation on arbitrary $v_1(\mathbf{r}, t)$ and use $\chi v_1 = \rho_1$:

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

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

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

Standard linear response formalism

$H(t_0)$ = full static Hamiltonian at t_0

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

full response function

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

\Rightarrow The exact linear density response

$$\rho_1(\omega) = \hat{\chi}(\omega) v_1(\omega)$$

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

Discrete excitation energies from TDDFT

Goal: Use exact TDDFT representation of linear density response to determine the poles of $\rho_1(\omega)$:

$$\rho_1(\omega) = \hat{\chi}_S(\omega) \left(v_1(\omega) + \hat{W}_C \rho_1(\omega) + \hat{f}_{xc}(\omega) \rho_1(\omega) \right)$$

“ \wedge ” denotes integral operator, e.g. $\hat{f}_{xc} \rho_1 \equiv \int f_{xc}(\vec{r}, \vec{r}') \rho_1(\vec{r}') d^3 r'$

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

$$\text{with } M_{jk}(\vec{r}, \vec{r}') = (f_k - f_j) \varphi_j(\vec{r}) \varphi_j^*(\vec{r}') \varphi_k(\vec{r}') \varphi_k^*(\vec{r})$$

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

$\epsilon_j - \epsilon_k$ KS excitation energy

$$\left(\hat{1} - \hat{\chi}_S(\omega) \left[\hat{W}_C + \hat{f}_{xc}(\omega) \right] \right) \rho_1(\omega) = \hat{\chi}_S(\omega) v_1(\omega)$$

$\rho_1(\omega) \rightarrow \infty$ for $\omega \rightarrow \Omega$ (exact excitation energy) but right-hand side remains finite for $\omega \rightarrow \Omega$

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

$\lambda(\omega) \rightarrow 0$ for $\omega \rightarrow \Omega$

This condition rigorously determines the exact excitation energies, i.e.,

$$\left(\hat{1} - \hat{\chi}_S(\Omega) \left[\hat{W}_C + \hat{f}_{xc}(\Omega) \right] \right) \xi(\Omega) = 0$$

This leads to the (non-linear) eigenvalue equation

(See T. Grabo, M. Petersilka, E. K. U. G., J. Mol. Struc. (Theochem) 501, 353 (2000))

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

where

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

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

$$\alpha_q = f_a - f_j$$

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

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

Atom	Experimental Excitation Energies $^1S \rightarrow ^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	$\Delta\epsilon_{KS} + K$
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)

$$\Delta E = \underbrace{\Delta\epsilon_{KS}}_{\epsilon_j - \epsilon_k} + K$$

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

Excitation energies of CO molecule

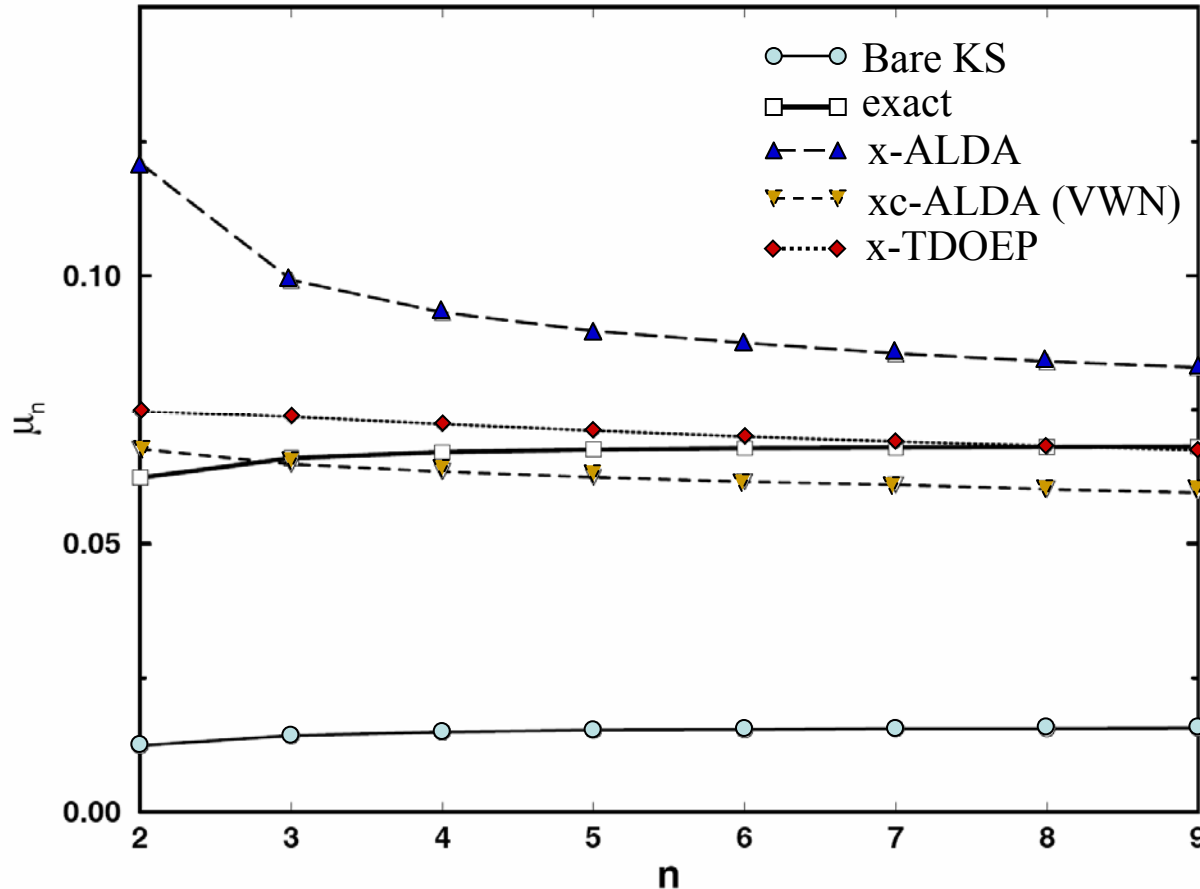
	State	Ω_{expt}	KS-transition	$\Delta\epsilon_{\text{KS}}$	$\Delta\epsilon_{\text{KS}} + \text{K}$
A	$^1\Pi$	0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	$^3\Pi$	0.2323			0.2238
I	$^1\Sigma^-$	0.3631	$1\Pi \rightarrow 2\Pi$	0.3626	0.3626
D	$^1\Delta$	0.3759			0.3812
a'	$^3\Sigma^+$	0.3127			0.3181
e	$^3\Sigma^-$	0.3631			0.3626
d	$^3\Delta$	0.3440			0.3404

T. Grabo, M. Petersilka and E.K.U. Gross, J. Mol. Struct. (Theochem) 501, 353 (2000)

approximations made: v_{xc}^{LDA} and f_{xc}^{ALDA}

Quantum defects in Helium $E_n = -\frac{1}{2(n - \mu_n)^2}$ [a.u.]

3P Series



M. Petersilka, U.J. Gossmann and E.K.U. Gross, in: *Electronic Density Functional Theory: Recent Progress and New Directions*, J.F. Dobson, G. Vignale, M.P. Das, ed(s), (Plenum, New York, 1998), p 177 - 197.

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, $f_{xc}^{\text{ALDA}}(q, \omega, \rho) = c(\rho)$ whereas,**

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

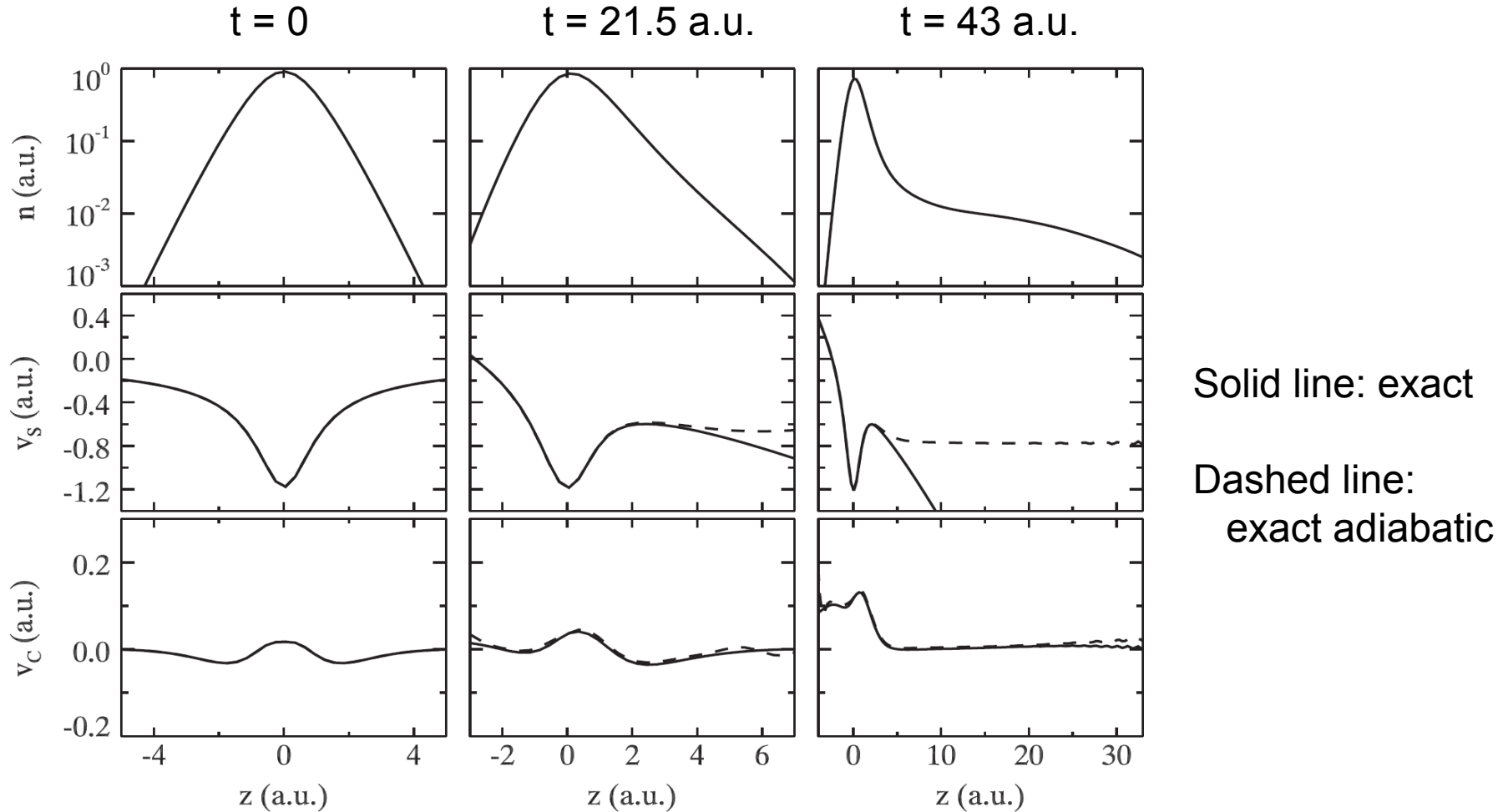
- **charge-transfer excitations not properly described**

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

**In the ALDA,
which problems come from ADIABATIC approximation, and
which come from LDA?**

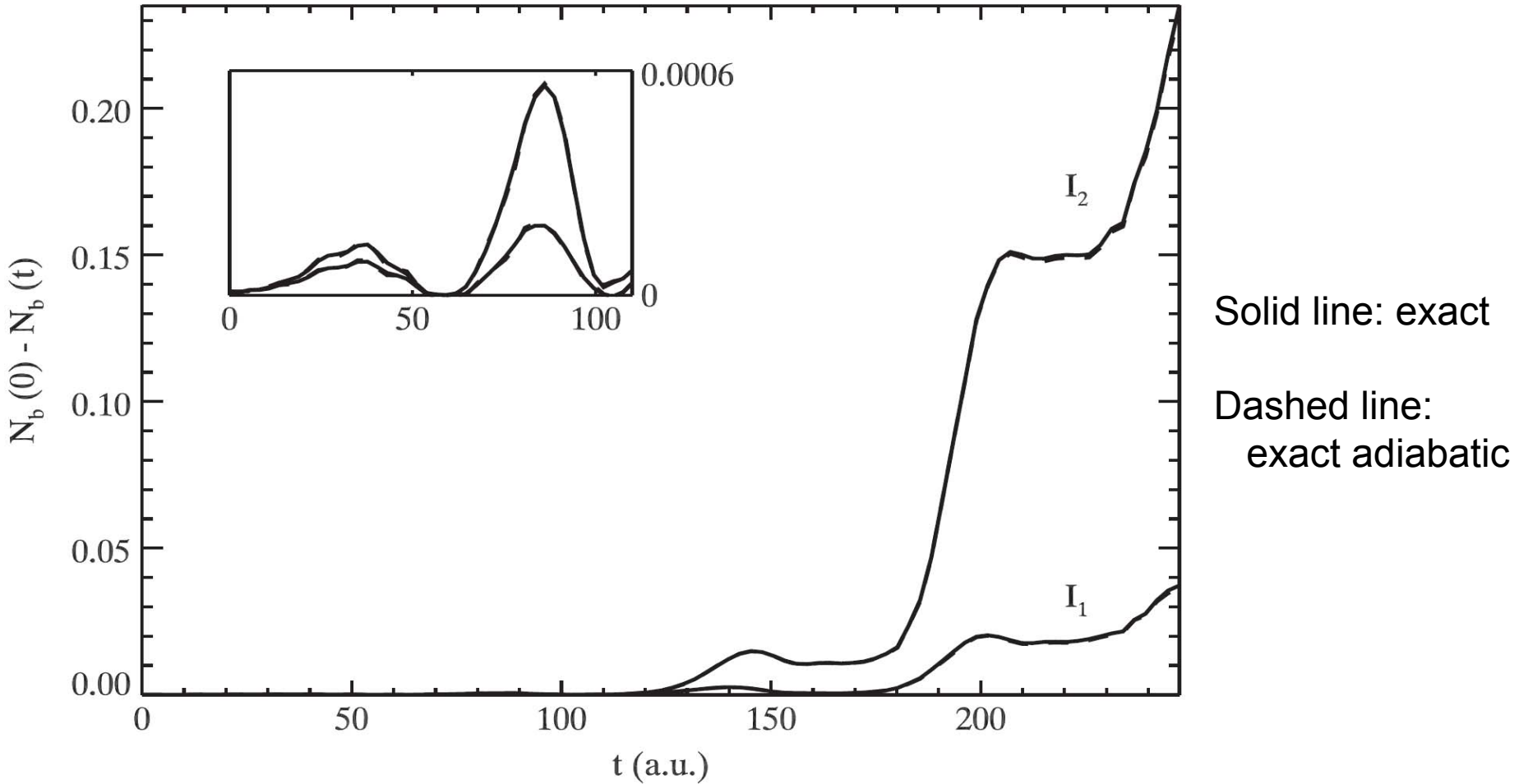
→ Investigate EXACT ADIABATIC approximation

$E(t)$ ramped over 27 a.u. (0.65 fs) to the value $E=0.14$ a.u. and then kept constant



M. Thiele, E.K.U.G., S. Kuemmel, PRL **100**, 153004 (2008)

4-cycle pulse with $\lambda = 780$ nm, $I_1 = 4 \times 10^{14}$ W/cm², $I_2 = 7 \times 10^{14}$ W/cm²



M. Thiele, E.K.U.G., S. Kuemmel, PRL **100**, 153004 (2008)