Time-dependent density functional theory



E.K.U. Gross

Max-Planck Institute of Microstructure Physics Halle (Saale)



OUTLINE

LECTURE I

- Phenomena to be described by TDDFT
- Some generalities on "functional theories"
- Basic framework of TDDFT
- TDDFT in the linear-response regime: Calculation of optical excitation spectra

LECTURE II:

- Approximations of the static xc energy functional derived from TDDFT
- **TD Electron Localization Function**
- Optimal Control Theory

What do we want to describe?

System in laser field: Generic situation



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

What do we want to describe?





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Electronic transport: Generic situation



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

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

Strong laser $(\mathbf{v}_{\text{laser}}(\mathbf{t}) \ge \mathbf{v}_{\text{en}})$:

Non-perturbative solution of full TDSE required

Weak laser ($\mathbf{v}_{laser}(\mathbf{t}) \ll \mathbf{v}_{en}$):Calculate1. Linear density response $\rho_1(\vec{r} t)$ 2. Dynamical polarizability $\alpha(\omega) = -\frac{e}{F} \int z \rho_1(\vec{r}, \omega) d^3 r$

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

Photo-absorption in weak lasers



Standard linear response formalism

$\mathbf{H}(\mathbf{t}_0) = \text{full static Hamiltonian at } \mathbf{t}_0$ $\mathbf{H}(\mathbf{t}_0) | \mathbf{m} \rangle = \mathbf{E}_{\mathbf{m}} | \mathbf{m} \rangle \quad \leftarrow \text{ exact many-body eigenfunctions} \text{ and energies of system}$

full response function

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

⇒ The exact linear density response

$$\rho_1(\omega) = \chi(\omega) \mathbf{v}_1$$

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

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

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 10²⁴ entries1 byte per entry: \Rightarrow 10²⁴ bytes10¹⁰ bytes per DVD: \Rightarrow 10¹⁴ DVDs10 g per DVD: \Rightarrow 10¹⁵ g DVDs

 $= 10^9 t DVDs$

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 <u>non-interacting particles</u>

ESSENCE OF DENSITY-FUNTIONAL THEORY

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

Walter Kohn, Nobel Laureate, UC Santa Barbara

Static Density Functional Theory: Some remarks

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

Hohenberg-Kohn-Theorem (1964)

G: v(r) $\rightarrow \rho$ (r) is invertible

HOHENBERG-KOHN THEOREM

1.
$$v(r) \leftarrow 1 \longrightarrow \rho(r)$$

one-to-one correspondence between external potentials v(r) and ground-state densities $\rho(r)$

2. <u>Variational principle</u>

Given a particular system characterized by the external potential $v_0(\mathbf{r})$. Then the solution of the Euler-Lagrange equation

$$\frac{\delta}{\delta\rho(\mathbf{r})} \mathbf{E}_{\mathrm{HK}}[\rho] = 0$$

yields the exact ground-state energy E_0 and ground-state density $\rho_0(r)$ of this system

3. $E_{HK}[\rho] = F[\rho] + \int \rho(r) \mathbf{v}_o(r) d^3 r$

 $F[\rho]$ is <u>UNIVERSAL</u>. In practice, $F[\rho]$ needs to be approximated

Expansion of F[\rho] in powers of e^2

 $F[\rho] = F^{(0)}[\rho] + e^2 F^{(1)}[\rho] + e^4 F^{(2)}[\rho] + \cdots$

where: $F^{(0)}[\rho] = T_s[\rho]$ (kinetic energy of <u>non</u>-interacting particles)

$$e^{2}F^{(1)}[\rho] = \frac{e^{2}}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^{3}r d^{3}r' + E_{x}[\rho] \quad (\text{Hartree} + \text{exchange energies})$$

 $\sum_{i=2}^{\infty} \left(e^{2}\right)^{i} F^{(i)}[\rho] = E_{c}[\rho] \qquad \text{(correlation energy)}$

$$\Rightarrow F[\rho] = T_s[\rho] + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' + E_x[\rho] + E_c[\rho]$$



Kohn-Sham Theorem

Let $\rho_0(r)$ be the ground-state density of interacting electrons moving in the external potential $v_0(r)$. Then there exists a local potential $v_{s,0}(r)$ such that non-interacting particles exposed to $v_{s,0}(r)$ have the ground-state density $\rho_0(r)$, i.e.

$$\left(-\frac{\nabla^{2}}{2}+\mathbf{v}_{s,o}\left(\mathbf{r}\right)\right)\boldsymbol{\varphi}_{j}\left(\mathbf{r}\right)=\boldsymbol{\varepsilon}_{j}\boldsymbol{\varphi}_{j}\left(\mathbf{r}\right),\quad\boldsymbol{\rho}_{o}\left(\mathbf{r}\right)=\sum_{\substack{j\left(\text{with}\\\text{lowest}\,\boldsymbol{\varepsilon}_{i}\right)}}^{N}\left|\boldsymbol{\varphi}_{j}\left(\mathbf{r}\right)\right|^{2}$$

<u>proof</u>: $\mathbf{v}_{s,o}(\mathbf{r}) = \mathbf{v}_{s}[\rho_{o}](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping Existence follows from V-representability theorem 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 $\rho(r)$).

<u>QUESTION</u>: Are all "reasonable" functions $\rho(r)$ V-representable?

V-representability theorem (Chayes, Chayes, Ruskai, J Stat. Phys. <u>38</u>, 497 (1985))

On a lattice (finite or infinite), any normalizable positive function $\rho(\mathbf{r})$, 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, $v_{ext}[\rho](r)$, 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 (<u>ensemble</u>-V-representable).

Define
$$\mathbf{v}_{xc}[\rho](\mathbf{r})$$
 by the equation
 $\mathbf{v}_{s}[\rho](\mathbf{r}) \coloneqq \mathbf{v}_{ext}[\rho](\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^{3}\mathbf{r}' + \mathbf{v}_{xc}[\rho](\mathbf{r})$
 $\mathbf{v}_{H}[\rho](\mathbf{r})$
 $\mathbf{v}_{s}[\rho]$ and $\mathbf{v}_{ext}[\rho]$ are well defined through HK.

KS equations



<u>Note</u>: The KS equations do <u>not</u> follow from the variational principle. They follow from the HK 1-1 mapping and the V-representability theorem.

Four steps needed

Step 1: Basic Theorems, exact features

<u>Step 2</u>: Find approximate functionals for $v_{xc} \left[\rho(r') \right] (r)$

<u>Step 3</u>: Write code that solves the equations

<u>Step 4</u>: Run code for interesting systems/questions

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



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MBPT DFT RDMFT $G(r, r', t-t') \quad \gamma(r, r') = G(r, r', 0^+) \quad \rho(r) = \gamma(r, r)$ **Functional: Functional:** Functional: $\Phi_{\rm xc}[G]$ $E_{xc}[\gamma]$ $E_{xc}[\rho]$ or $\Sigma_{\rm xc}[G]$ or $v_{xc}[\rho]$ easy (e.g. GW) difficult very difficult numerically moderate heavy light



For each of these functional theories there exist static and TD versions

Time-dependent density-functional formalism (E. Runge, E.K.U.G., PRL <u>52</u>, 997 (1984))

Basic 1-1 correspondence:

 $v(rt) \xleftarrow{1-1} \rho(rt)$ 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 <u>interacting</u> system of interest can be calculated as density

$$\varphi(\mathbf{rt}) = \sum_{j=1}^{N} \left| \varphi_{j}(\mathbf{rt}) \right|^{2}$$

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 <u>local</u> potential

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

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

define maps

pot

V

$$\begin{array}{ccc} \text{aps} & F: v(\vec{r}t) \mapsto \Psi(t) & \tilde{F}: \Psi(t) \mapsto \rho(\vec{r}t) \\ \hline G \\ \hline G \\ \hline ft \\ \vec{r}t \\ \psi(t_{o}) = \Psi_{o} \\ \hline G: v(\vec{r}t) \mapsto \rho(\vec{r}t) \\ \hline G: v(\vec{r}t) \mapsto \rho(\vec{r}t) \end{array}$$

The TDKS equations follow (like in the static case) from:

- i. the basic 1-1 mapping and
- ii. the TD V-representability theorem (R. van Leeuwen, PRL <u>82</u>, 3863 (1999)).

Reminder: Photo-absorption in weak lasers



No absorption if ω < lowest excitation energy

LINEAR RESPONSE THEORY

$$\begin{split} t &= t_0: \text{Interacting system in ground state of potential } v_0(r) \text{ with density } \rho_0(r) \\ t &> t_0: \text{Switch on perturbation } v_1(r \ t) \ (\text{with } v_1(r \ t_0) = 0). \\ \text{Density: } \rho(r \ t) &= \rho_0(r) + \delta\rho(r \ t) \end{split}$$

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

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

$$\begin{split} \rho[\mathbf{v}] (\mathbf{rt}) &= \rho[\mathbf{v}_0 + \mathbf{v}_1] (\mathbf{rt}) \\ &= \rho[\mathbf{v}_0](\mathbf{rt}) & \longrightarrow \rho_o(\mathbf{r}) \\ &+ \int \frac{\delta \rho[\mathbf{v}](\mathbf{rt})}{\delta \mathbf{v}(\mathbf{r't'})} \bigg|_{\mathbf{v}_0} \mathbf{v}_1(\mathbf{r't'}) \mathbf{d}^3 \mathbf{r'} \mathbf{dt'} & \longrightarrow \rho_1(\mathbf{rt}) \\ &+ \frac{1}{2} \int \int \frac{\delta^2 \rho[\mathbf{v}](\mathbf{rt})}{\delta \mathbf{v}(\mathbf{r't'}) \delta \mathbf{v}(\mathbf{r''t''})} \bigg|_{\mathbf{v}_0} \mathbf{v}_1(\mathbf{r'}, \mathbf{t'}) \mathbf{v}_1(\mathbf{r''}, \mathbf{t''}) \mathbf{d}^3 \mathbf{r'} \mathbf{dt'} \mathbf{dt''} & \longrightarrow \rho_2(\mathbf{rt}) \\ &\vdots \end{split}$$

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

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

Analogous function $\rho_s[v_s](r t)$ for <u>non</u>-interacting system

$$\rho_{S} \left[v_{S} \right] \left(rt \right) = \rho_{S} \left[v_{S,0} + v_{S,1} \right] \left(rt \right) = \rho_{S} \left[v_{S,0} \right] \left(rt \right) + \int \frac{\delta \rho_{S} \left[v_{S} \right] \left(rt \right)}{\delta v_{S} \left(r't' \right)} \bigg|_{\mathbf{v}_{S,0}} \mathbf{v}_{S,1} \left(r't' \right) d^{3}r'dt' + \cdots$$

$$\chi_{s}(\mathbf{rt},\mathbf{r't'}) \coloneqq \frac{\delta \rho_{s}[\mathbf{v}_{s}](\mathbf{rt})}{\delta \mathbf{v}_{s}(\mathbf{r't'})} \bigg|_{\mathbf{v}_{s,0}} =$$

density-density response function of <u>non</u>-interacting system

<u>GOAL</u>: Find a way to calculate $\rho_1(r t)$ without explicitly evaluating $\chi(r t, r't')$ of the <u>interacting</u> system

starting point: Definition of xc potential

$$\mathbf{v}_{xc}[\rho](\mathbf{rt}) \coloneqq \mathbf{v}_{s}[\rho](\mathbf{rt}) - \mathbf{v}_{ext}[\rho](\mathbf{rt}) - \mathbf{v}_{H}[\rho](\mathbf{rt})$$

<u>Notes</u>: • v_{xc} is well-defined through non-interacting/ interacting 1-1 mapping.

$$\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')}\bigg|_{\rho_{0}} = \frac{\delta v_{s}[\rho](rt)}{\delta \rho(r't')}\bigg|_{\rho_{0}} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')}\bigg|_{\rho_{0}} - \frac{\delta(t-t')}{|r-r'|}$$





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



$$\chi_{\mathbf{S}} \bullet \left| \mathbf{f}_{\mathbf{x}\mathbf{c}} + \mathbf{W}_{\mathbf{C}} = \chi_{\mathbf{S}}^{-1} - \chi^{-1} \right| \bullet \chi$$

$$\begin{split} \frac{\delta v_{xc} \left[\rho\right](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} &= \frac{\delta v_{s} \left[\rho\right](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext} \left[\rho\right](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|} \\ \uparrow & \uparrow & \uparrow & \uparrow \\ f_{xc} \left(rt, r't'\right) & \chi_{s}^{-1} \left(rt, r't'\right) & \chi^{-1} \left(rt, r't'\right) & W_{C} \left(rt, r't'\right) \\ \chi_{S} \bullet \bigg| f_{xc} + W_{C} &= \chi_{S}^{-1} - \chi^{-1} \bigg| \bullet \chi \\ \chi_{S} \left(f_{xc} + W_{C}\right) \chi &= \chi - \chi_{S} \end{split}$$

$$\chi = \chi_{S} + \chi_{S} \left(W_{C} + f_{xc} \right) \chi$$

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

$$\rho_{1}(\mathbf{rt}) = \int d^{3}\mathbf{r}' dt' \chi_{s}(\mathbf{rt}, \mathbf{r't'}) \left[v_{1}(\mathbf{rt}) + \int d^{3}\mathbf{r}'' dt'' \left\{ W_{C}(\mathbf{r't'}, \mathbf{r''t''}) + f_{xc}(\mathbf{r't'}, \mathbf{r''t''}) \right\} \rho_{1}(\mathbf{r''t''}) \right]$$

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

• Need approximation for
$$f_{xc}(\mathbf{r't'},\mathbf{r''t''}) = \frac{\delta v_{xc}[\rho](\mathbf{r't'})}{\delta \rho(\mathbf{r''t''})}\Big|_{\rho_{t}}$$

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

Adiabatic approximation

$$v_{xc}^{adiab}\left[\rho\right]\left(rt\right) := v_{xc}^{static DFT}\left[\rho(t)\right]\left(rt\right)$$

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.

e.g. adiabatic LDA:
$$v_{xc}^{ALDA}(rt) \coloneqq v_{xc}^{LDA}(\rho(rt)) = -\alpha \rho(rt)^{1/3} + \cdots$$

$$\Rightarrow f_{xc}^{ALDA}(rt, r't') = \frac{\delta v_{xc}^{ALDA}(rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \delta(r - r') \delta(t - t') \frac{\partial v_{xc}^{ALDA}}{\partial \rho(r)} \bigg|_{\rho_0(r)}$$
$$= \delta(r - r') \delta(t - t') \frac{\partial^2 e_{xc}^{hom}}{\partial n^2} \bigg|_{\rho_0(r)}$$

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)]

Photo-absorption in weak lasers





Ribbon diagram of the wt-GFP structure. The α -helices are shown in red, the β -strands are shown in green, and the chromophore is shown as a ball-and-stick model.

Brejc et al., Proc. Natl. Acad. Sci. <u>94</u>, 2306 (1997)







Computed photoabsorption cross section of the neutral (thick solid line) and anionic (thick dashed line) GFP chromophores, along with experimental results (thin solid line and crosses, respectively).

For comparative purposes, the anionic results is divided by 4 with respect to the neutral results.

Inset: decomposition of the computed spectra of the neutral chromophore in the three directions, showing the inherent anisotropy of the GFP molecule.

Marques et al., PRL <u>90</u>, 258101 (2003)



Photo-absorption in weak lasers



Looking at those frequencies, Ω , for which $\rho_1(\omega)$ has poles, leads to the (non-linear) eigenvalue equation

(T. Grabo, M. Petersilka, EKUG, J. Mol. Struc. (Theochem) <u>501</u>, 353 (2000))

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

where

$$\begin{split} \mathbf{A}_{qq'} &= \alpha_{q'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \, \Phi_q \left(\mathbf{r} \right) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \mathbf{f}_{xc} \left(\mathbf{r}, \mathbf{r}', \Omega \right) \right) \Phi_{q'} \left(\mathbf{r}' \right) \\ & \mathbf{q} = \left(\mathbf{j}, \mathbf{a} \right) \text{ double index} \qquad \alpha_q = \mathbf{f}_a - \mathbf{f}_j \\ & \Phi_q \left(\mathbf{r} \right) = \phi_a^* \left(\mathbf{r} \right) \phi_j \left(\mathbf{r} \right) \qquad \omega_q = \varepsilon_a - \varepsilon_j \end{split}$$

Atom	Experimental Excitation Energies ¹ S→ ¹ P (in Ry)	KS energy differences ∆∈ _{KS} (Ry)	$\Delta \epsilon_{\mathrm{KS}} + \mathbf{K}$
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)

 $\Delta \mathbf{E} = \underbrace{\Delta \boldsymbol{\epsilon}_{\mathrm{KS}}}_{\boldsymbol{\epsilon}_{j} \cdot \boldsymbol{\epsilon}_{k}} + \mathbf{K}$

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

Excitation energies of CO molecule

State		Ω_{expt}	KS-transition	$\Delta \in_{\mathrm{KS}}$	$\Delta \in_{\mathrm{KS}} + \mathrm{K}$
A	$^{1}\Pi$	0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	³ П	0.2323			0.2238
Ι	$^{1}\Sigma$	0.3631	1 Π→2 Π	0.3626	0.3626
D	$^{1}\Delta$	0.3759			0.3812
a'	$^{3}\Sigma^{+}$	0.3127			0.3181
e	³ Σ ⁻	0.3631			0.3626
d	³ Д	0.3440			0.3404

T. Grabo, M. Petersilka and E.K.U. Gross, J. Mol. Struct. (Theochem) <u>501</u>, 353 (2000) approximations made: v_{xc}^{LDA} and f_{xc}^{ALDA}



M. Petersilka, U.J. Gossmann and E.K.U.G., 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.



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.

(M. Petersilka, E.K.U.G., K. Burke, Int. J. Quantum Chem. <u>80</u>, 534 (2000))

Failures of ALDA in the linear response regime

• H₂ dissociation is incorrect:

$$E\binom{1}{\Sigma_{u}^{+}} - E\binom{1}{\Sigma_{g}^{+}} \xrightarrow[R \to \infty]{(in ALDA)}$$

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

- response of long chains strongly overestimated (see: Champagne et al., JCP <u>109</u>, 10489 (1998) and <u>110</u>, 11664 (1999))
- in periodic solids, $f_{xc}^{ALDA}(q, \omega, \rho) = c(\rho)$ whereas, for insulators, $f_{xc}^{exact} \xrightarrow[q \to 0]{} 1/q^2$ divergent.
- charge-transfer excitations not properly described (see: Dreuw et al., JCP <u>119</u>, 2943 (2003))

Solid Argon



L. Reining, V. Olevano, A. Rubio, G. Onida, PRL <u>88</u>, 066404 (2002)

Excitons are <u>completely missing</u> for simple xc functionals like ALDA!





