Time-dependent density-functional formalism

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

Basic 1-1 correspondence:

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

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

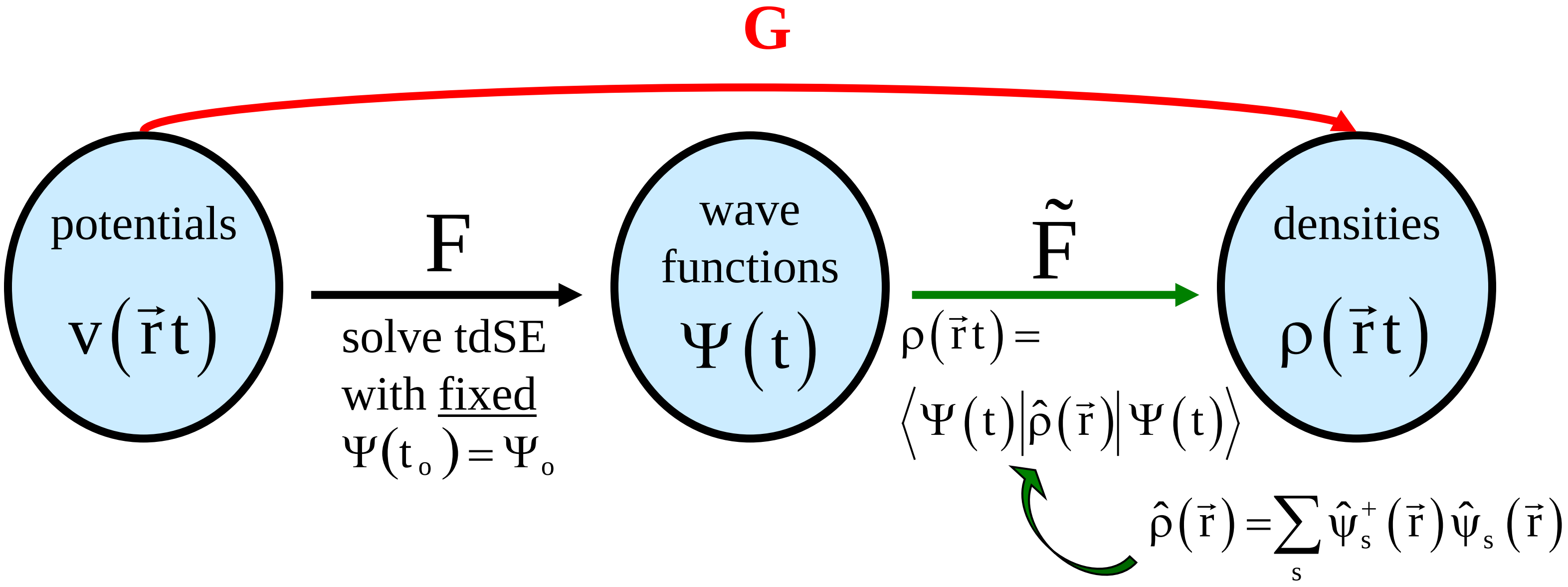
$$i\hbar\frac{\partial}{\partial t}\varphi_j(rt) = \left(-\frac{\hbar^2\nabla^2}{2m} + v_S[\rho](rt)\right)\varphi_j(rt)$$

with the local potential

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

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

<u>define maps</u> $\boxed{F:\ v(\vec{r}\,t) \mapsto \Psi(t)}$ $\boxed{\tilde{F}:\ \Psi(t) \mapsto \rho(\vec{r}\,t)}$



solve tdSE
with <u>fixed</u>
$\Psi(t_o) = \Psi_o$

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

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

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

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

1. **the basic 1-1 mapping and**
2. **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, PRL 80, 1280 (1998)).

complete 1 - 1 correspondence not to be expected!

$$i\frac{\partial}{\partial t}\Psi(t)=\left(\hat{T}+\underline{\underline{\hat{V}(t)}}+\hat{W}\right)\Psi(t) \qquad \Psi(t_o)=\Psi_o$$

$$i\frac{\partial}{\partial t}\Psi'(t)=\left(\hat{T}+\underline{\underline{\hat{V}'(t)}}+\hat{W}\right)\Psi'(t) \qquad \Psi'(t_o)=\Psi_o$$

$$\hat{V}'(t)=\hat{V}(t)+\underset{\substack{\uparrow\\ \text{“no operator”}}}{C(t)} \;\Leftrightarrow\; \Psi'(t)=e^{-i\alpha(t)}\Psi(t)$$

with $\boxed{\dot{\alpha}(t)=C(t)}$

$$\Rightarrow \underline{\underline{\rho'(\vec{r}t)=\rho(\vec{r}t)}}$$

i.e. $\left\{\hat{V}(t)+C(t)\right\} \rightarrow \rho(\vec{r}t)$

If G invertible up to within time-dependent function C(t)

$$\Rightarrow \Psi = FG^{-1}\rho$$ fixed up to within time-dependent phase

i.e. $$\Psi = e^{-i\alpha(t)}\Psi[\rho]$$

For any observable $\hat{O}$

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

is functional of the density

THEOREM (time-dependent analogue of Hohenberg-Kohn theorem)

The map

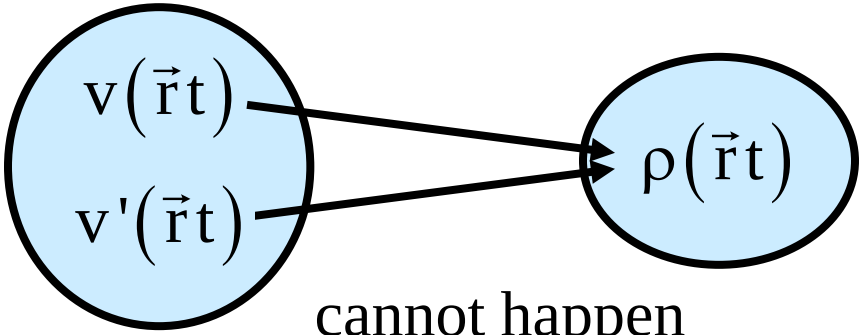
$$G: \quad v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

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_o

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

Proof:

to be shown:



cannot happen

i.e. $$\underline{\underline{\hat{v}(\vec{r}t) \neq \hat{v}'(\vec{r}t) + c(t)}} \overset{!}{\Rightarrow} \rho(\vec{r}t) \neq \rho'(\vec{r}t)$$

$\Downarrow$ potential expandable into Taylor series

$$\boxed{\exists\, k \geq 0 \quad : \quad \frac{\partial^k}{\partial t^k}\left[v(\vec{r}t) - v'(\vec{r}t)\right]_{t=t_o} \neq \text{constant}}$$

$\Downarrow$ step 1

$$\vec{j}(\vec{r}t) \neq \vec{j}'(\vec{r}t)$$

$\Downarrow$ step 2

$$\rho(\vec{r}t) \neq \rho'(\vec{r}t)$$

Step 1: Current densities

$$\vec{j}(\vec{r}t) = \left\langle \Psi(t) \middle| \hat{\vec{j}}(\vec{r}) \middle| \Psi(t) \right\rangle$$

$$\text{with} \quad \hat{\vec{j}}(\vec{r}) = -\frac{1}{2i} \sum_s \left(\left[\vec{\nabla} \hat{\psi}_s^+(\vec{r}) \right] \hat{\psi}_s(\vec{r}) - \hat{\psi}_s^+(\vec{r}) \left[\vec{\nabla} \hat{\psi}_s(\vec{r}) \right] \right)$$

Use equation of motion:

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

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

$$i \frac{\partial}{\partial t} \vec{j}'(\vec{r}t) = \left\langle \Psi'(t) \middle| \left[\hat{\vec{j}}(\vec{r}), \hat{H}'(t) \right] \middle| \Psi'(t) \right\rangle$$

note:

$$\vec{j}(\vec{r}\underline{\underline{t_o}}) = \vec{j}'(\vec{r}\underline{\underline{t_o}}) = \left\langle \Psi_o \middle| \hat{\vec{j}}(\vec{r}) \middle| \Psi_o \right\rangle \equiv \vec{j}_o(\vec{r})$$

$$\rho(\vec{r}\underline{\underline{t_o}}) = \rho'(\vec{r}\underline{\underline{t_o}}) = \left\langle \Psi_o \middle| \hat{\rho}(\vec{r}) \middle| \Psi_o \right\rangle \equiv \rho_o(\vec{r})$$

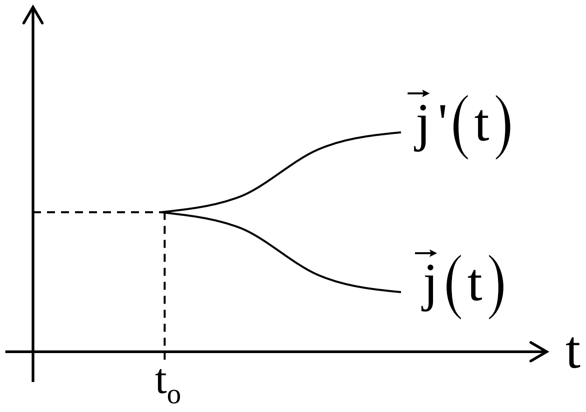
$$i\frac{\partial}{\partial t}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]_{t=t_o} = \left\langle \Psi_o \left\| \left[\hat{\vec{j}}(\vec{r}), \hat{H}(t_o)-\hat{H}'(t_o)\right] \right\| \Psi_o \right\rangle$$

$$= \left\langle \Psi_o \left\| \left[\hat{\vec{j}}(\vec{r}), V(t_o)-V'(t_o)\right] \right\| \Psi_o \right\rangle$$

$$= i\rho_o(\vec{r})\vec{\nabla}\big(v(\vec{r}t_o)-v'(\vec{r}t_o)\big)$$

if $\quad \frac{\partial^k}{\partial t^k}\left[v(\vec{r}t)-v'(\vec{r}t)\right]_{t=t_o} \neq \text{constant}$ holds for k=0

then $\quad i\frac{\partial}{\partial t}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]_{t=t_o} \neq 0$



$$\Rightarrow \quad \underline{\underline{\vec{j}(\vec{r}t) \neq \vec{j}'(\vec{r}t)}}$$

q.e.d.

if $\frac{\partial^k}{\partial t^k}\left[v(\vec{r}t)-v'(\vec{r}t)\right]_{t=t_o} \neq \text{constant}$ holds for k>0

→ use equation of motion k+1 times:

$$\left(i\frac{\partial}{\partial t}\right)^2 \vec{j}(\vec{r}t) = i\frac{\partial}{\partial t}\left\langle \Psi(t)\middle|\left[\hat{\vec{j}},\hat{H}(t)\right]\middle|\Psi(t)\right\rangle$$

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

$$\left(i\frac{\partial}{\partial t}\right)^3 \vec{j}(\vec{r}t) = i\frac{\partial}{\partial t}\left\langle \Psi(t)\middle| i\frac{\partial}{\partial t}\left[\vec{j},\hat{H}(t)\right] + \left[\left[\vec{j},H(t)\right],\hat{H}(t)\right]\middle|\Psi(t)\right\rangle$$

H‖ | |

$$\left(i\frac{\partial}{\partial t}\right)^{k+1}\left[\vec{j}(\vec{r}t)-\vec{j}\,'(\vec{r}t)\right]_{t=t_o} = i\rho_o(\vec{r})\vec{\nabla}\underbrace{\left(\left(i\frac{\partial}{\partial t}\right)^{k}\left[v(\vec{r}t)-v'(\vec{r}t)\right]_{t_o}\right)}_{\neq\ \text{constant}} \neq 0$$

$\Rightarrow$ $\underline{\vec{j}(\vec{r}t) \neq \vec{j}\,'(\vec{r}t)}$ q.e.d.

Step 2: densities

Use continuity equation:

$$\frac{\partial}{\partial t}\left[\rho(\vec{r}t)-\rho'(\vec{r}t)\right]=-\mathrm{div}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]$$

$$\Rightarrow \quad \frac{\partial^{k+2}}{\partial t^{k+2}}\left[\rho(\vec{r}t)-\rho'(\vec{r}t)\right]_{t=t_o}=-\mathrm{div}\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]_{t=t_o}$$

$$=-\mathrm{div}\;\rho_o(\vec{r})\vec{\nabla}\left(\underbrace{\frac{\partial^{k}}{\partial t^{k}}\left[v(\vec{r}t)-v'(\vec{r}t)\right]_{t=t_o}}_{\neq\,\mathrm{constant}}\right)$$

remains to be shown:

$$\mathrm{div}\left[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})\right]\neq 0 \qquad \text{if} \qquad u(\vec{r})\neq \text{constant}$$

Proof: by reductio ad absurdum

Assume: $\operatorname{div}\left[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})\right]=0$ with $u(\vec{r})\neq \text{constant}$

$$\int dr^3\rho_o(\vec{r})\;\left(\vec{\nabla}u(\vec{r})\right)^2$$

$$=-\int dr^3u(\vec{r})\underbrace{\operatorname{div}\left[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})\right]}_{0}+\underbrace{\int\rho_o(\vec{r})u(\vec{r})\vec{\nabla}u(\vec{r})\cdot d\vec{S}}_{0}=0$$

$$\Rightarrow\quad \rho_o(\vec{r})\left(\vec{\nabla}u(\vec{r})\right)^2\equiv 0 \quad\longrightarrow$$

contradiction to
$u(\vec{r})\neq \text{constant}$

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**

Approximation with correct asymptotic -1/r behavior: time-dependent optimized effective potential

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

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:

$$\rho[v]\,(rt) = \rho[v_0 + v_1]\,(rt)$$

$$= \rho[v_0](rt) \longrightarrow \rho_o(r)$$

$$+\int \left.\frac{\delta\rho[v](rt)}{\delta v(r't')}\right|_{v_0} v_1(r't')\,d^3r'dt' \longrightarrow \rho_1(rt)$$

$$+\frac{1}{2}\int\int \left.\frac{\delta^2\rho[v](rt)}{\delta v(r't')\,\delta v(r''t'')}\right|_{v_0} v_1(r',t')\,v_1(r'',t'')\,d^3r'd^3r''dt'dt'' \longrightarrow \rho_2(rt)$$

$$\vdots$$

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

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

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

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

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

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 Φ_0.
- $v_{ext}[\rho]$ 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.

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

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

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

$$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ f_{xc}(rt,r't') & \chi_S^{-1}(rt,r't') & \chi^{-1}(rt,r't') & W_C(rt,r't') \end{array}$$

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

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

$$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ f_{xc}(rt,r't') & \chi_S^{-1}(rt,r't') & \chi^{-1}(rt,r't') & W_C(rt,r't') \end{array}$$

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

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

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

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

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

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

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

- Exact integral equation for $\rho_1(r\,t)$, to be solved iteratively
- Need approximation for $f_{xc}(r't', r''t'') = \left. \frac{\delta v_{xc}[\rho](r't')}{\delta\rho(r''t'')} \right|_{\rho_0}$

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

Adiabatic approximation

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

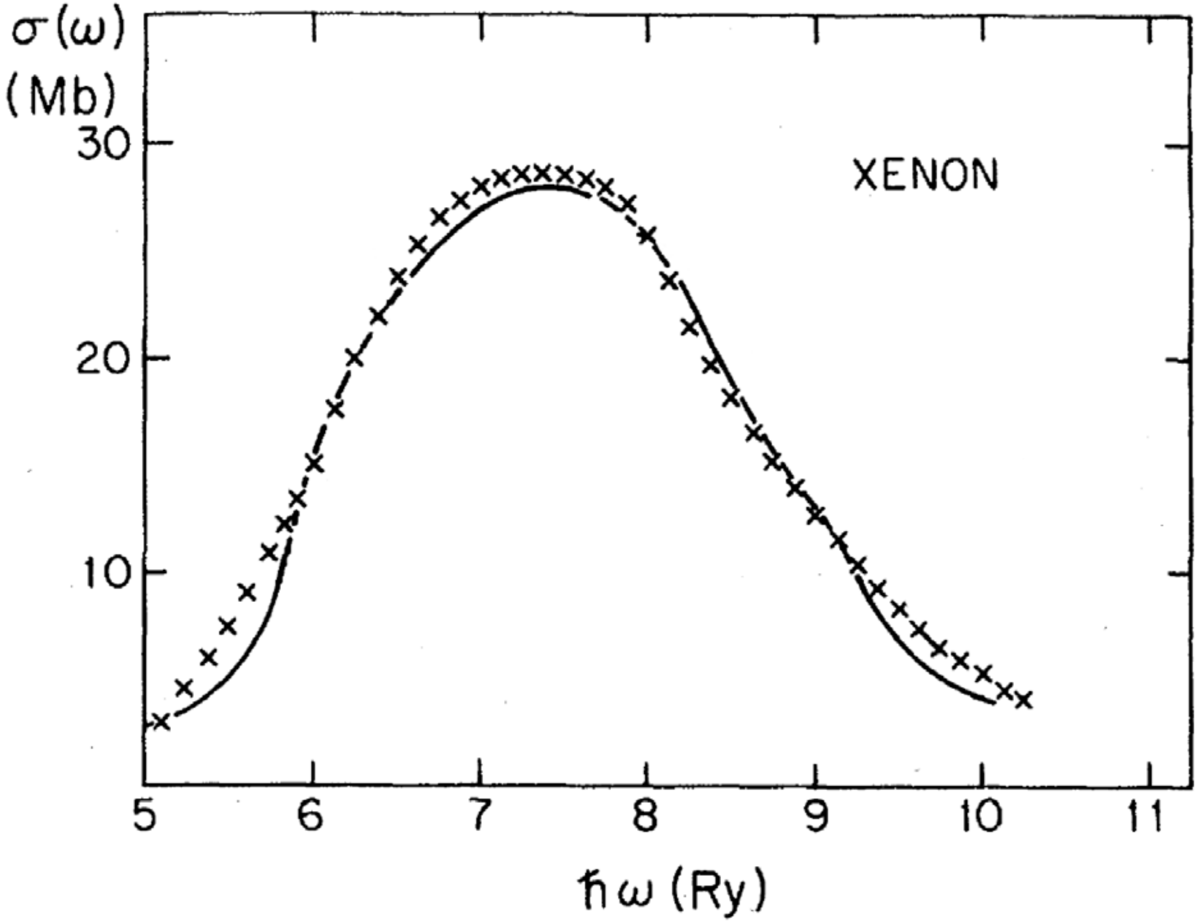
In the adiabatic approximation, the xc potential $v_{xc}(t)$ at time t only depends on the density ρ(t) at the very same point in time.

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

$$\Rightarrow\; f_{xc}^{\text{ALDA}}(rt, r't') = \left.\frac{\delta v_{xc}^{\text{ALDA}}(rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho}_0} = \delta(r-r')\delta(t-t')\left.\frac{\partial v_{xc}^{\text{ALDA}}}{\partial\rho(r)}\right|_{\boldsymbol{\rho}_0(\mathbf{r})}$$

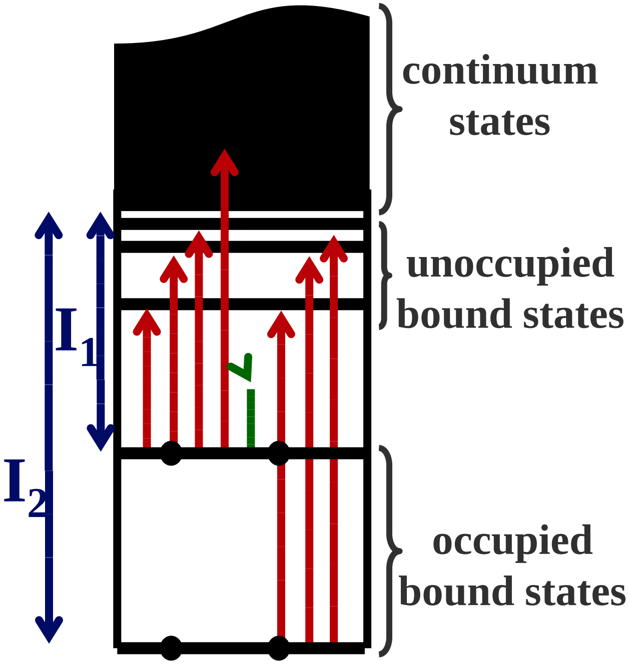
$$= \delta(r-r')\delta(t-t')\left.\frac{\partial^2 e_{xc}^{\text{hom}}}{\partial n^2}\right|_{\boldsymbol{\rho}_0(\mathbf{r})}$$

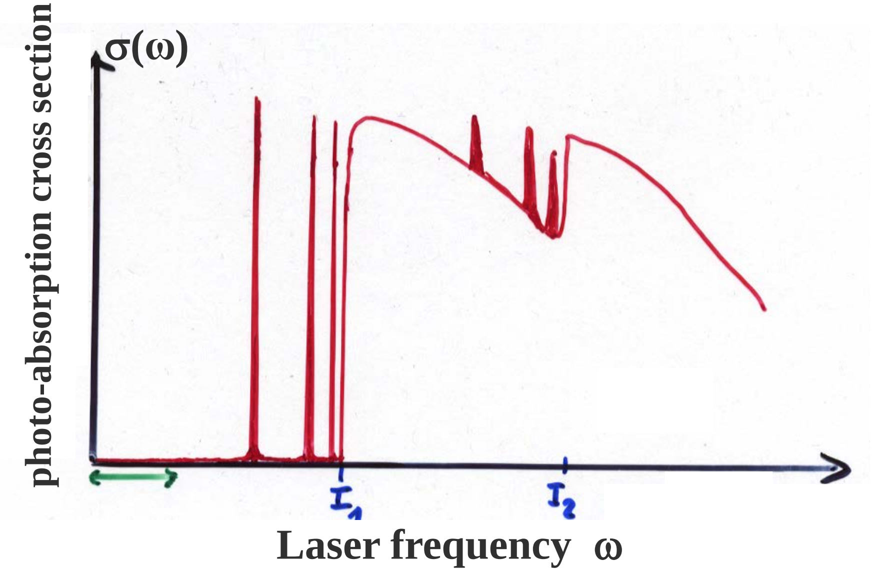
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.



Solid line: self-consistent time-dependent KS calculation [A. Zangwill and P. Soven, PRA 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





No absorption if ω < lowest excitation energy

Standard linear response formalism

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

$$H(t_0)|m\rangle = E_m|m\rangle$$ ← **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

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

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

Discrete excitation energies from TDDFT

exact representation of linear density response:

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

"^" denotes integral operators, i.e. $\hat{f}_{xc}\rho_1 \equiv \int f_{xc}(\vec{r},\vec{r}\,')\rho_1(\vec{r}\,')d^3r'$

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

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

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

$\varepsilon_j - \varepsilon_k$ KS excitation energy

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

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

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

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

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))

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

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

$$\alpha_q=f_a-f_j$$

$$\Phi_q(r)=\varphi_a^*(r)\varphi_j(r)$$

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

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)

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

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

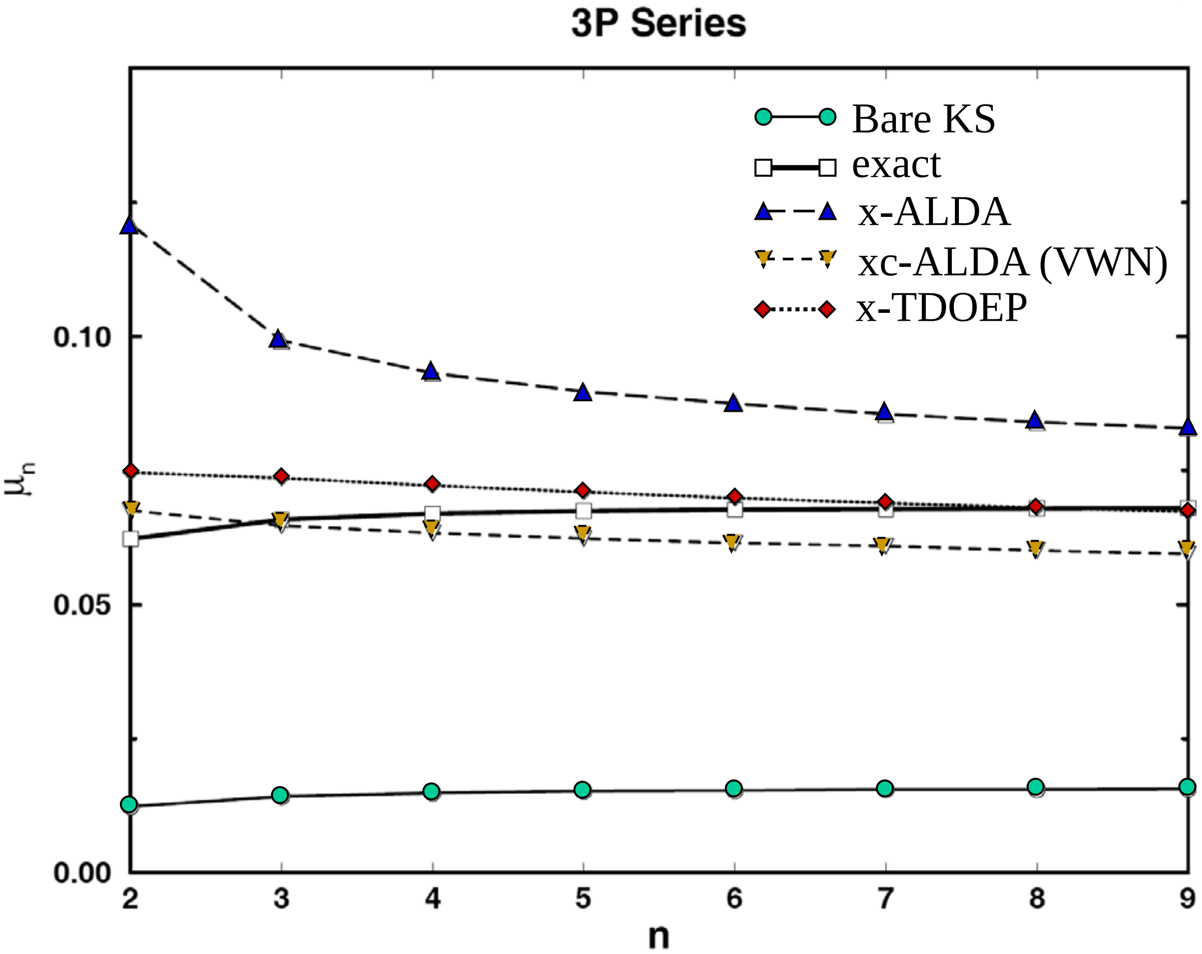
Excitation energies of CO molecule

State		Ω_{expt}	KS-transition	$\Delta\epsilon_{KS}$	$\Delta\epsilon_{KS} + K$
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.]



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.

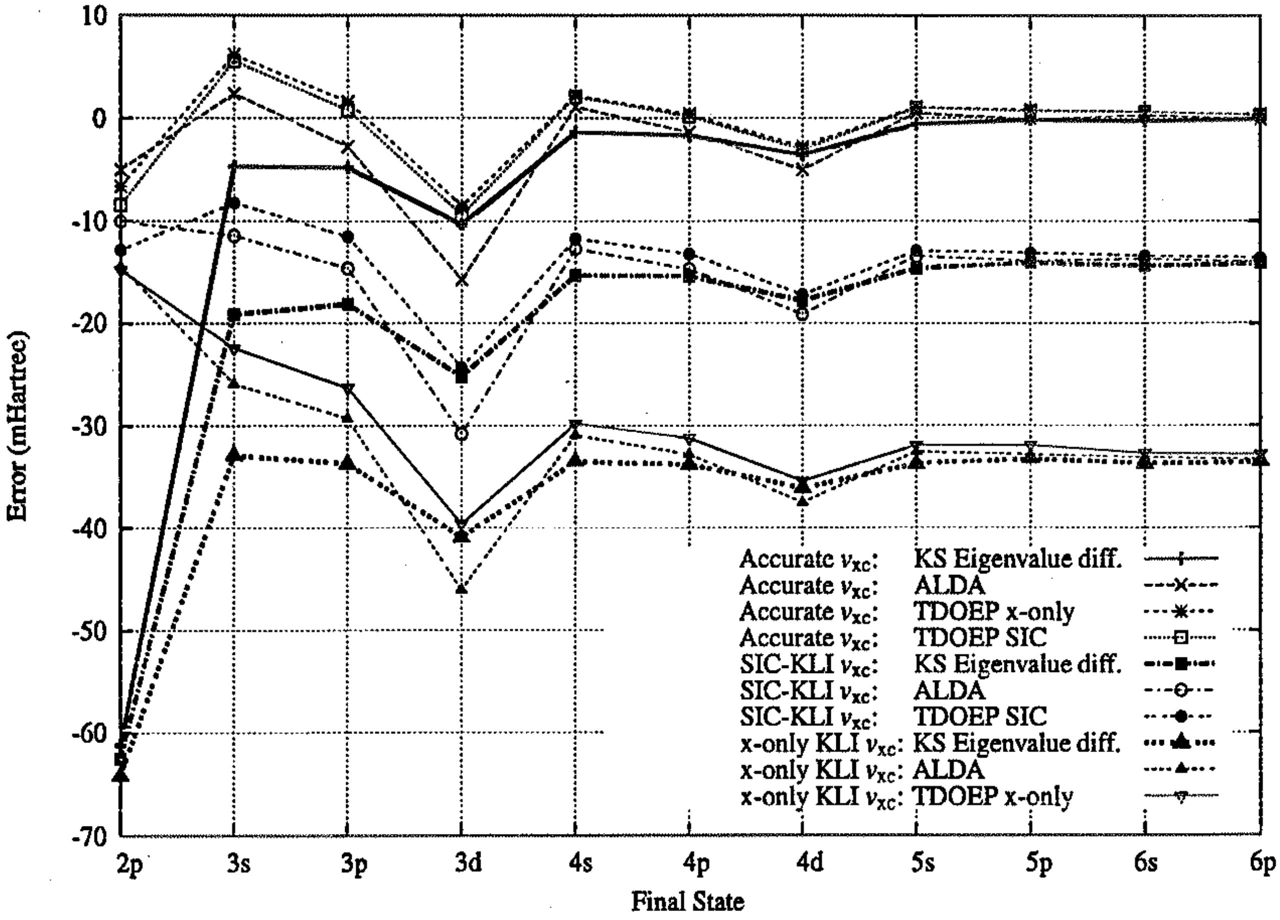


Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye,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

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

Failures of ALDA in the linear response regime

- **H$_2$ dissociation is incorrect:**

$$E\left({}^1\Sigma_u^+\right) - E\left({}^1\Sigma_g^+\right) \xrightarrow[R\to\infty]{} 0$$ **(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))

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

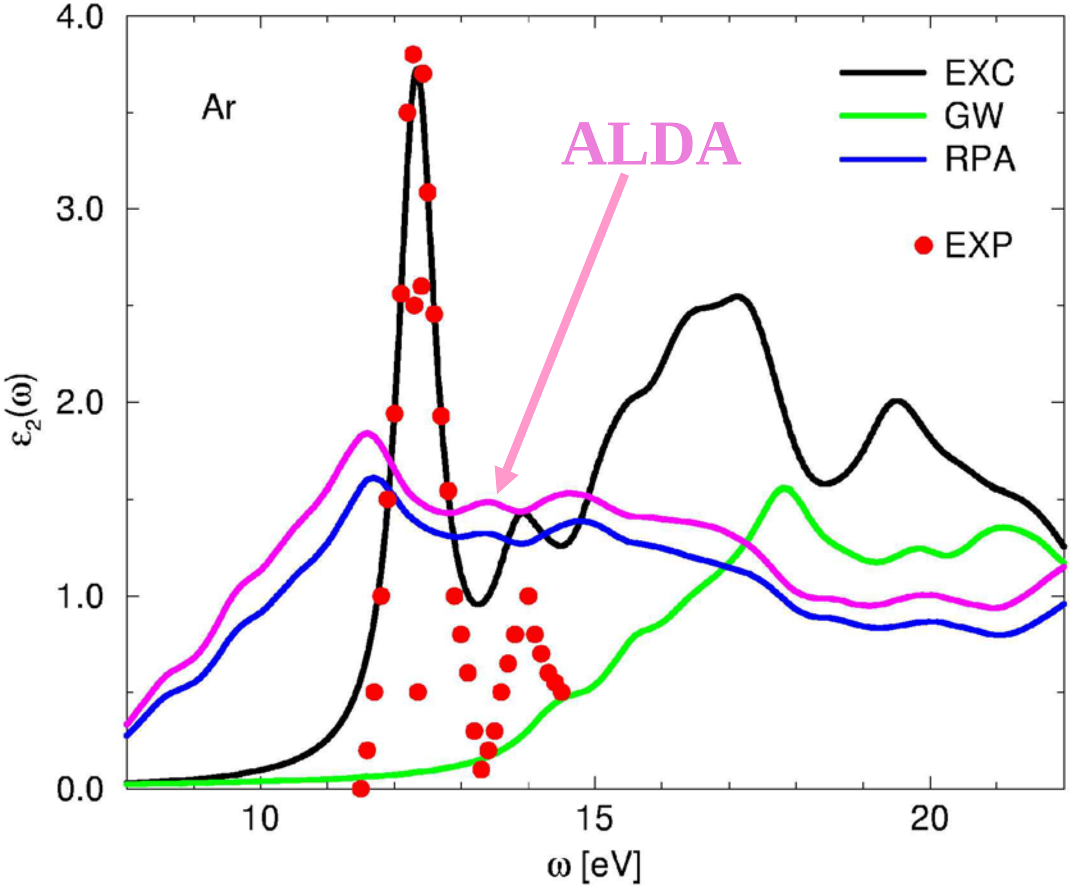
for insulators, $f_{xc}^{exact} \xrightarrow[q\to 0]{} 1/q^2$ **divergent.**

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

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

How good is ALDA for solids?

optical absorption (q=0)



Solid Argon

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

OBSERVATION:

In the long-wavelength-limit (q = 0), relevent for optical absorption, ALDA is not reliable. In particular, excitonic lines are completely missed. Results are very close to RPA.

EXPLANATION:

In the TDDFT response equation, the bare Coulomb interaction and the xc kernel only appear as sum ($W_C + f_{xc}$). For $q \rightarrow 0$, W_C 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 $q \rightarrow 0$ limit.

CONCLUSION:

Approximations for f_{xc} are needed which, for $q \rightarrow 0$, 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)).

A numerically inexpensive approximation for f_{xc} that works:

Exact relation between ε^{-1} and f_{xc} :

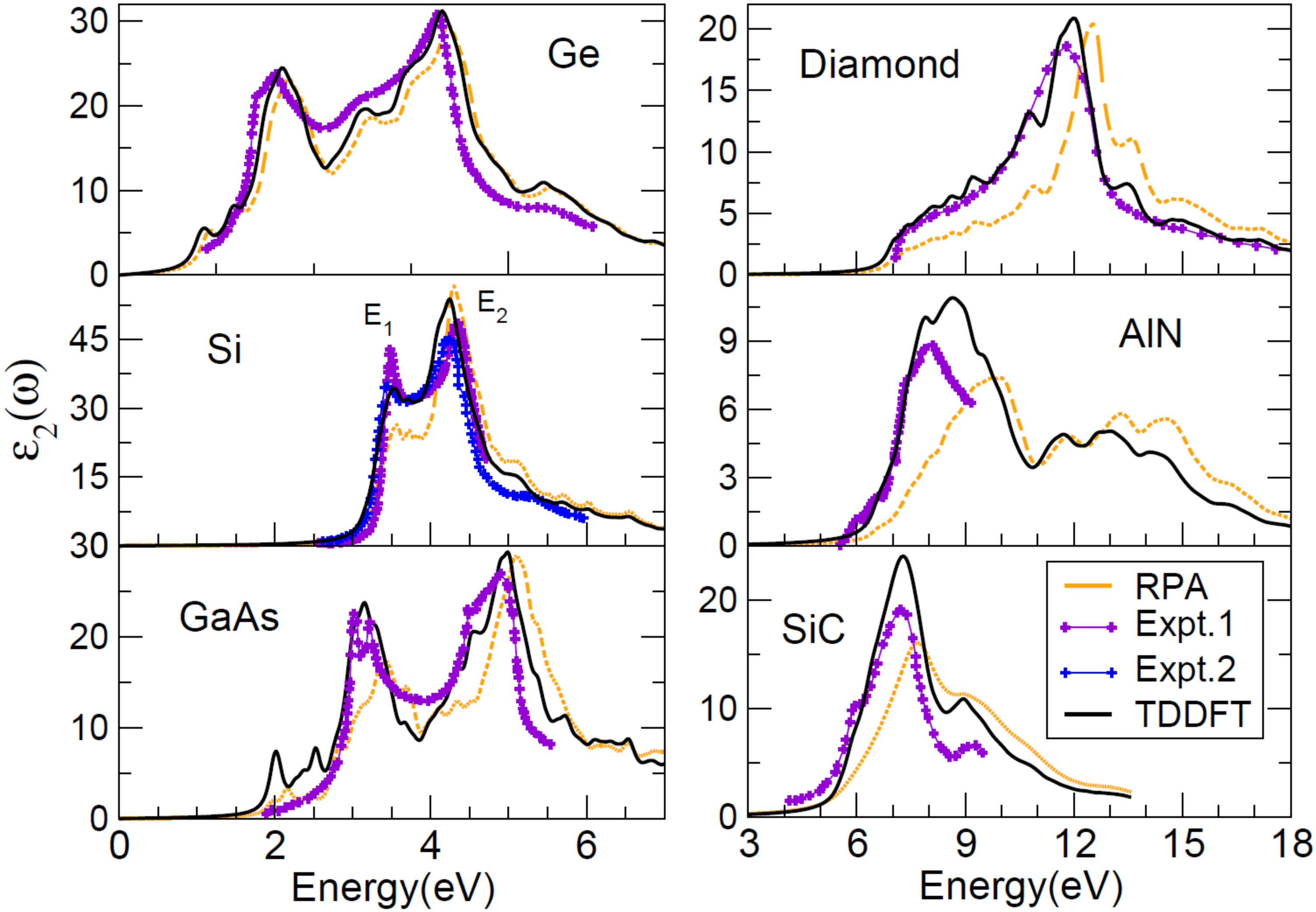
$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v(\mathbf{q})\,\chi(\mathbf{q},\omega)$$

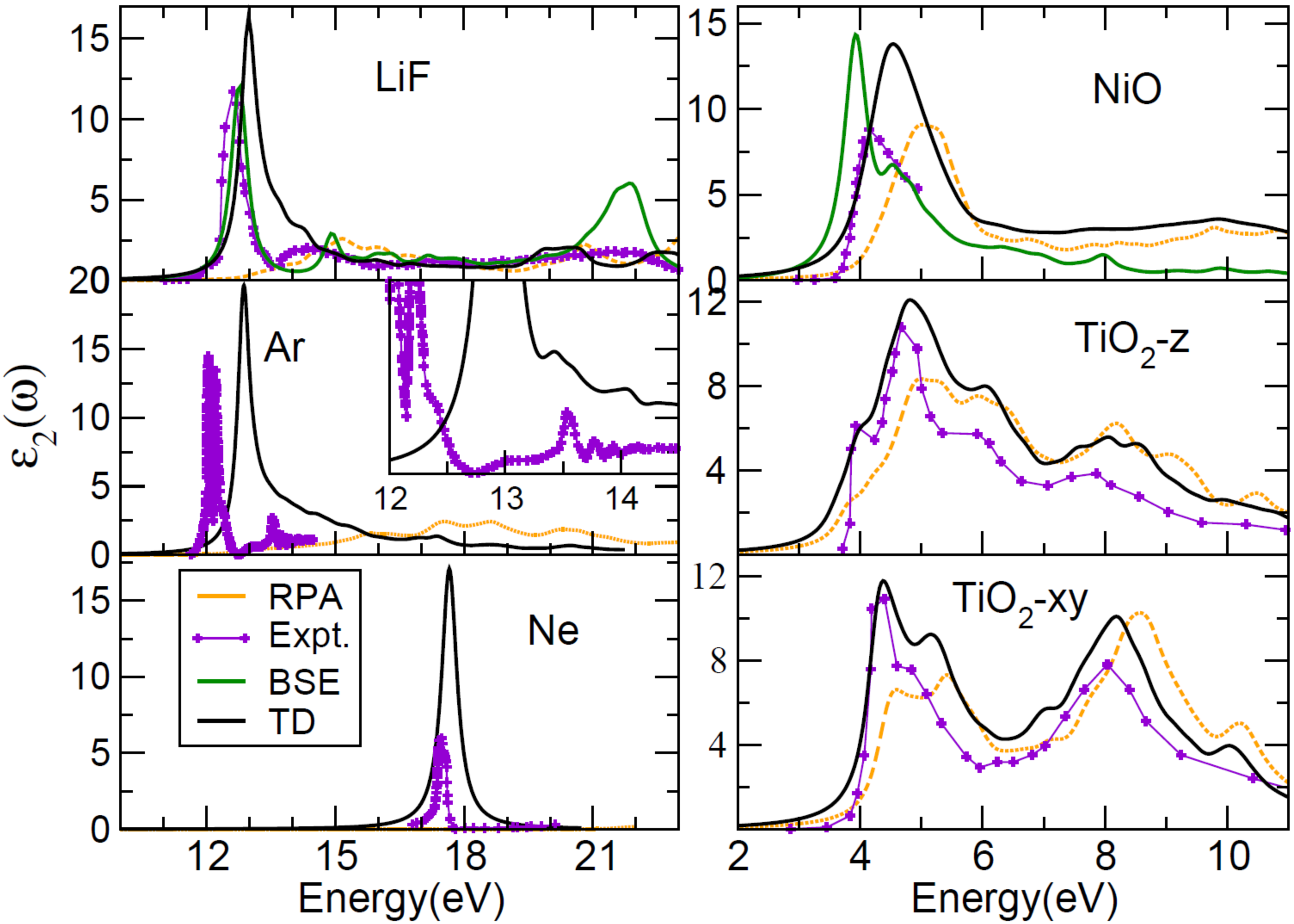
$$= 1 + \frac{v(\mathbf{q})\,\chi_s(\mathbf{q},\omega)}{1-\left[v(\mathbf{q})\; f_{xc}(\mathbf{q},\omega)\right]\chi_s(\mathbf{q},\omega)}$$

Bootstrap approximation for f_{xc} :

$$f_{xc}^{\text{bootstrap}}(\mathbf{q},\omega) = \frac{\varepsilon^{-1}(\mathbf{q},\omega=0)}{\chi_s^{00}(\mathbf{q},\omega=0)}$$

S. Sharma, K. Dewhurst, A. Sanna, E.K.U.G.,
Phys. Rev. Lett. 107, 186401 (2011)


Ge
Diamond
Si
E_1
E_2
AlN
GaAs
SiC
RPA
Expt.1
Expt.2
TDDFT
$\varepsilon_2(\omega)$
30
20
10
0
45
30
15
30
20
10
0
20
15
10
5
0
9
6
3
0
20
10
0
0
2
4
6
3
6
9
12
15
18
Energy(eV)
Energy(eV)


$\varepsilon_2(\omega)$
LiF
Ar
Ne
NiO
TiO_2-z
TiO_2-xy
RPA
Expt.
BSE
TD
0
5
10
15
20
12
13
14
12
15
18
21
2
4
6
8
10
12
Energy(eV)
Energy(eV)