Time-dependent density functional theory

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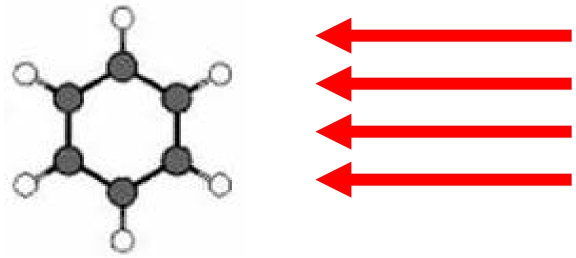
OUTLINE

- **Phenomena to be described by TDDFT**
- **Basic theorems of TDDFT**
- **Approximate xc functionals: "Exact adiabatic" approximation**
- **TDDFT in the linear-response regime:**
  -- Optical excitation spectra of molecules
  -- Excitonic effects in the optical spectra of solids
  -- Charge-transfer excitations and the discontinuity of the xc kernel

Time-dependent systems

Generic situation:
Molecule in laser field



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

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

Non-perturbative solution of full TDSE required

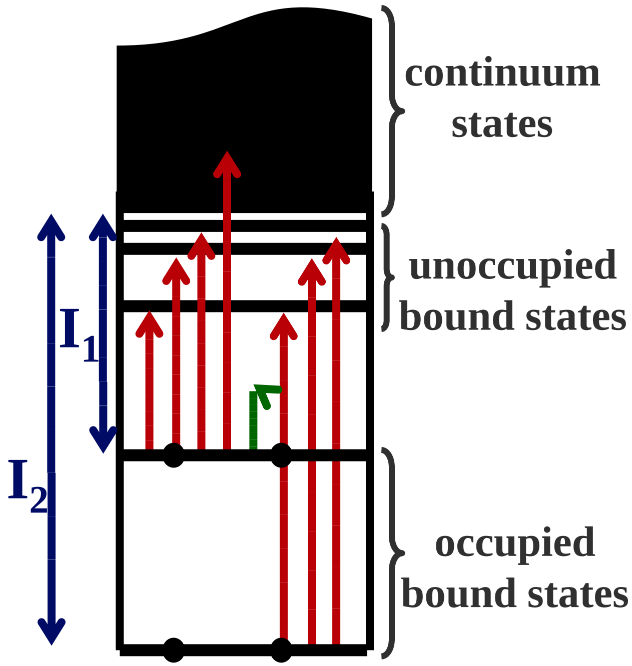
Weak laser ($v_{laser}(t) << v_{en}$) :

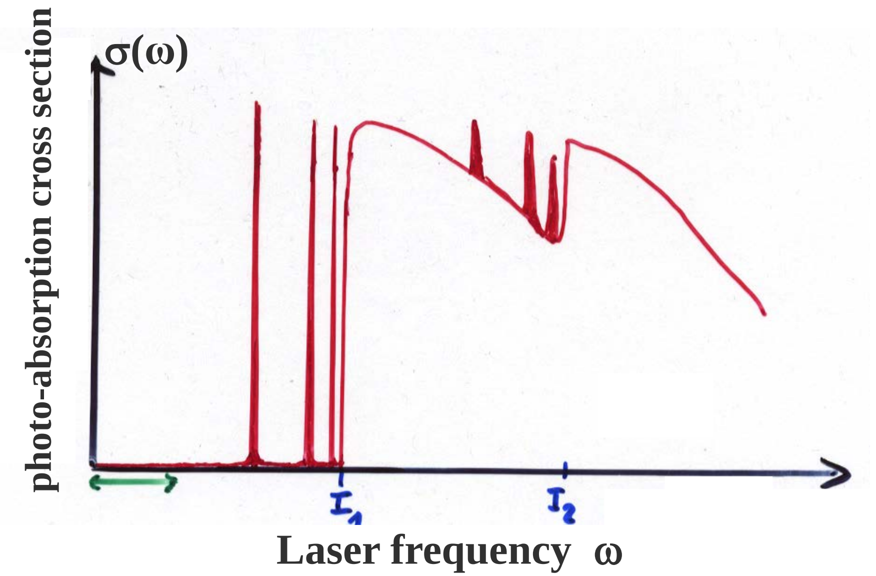
Calculate **1. Linear density response** $\rho_1(\vec{r}\ t)$

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





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

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

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

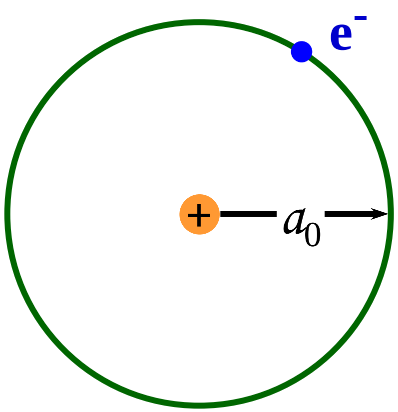
Strong Laser Fields

Intensities in the range of 10^{13} …10^{16} W/cm^2

Comparison: Electric field on 1st Bohr-orbit in hydrogen

$$E = \frac{1}{4\pi\varepsilon_0}\frac{e}{a_0^2} = 5.1\times10^9\ \mathrm{V/m}$$

$$I = \frac{1}{2}\varepsilon_0 c E^2 = 3.51\times10^{16}\ \mathrm{W/cm^2}$$



Three quantities to look at:

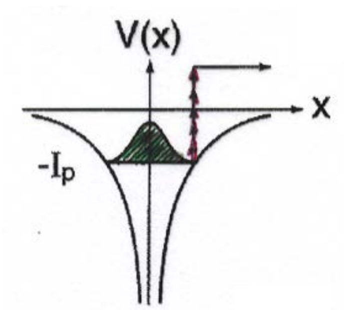
I. **Emitted ions**
II. **Emitted electrons**
III. **Emitted photons**

I. Emitted Ions

Three regimes of ionization, depending on Keldysh parameter

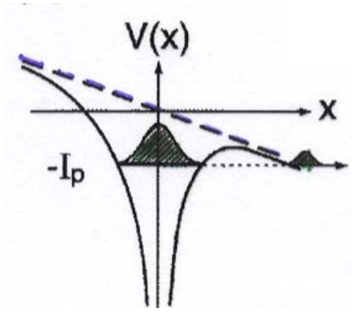
$$\gamma := \frac{\omega}{E} (\text{a.u.})$$

Multiphoton



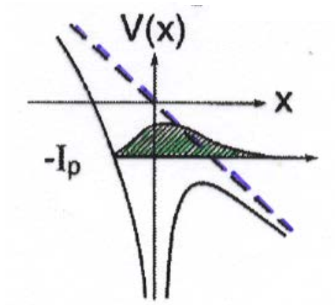
$\gamma >> 1$

Tunneling



$\gamma \approx 1$

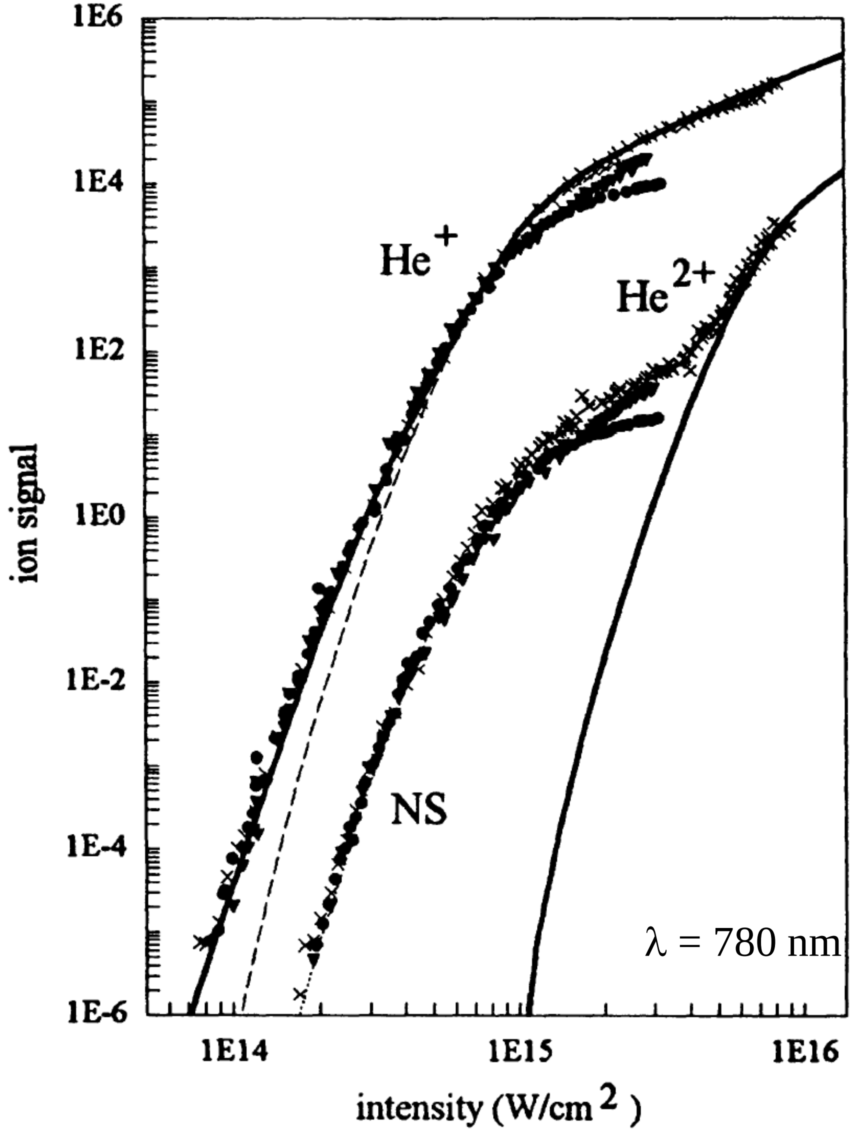
Over the barrier



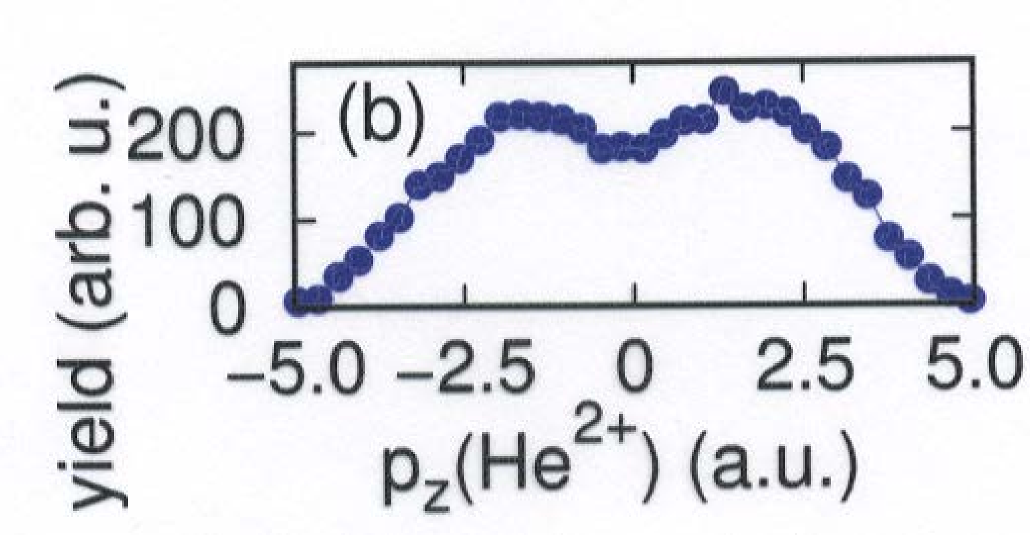
$\gamma << 1$

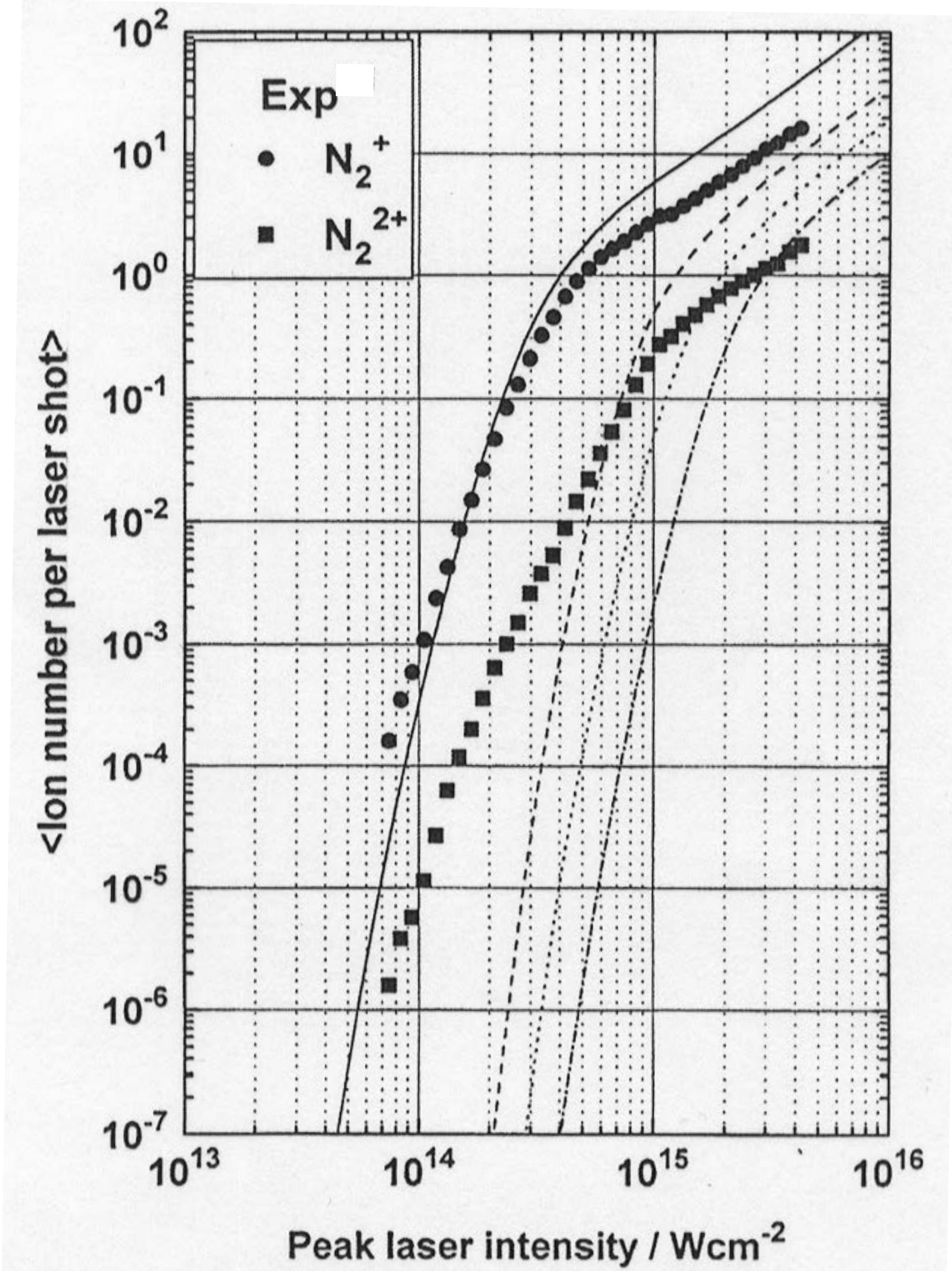
Multiphoton-Ionization (He)

Walker et al.,
PRL 73, 1227 (1994)



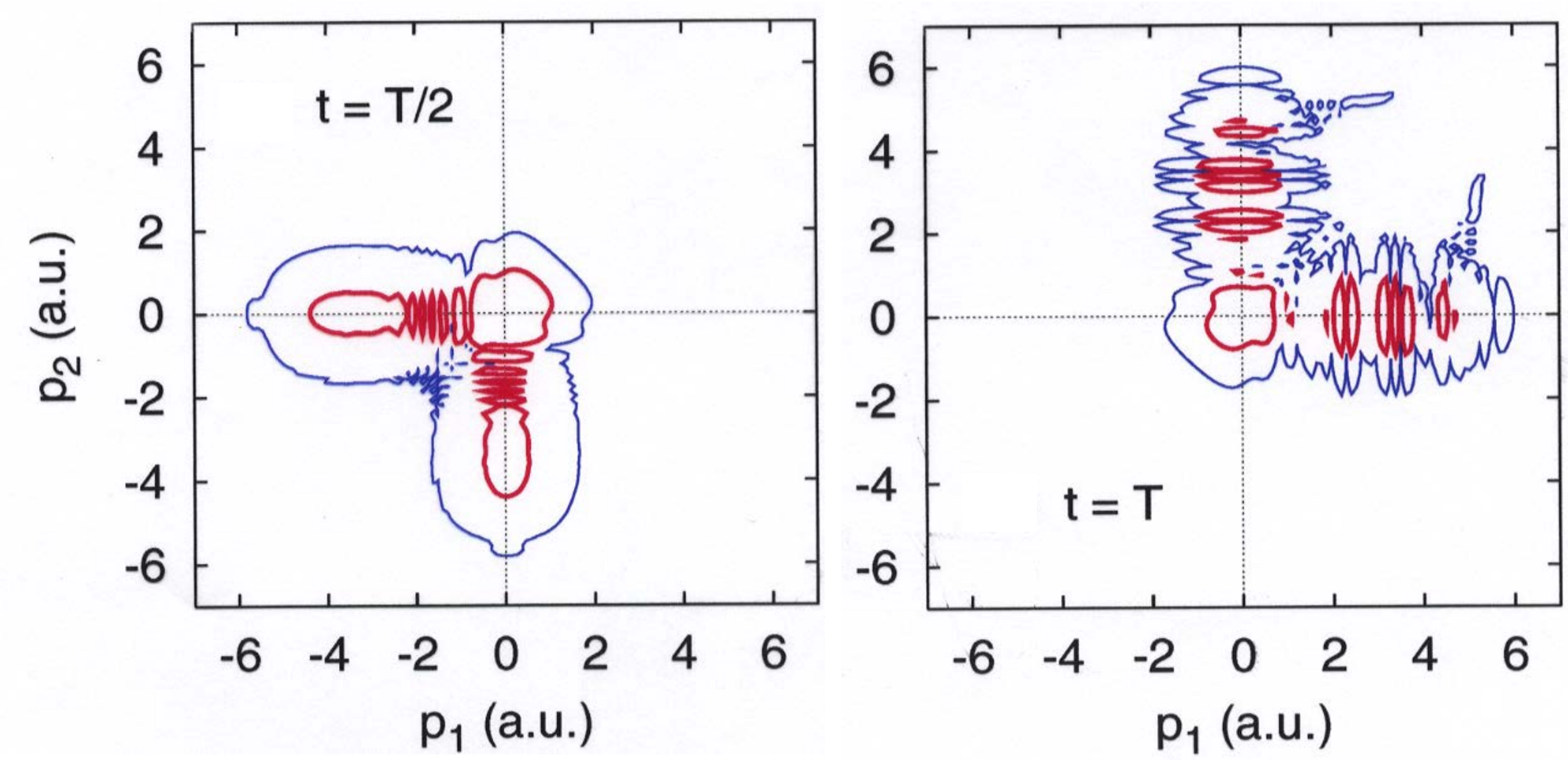
Momentum Distribution of the He^{2+} recoil ions




Exp
N_2^+
N_2^{2+}
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
<Ion number per laser shot>
10^{13}
10^{14}
10^{15}
10^{16}
Peak laser intensity / Wcm^{-2}

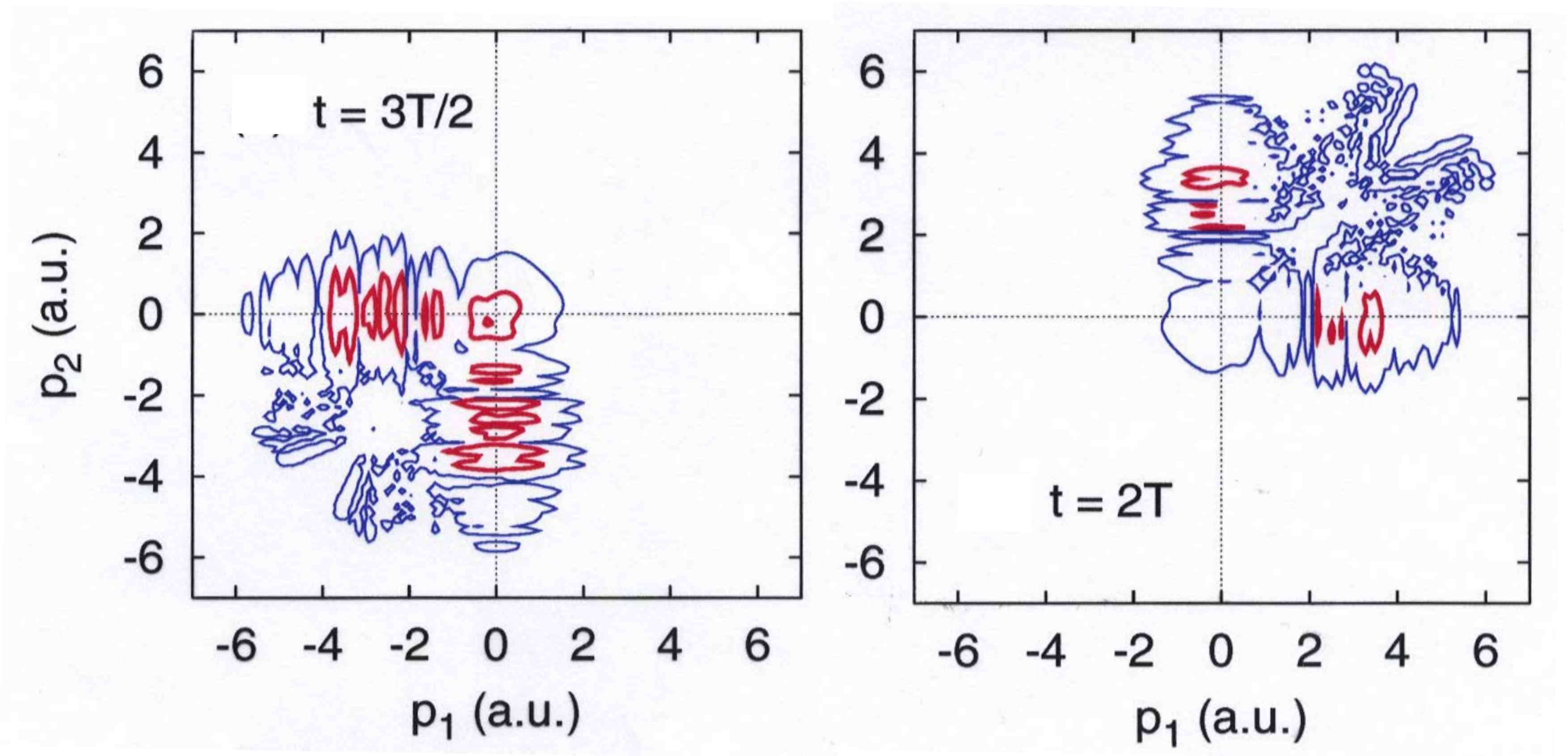
$\left|\Psi\left(p_1, p_2, t\right)\right|^2$ of the He atom

(M. Lein, E.K.U.G., V. Engel, J. Phys. B <u>33</u>, 433 (2000))



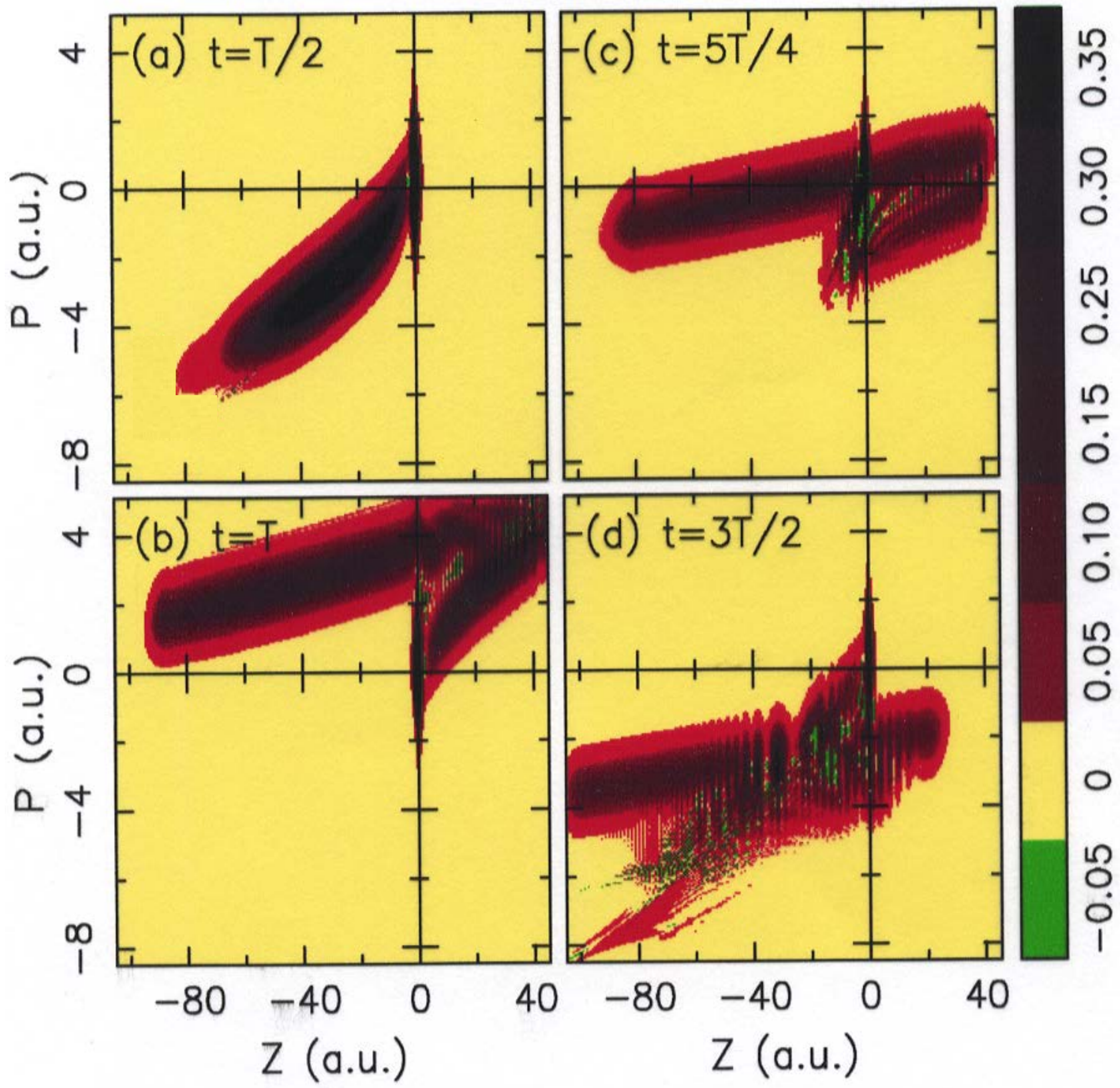
$$\left|\Psi\left(p_1, p_2, t\right)\right|^2 \quad \text{of the He atom}$$

(M. Lein, E.K.U.G., V. Engel, J. Phys. B <u>33</u>, 433 (2000))



Wigner distribution
W(Z,P,t) of the
electronic center
of mass for He atom

(M. Lein, E.K.U.G., V. Engel, PRL <u>85</u>, 4707 (2000))



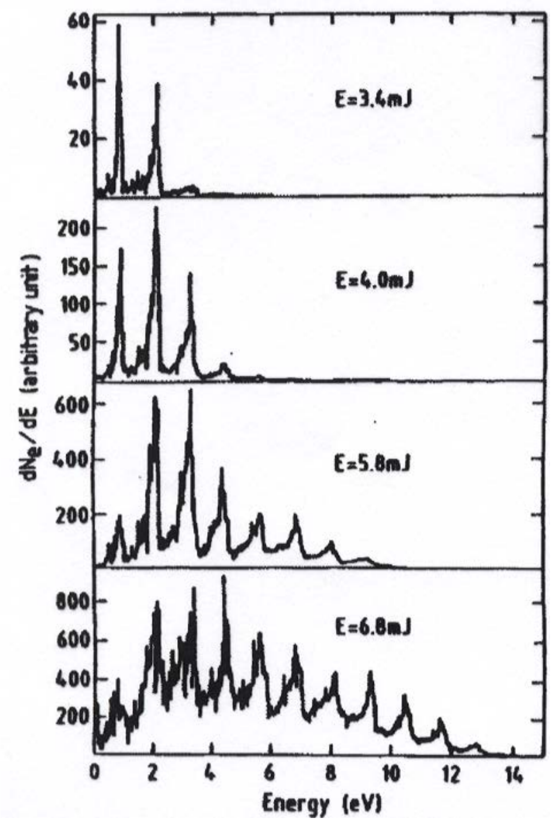
$v_{Laser}(z,t) = E\, z \sin \omega t$ $I = 10^{15}\ W/cm^2$ $\lambda = 780$ nm

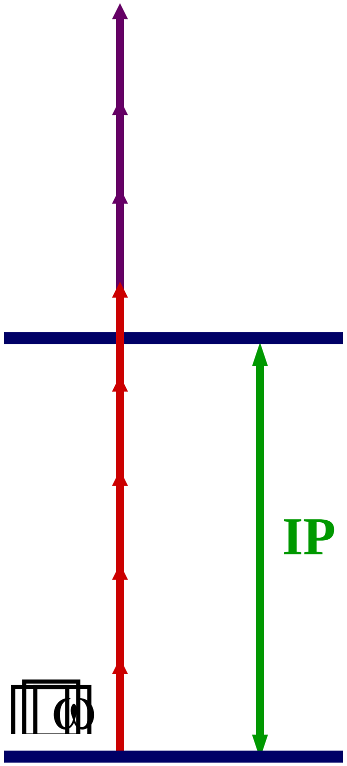
II. Electrons: Above-Threshold-Ionization (ATI)

Ionized electrons absorb more photons than necessary to overcome the ionization potential (IP)

Photoelectrons: $E_{kin} = (n+s)\hbar\omega - IP$

$\Rightarrow$ Equidistant maxima in intervals of $\hbar\omega$:

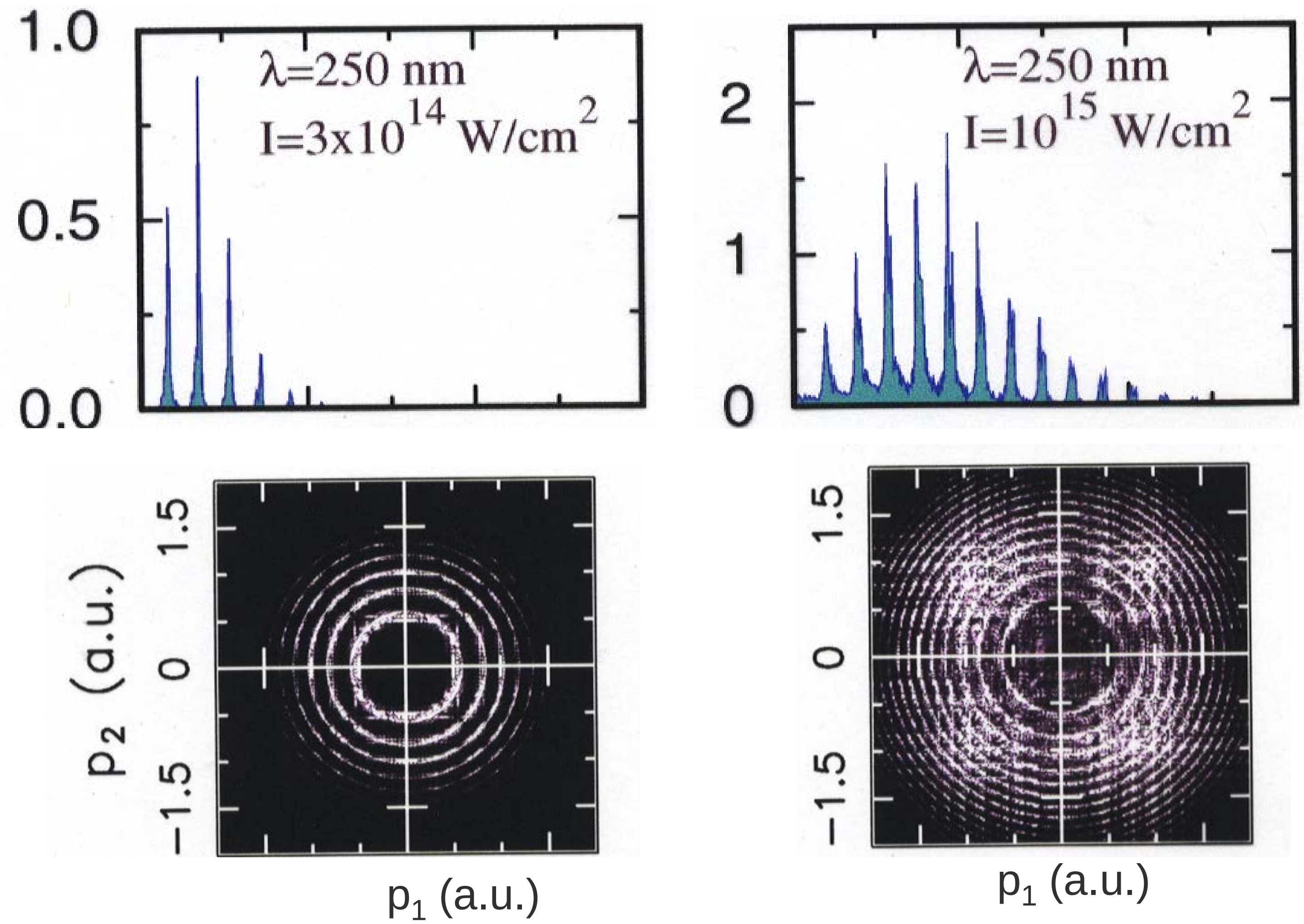




Agostini et al., PRL 42, 1127 (1979)

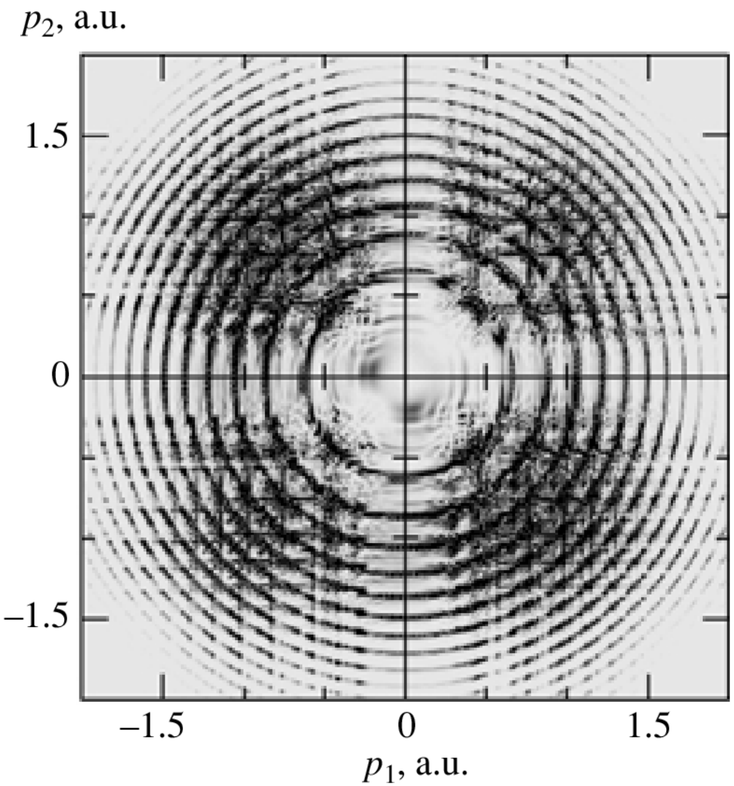
He: Above threshold double ionization

M. Lein, E.K.U.G., V. Engel, PRA 64, 23406 (2001)

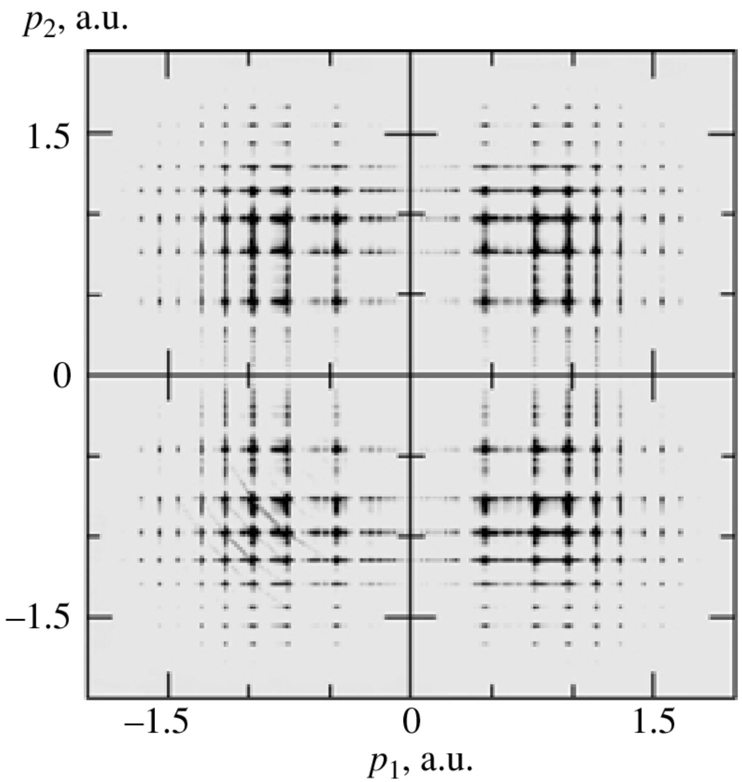


Role of electron-electron interaction

M. Lein, E.K.U.G., and V. Engel, Laser Physics 12, 487 (2002)



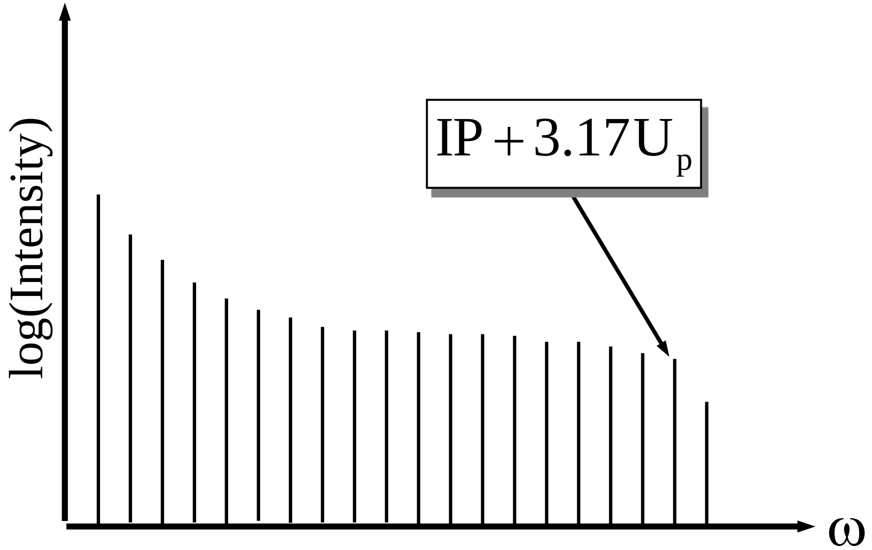
Two-electron momentum distribution for double ionization of the He model atom by a 250 nm pulse with intensity 10^{15} W/cm^2.

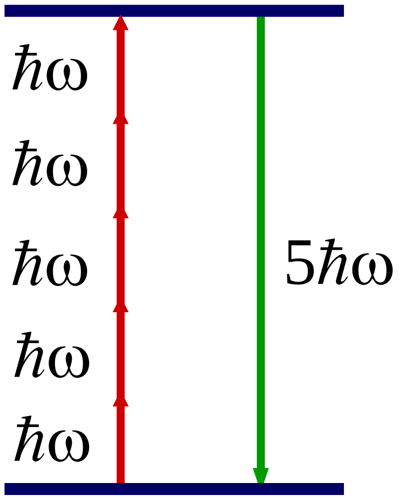


Two-electron momentum distribution for double ionization of the He model atom with non-interaction electrons by a 250 nm pulse with intensity 10^{15} W/cm^2.

III. Photons: High-Harmonic Generation

Emission of photons whose frequencies are integer multiples of the driving field. Over a wide frequency range, the peak intensities are almost constant (plateau).

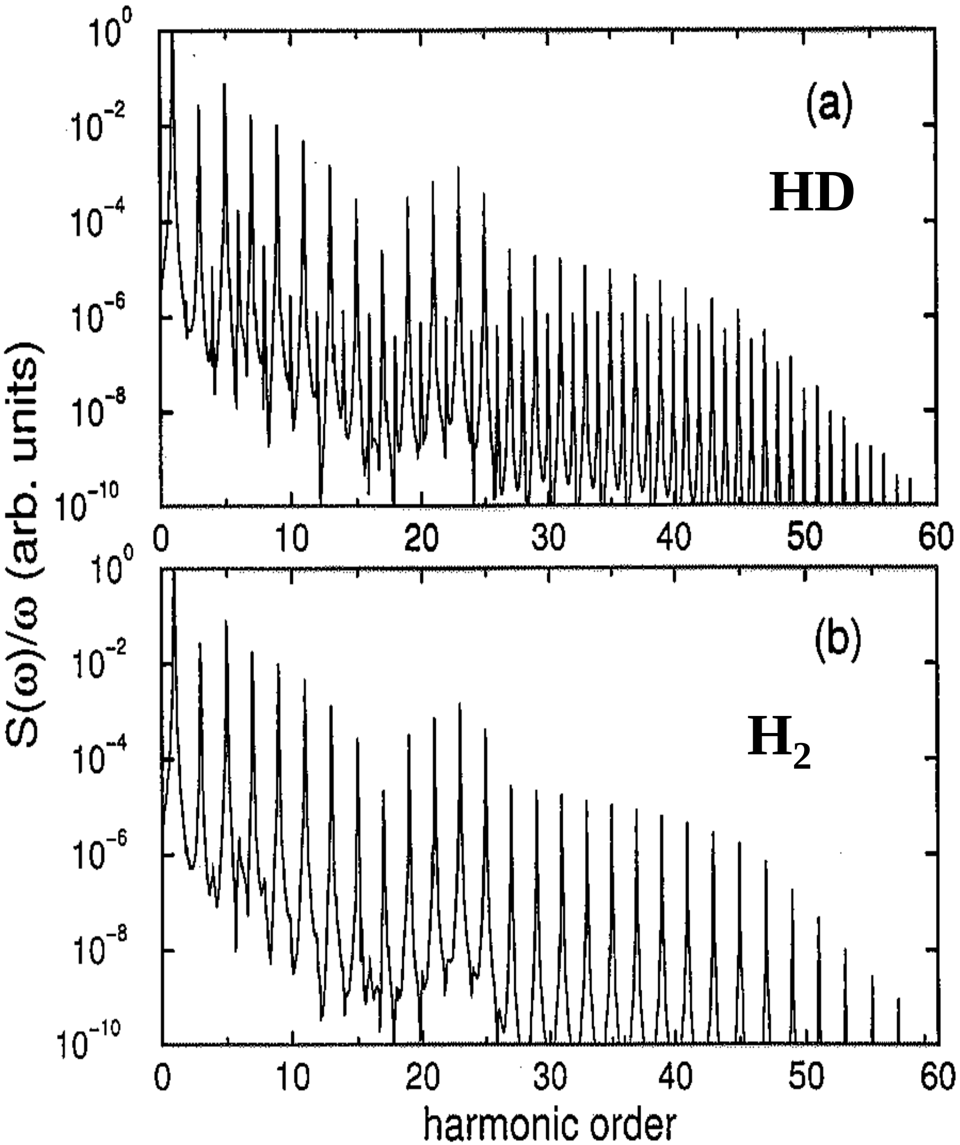




Even harmonic generation due to nuclear motion

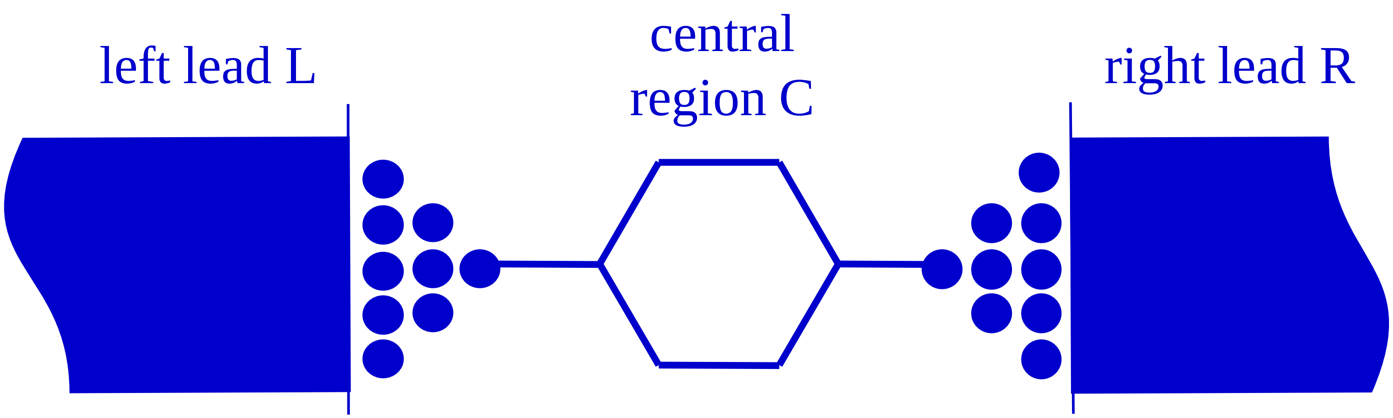
(a) Harmonic spectrum generated from the model HD molecule driven by a laser with peak intensity 10^{14} W/cm^2 and wavelength 770 nm. The plotted quantity is proportional to the number of emitted phonons. (b) Same as panel (a) for the model H_2 molecule.

T. Kreibich, M. Lein, V. Engel, E.K.U.G., PRL <u>87</u>, 103901 (2001)



Molecular Electronics

Dream: Use single molecules as basic units (transistors, diodes, …) of electronic devices



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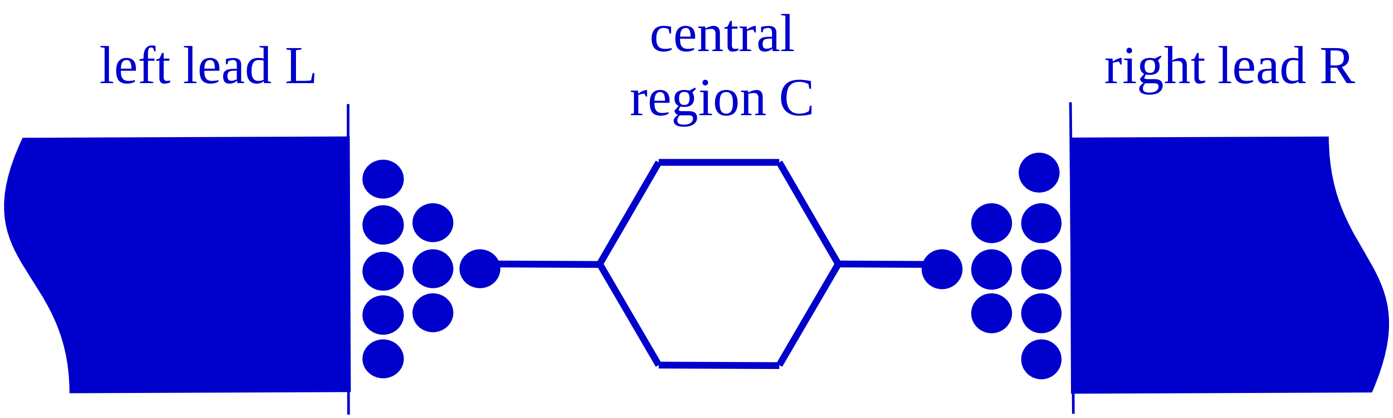


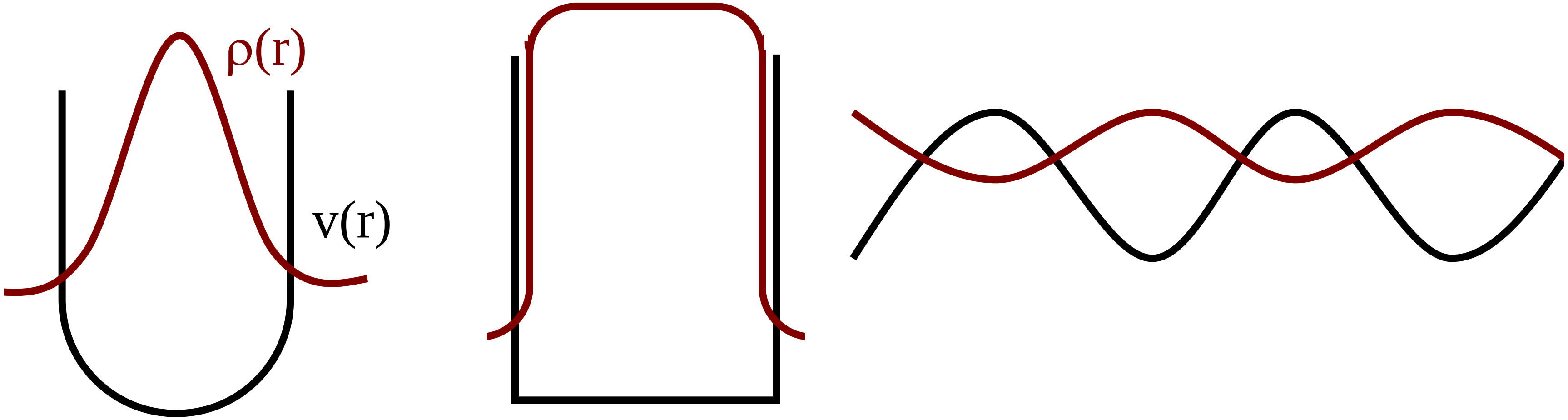
Bias between L and R is turned on: $U(t) \longrightarrow V$ for large t

A steady current, I, may develop as a result.

- **Calculate current-voltage characteristics I(V)**
- **Investigate cases where no steady state is achieved**

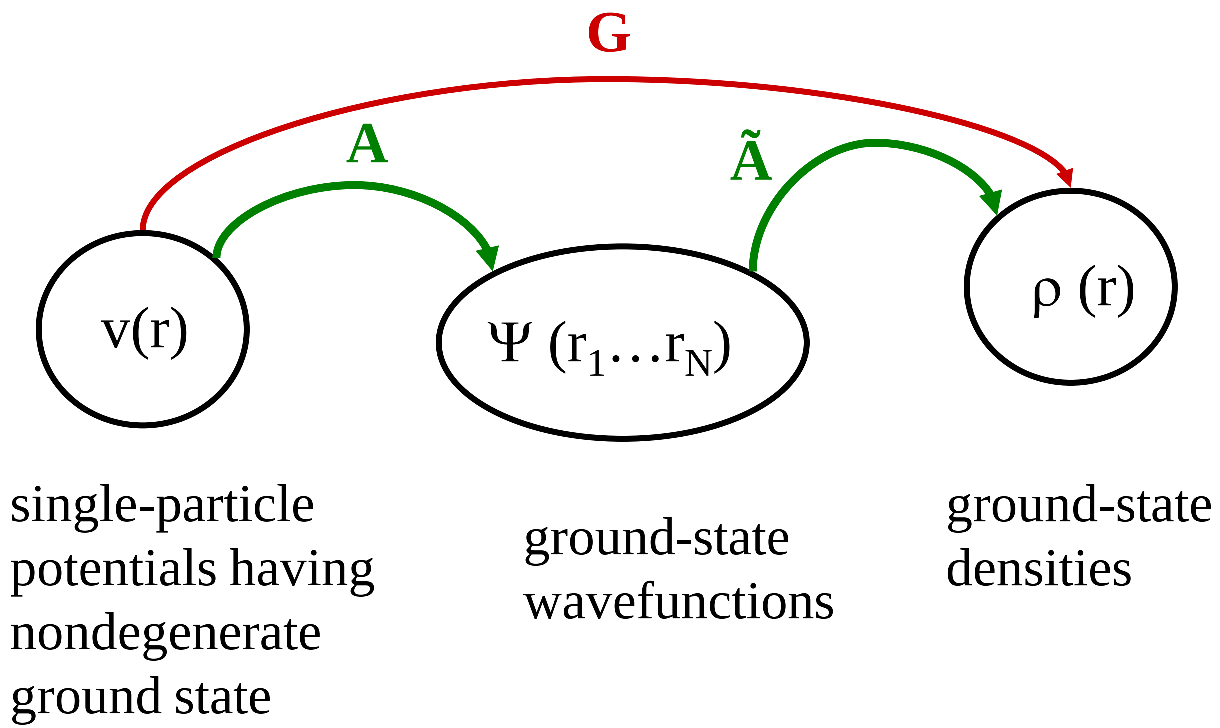
Ground-State Density Functional Theory

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?

Ground-State Density Functional Theory



<u>Hohenberg-Kohn-Theorem (1964)</u>

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

By construction, the HK mapping is well-defined for all those functions ρ(r) that are ground-state densities of some potential (so called V-representable functions ρ(r)).

QUESTION: Are all "reasonable" functions ρ(r) V-representable?

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

On a lattice (finite or infinite), any normalizable positive function ρ(r), that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable.

In other words: For any given ρ(r) (normalizable, positive, compatible with Pauli principle) there exists a potential, $v_{ext}[\rho](r)$, yielding ρ(r) as interacting ground-state density, and there exists another potential, $v_s[\rho](r)$, yielding ρ(r) as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given ρ(r) is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).

$$v_{ext}[\rho](\mathbf{r}) \; \overbrace{\longleftrightarrow}^{\boxed{\text{HK 1-1 mapping for interacting particles}}} \; \rho(\mathbf{r}) \; \overbrace{\longleftrightarrow}^{\boxed{\text{HK 1-1 mapping for non-interacting particles}}} \; v_s[\rho](\mathbf{r})$$

<u>**Kohn-Sham Theorem**</u>

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

$$\left(-\frac{\nabla^2}{2} + v_{s,o}(\mathbf{r})\right)\varphi_j(\mathbf{r}) = \epsilon_j\,\varphi_j(\mathbf{r}), \qquad \rho_o(\mathbf{r}) = \sum_{\substack{j\,(\text{with} \\ \text{lowest}\,\epsilon_j)}}^{N} \left|\varphi_j(\mathbf{r})\right|^2$$

<u>**proof**</u>: $v_{s,o}(\mathbf{r}) = v_s[\rho_o](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

<u>**Note: The KS equations do not follow from the variational principle!!**</u>

Time-dependent density-functional formalism

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

Basic 1-1 correspondence:

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

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

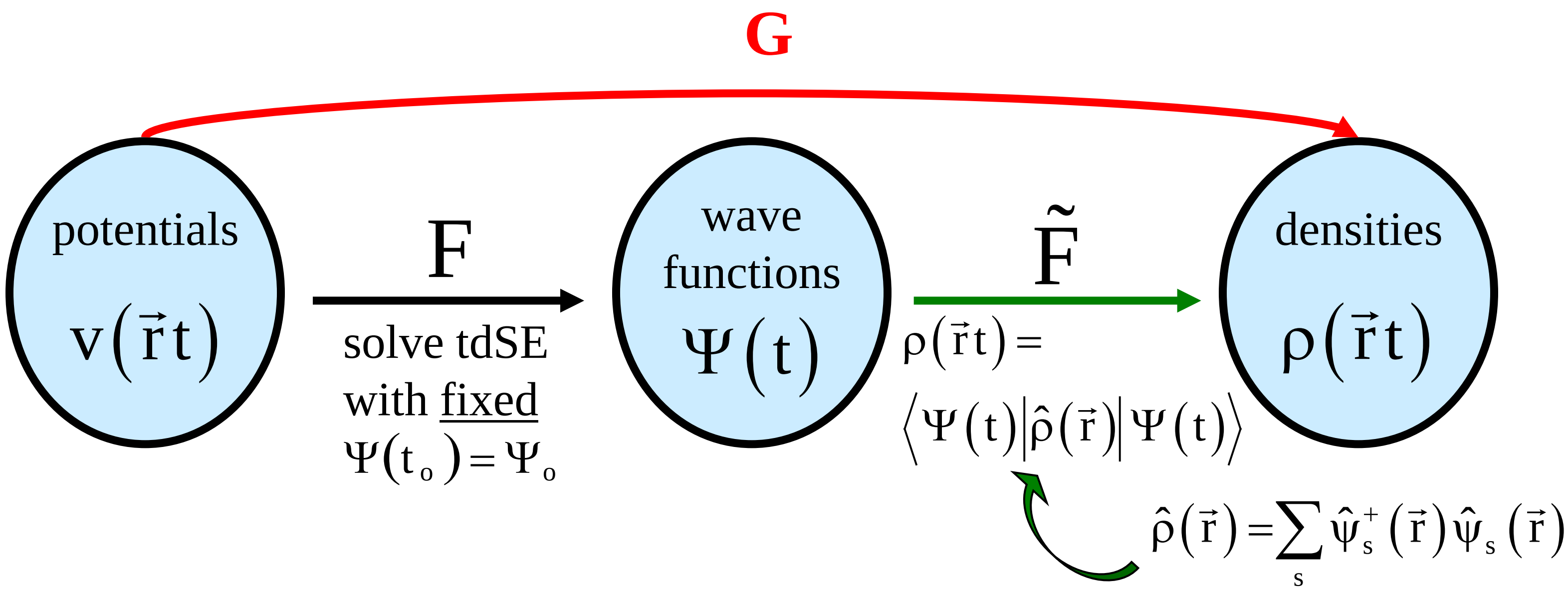
$$i\hbar \frac{\partial}{\partial t}\varphi_j(rt) = \left(-\frac{\hbar^2\nabla^2}{2m} + v_S[\rho](rt)\right)\varphi_j(rt)$$

with the local potential

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

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

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



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

<u>complete</u> 1 - 1 correspondence <u>not</u> to be expected!

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

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

$$\hat{V}'(t) = \hat{V}(t) + C(t) \;\Leftrightarrow\; \Psi'(t) = e^{-i\alpha(t)}\Psi(t)$$

"no operator"

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

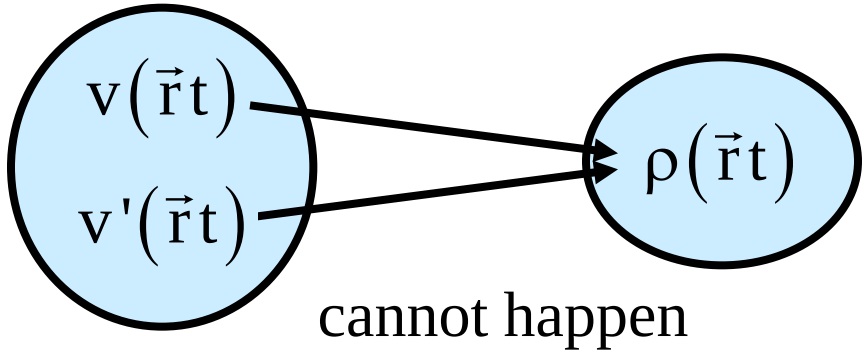
$$G: \ v(\vec{r}t) \mapsto \rho(\vec{r}t)$$

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:



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

$\Downarrow$

potential expandable into Taylor series

$\Downarrow$

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

$\Downarrow$ 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

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

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

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:

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

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

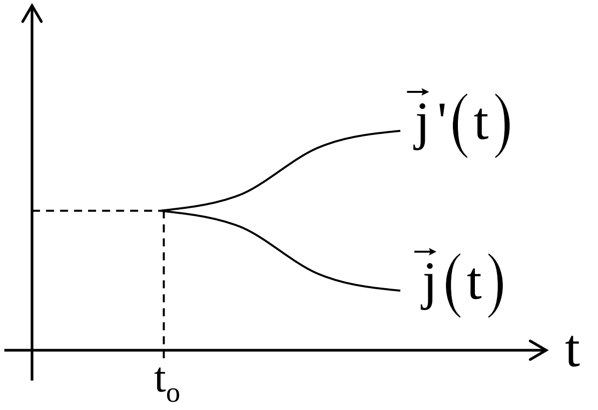
$$i\frac{\partial}{\partial t}\left[\vec{j}(\vec{r}t)-\vec{j}'(\vec{r}t)\right]_{t=t_o} = \left\langle \Psi_o \middle\| \left[\hat{\vec{j}}(\vec{r}),\hat{H}(t_o)-\hat{H}'(t_o)\right] \middle\| \Psi_o \right\rangle$$

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

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

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

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



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

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

$\longrightarrow$ <u>use equation of motion k+1 times</u>:

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

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

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

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

$\Rightarrow \quad \underline{\vec{j}(\vec{r}t) \neq \vec{j}\,'(\vec{r}t)}$ $\qquad$ 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: $\mathrm{div}\left[\rho_o(\vec{r})\vec{\nabla}u(\vec{r})\right]=0$ with $u(\vec{r})\neq \text{constant}$

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

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

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

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

i. **the basic 1-1 mapping for interacting and non-interacting particles**
ii. **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
S. Mukamel
T. Gal
G. Vignale
.
.

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

Adiabatic Approximation:

$$v_{xc}^{adiab}(\vec{r}t) := v_{xc}^{stat}[n](r)\Big|_{n=\rho(\vec{r}'t)}$$

where V_{xc}^{stat} **= xc potential of ground-state DFT**

Example:

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

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))

Assess the quality of the adiabatic approximation by the following steps:

- **Solve 1D model for He atom in strong laser fields (numerically) exactly. This yields exact TD density $\rho(r,t)$.**

- **Inversion of one-particle TDSE yields exact TDKS potential. Then, subtracting the laser field and the TD-Hartree term, yields the <u>exact TD xc potential</u> .**

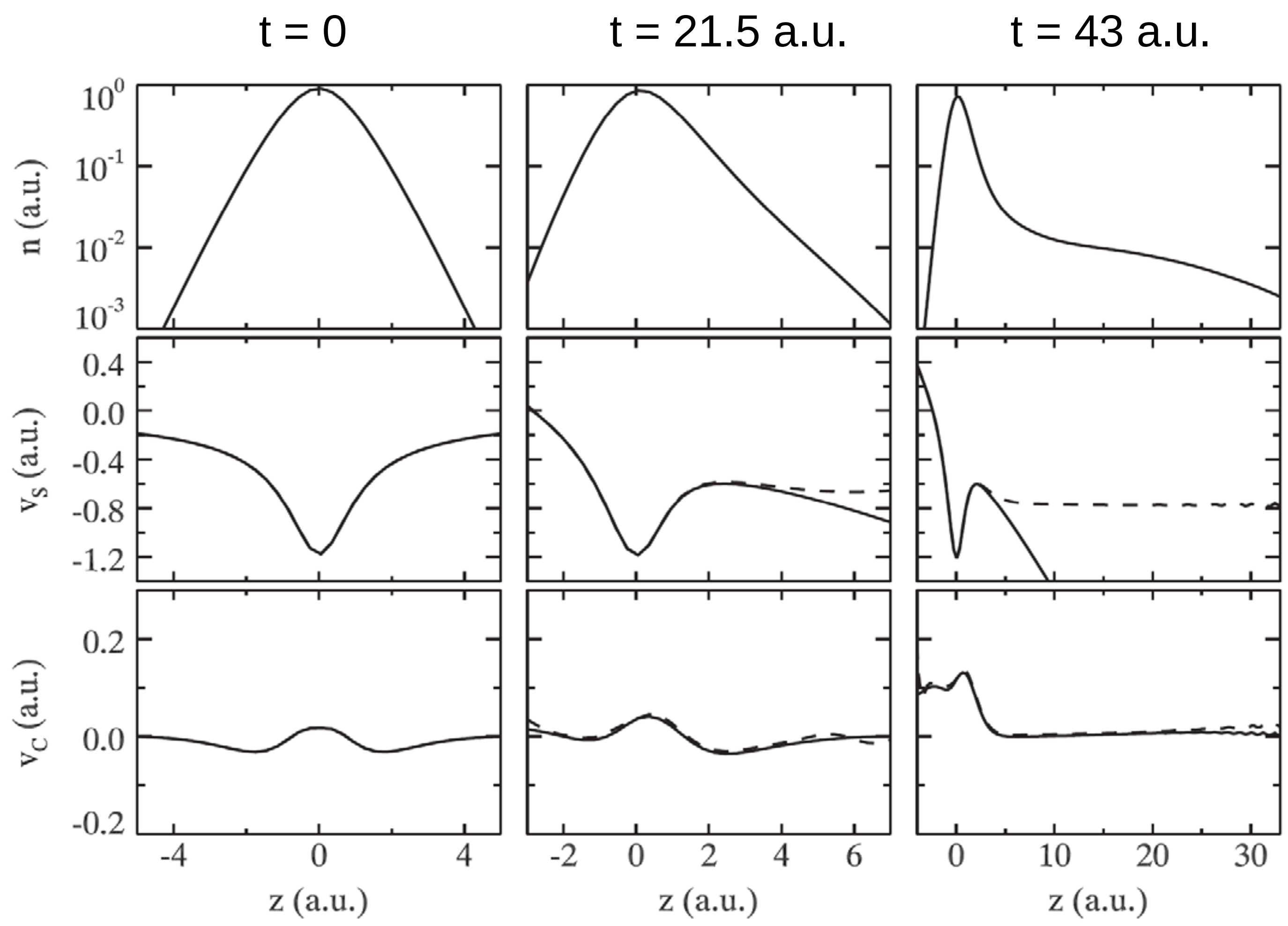
- **Inversion of one-particle ground-state SE yields the exact static KS potential, $v_{KS\text{-}static}[\rho(t)]$, that gives (for each separate t) $\rho(r,t)$ as ground-state density.**

- **Inversion of the many-particle ground-state SE yields the static external potential, $v_{ext\text{-}static}[\rho(t)]$, that gives (for each separate t) $\rho(r,t)$ as interacting ground-state density .**

- **Compare the exact TD xc potential of step 1 with the exact adiabatic approximation which is obtained by subtraction :**

$$v_{xc\text{-}exact\text{-}adiab}(t) = v_{KS\text{-}static}[\rho(t)] - v_H[\rho(t)] - v_{ext\text{-}static}[\rho(t)]$$

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

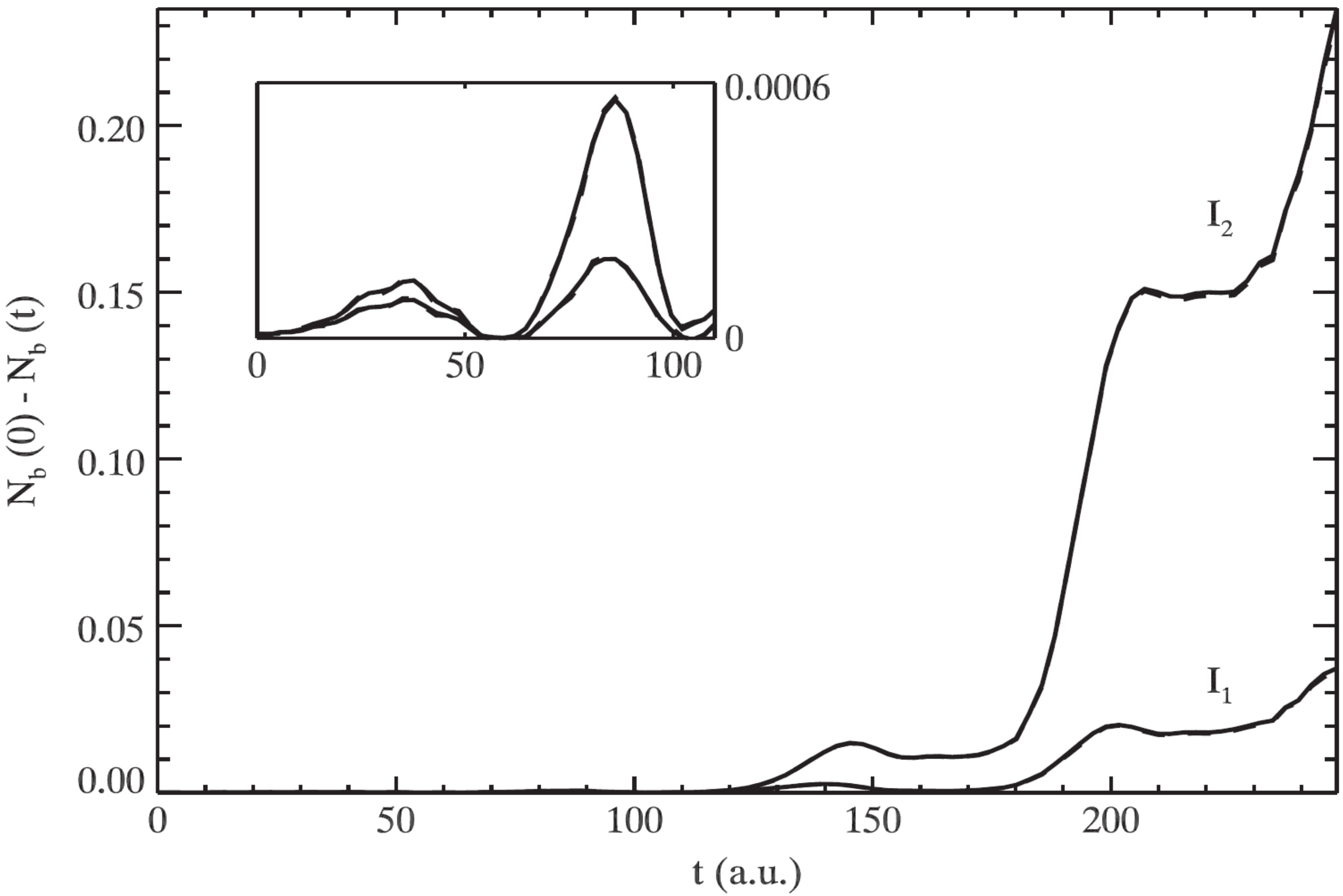


Solid line: exact

Dashed line:
exact adiabatic

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

4-cycle pulse with λ = 780 nm, I_1= 4x10^{14}W/cm^2, I_2=7x10^{14}W/cm^2



Solid line: exact

Dashed line:
exact adiabatic

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

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

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

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

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

starting point: Definition of xc potential

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

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.

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

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

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

$$f_{xc}(rt, r't') \qquad \chi_S^{-1}(rt, r't') \qquad \chi^{-1}(rt, r't') \qquad W_C(rt, r't')$$

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

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

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$f_{xc}(rt, r't') \qquad \chi_S^{-1}(rt, r't') \qquad \chi^{-1}(rt, r't') \qquad W_C(rt, r't')$$

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

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

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

$$\color{red}{\chi_S \bullet \Big|}\; f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \;\color{red}{\Big| \bullet \chi}$$

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

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

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

Adiabatic approximation

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

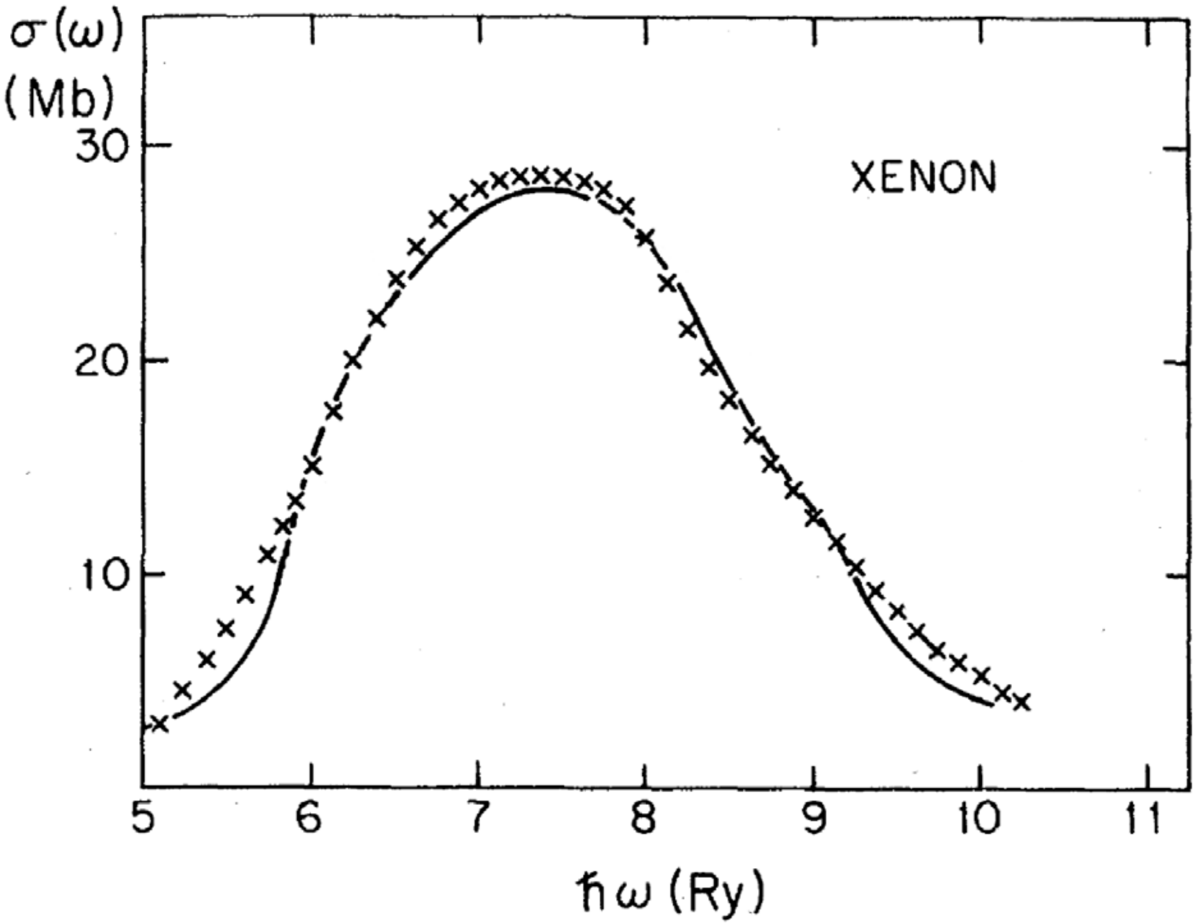
In the adiabatic approximation, the xc potential $v_{xc}(t)$ at time t only depends on the density $\rho(t)$ at the very same point in time.

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

$$\Rightarrow f_{xc}^{ALDA}(\mathbf{r}t,\mathbf{r}'t') = \left.\frac{\delta v_{xc}^{ALDA}(\mathbf{r}t)}{\delta\rho(\mathbf{r}'t')}\right|_{\rho_0} = \delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')\left.\frac{\partial v_{xc}^{ALDA}}{\partial\rho(\mathbf{r})}\right|_{\rho_0(\mathbf{r})}$$

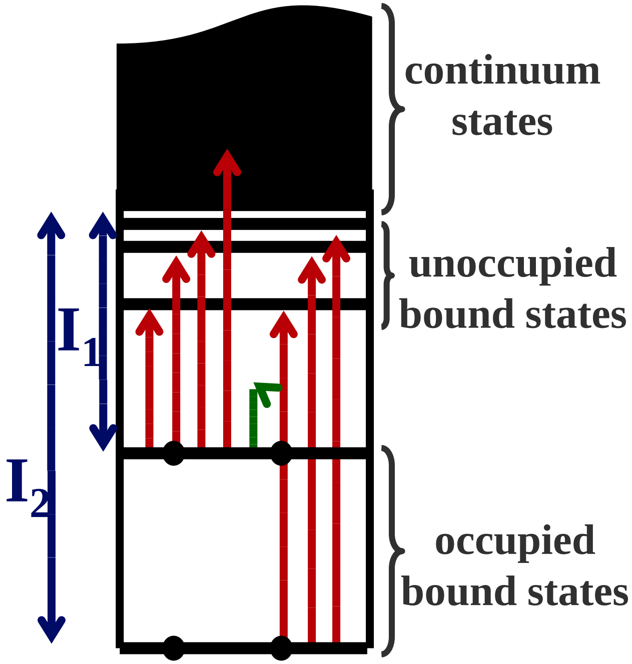
$$= \delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')\left.\frac{\partial^2 e_{xc}^{hom}}{\partial n^2}\right|_{\rho_0(\mathbf{r})}$$

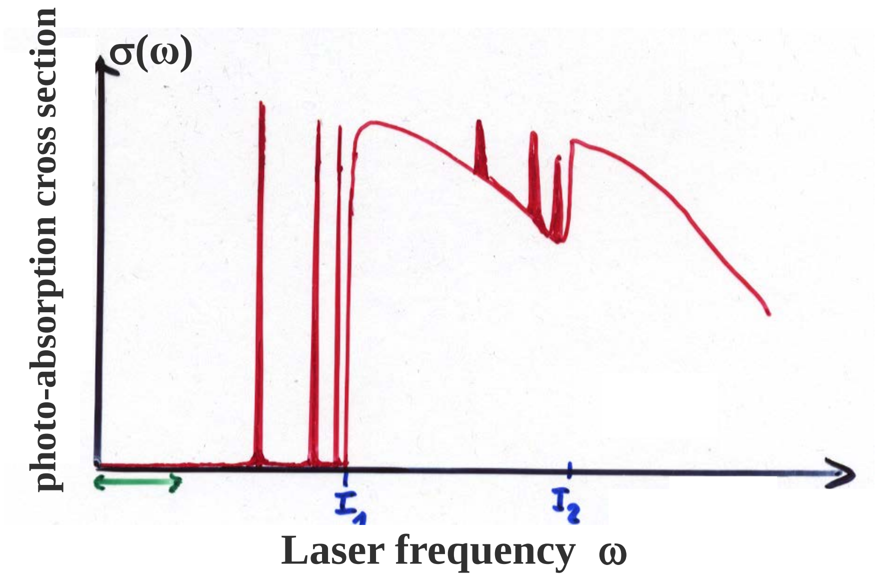
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.



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

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

$\rho_1(\omega) \;\rightarrow \infty$ 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))

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

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

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

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

Equivalent to Casida equations if:

- **ω-dependence of f_{xc} is neglected**
- **orbitals are real-valued**
- **pure density-response is considered in Casida eqs.**

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)

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

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

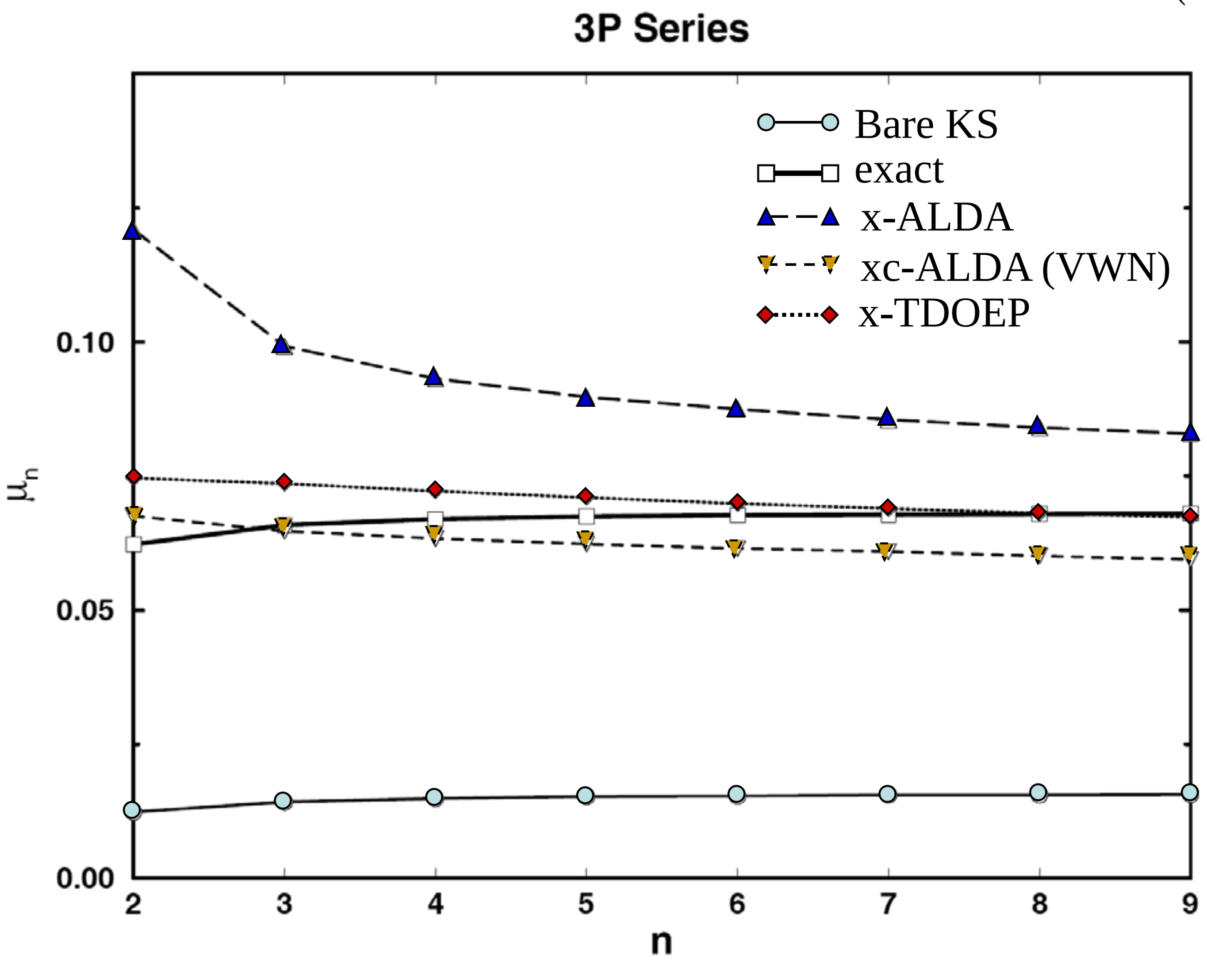
Excitation energies of CO molecule

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.

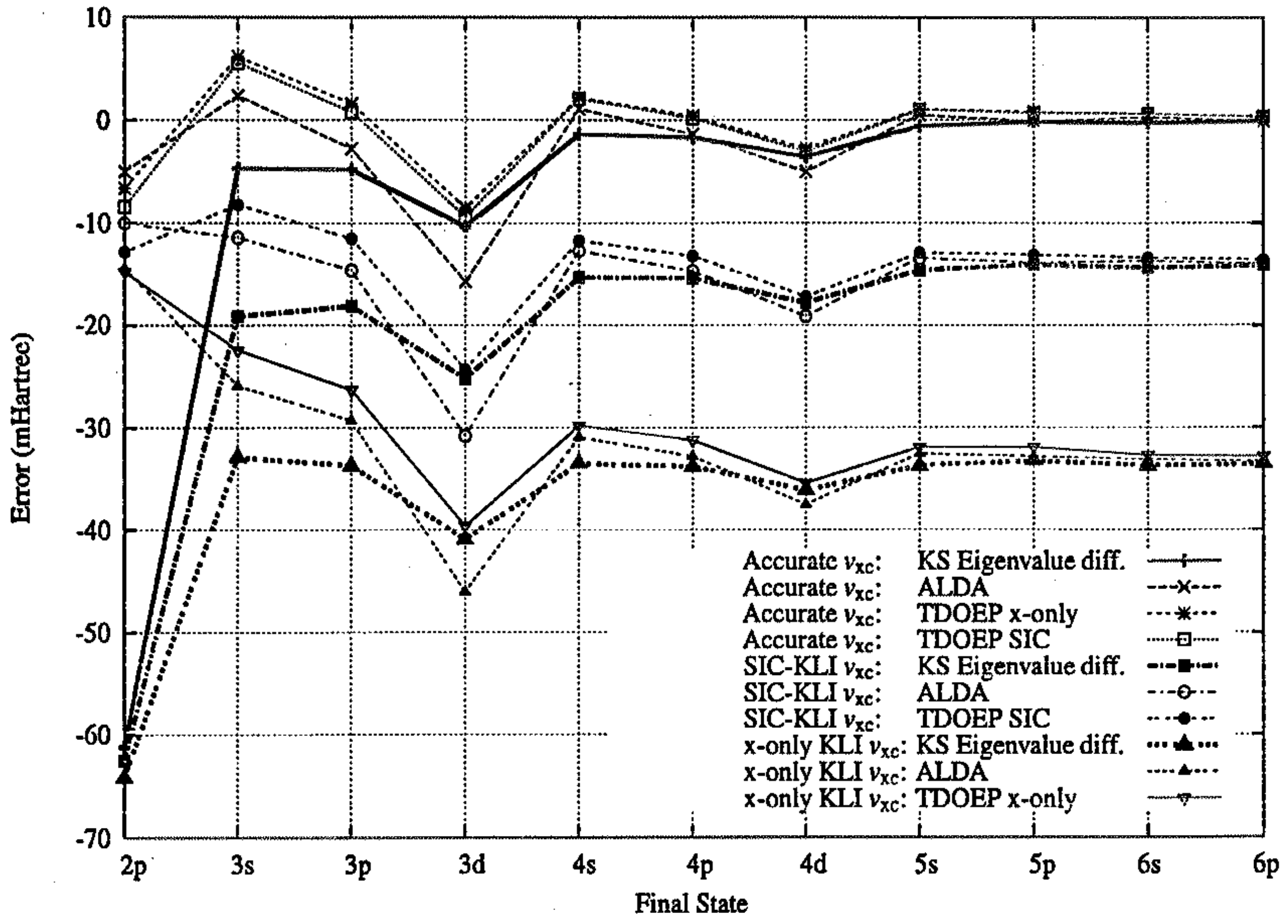


Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye, 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,** $f_{\mathbf{xc}}^{\mathbf{ALDA}}\left(q,\omega,\rho\right) = c\left(\rho\right)$ **whereas,**

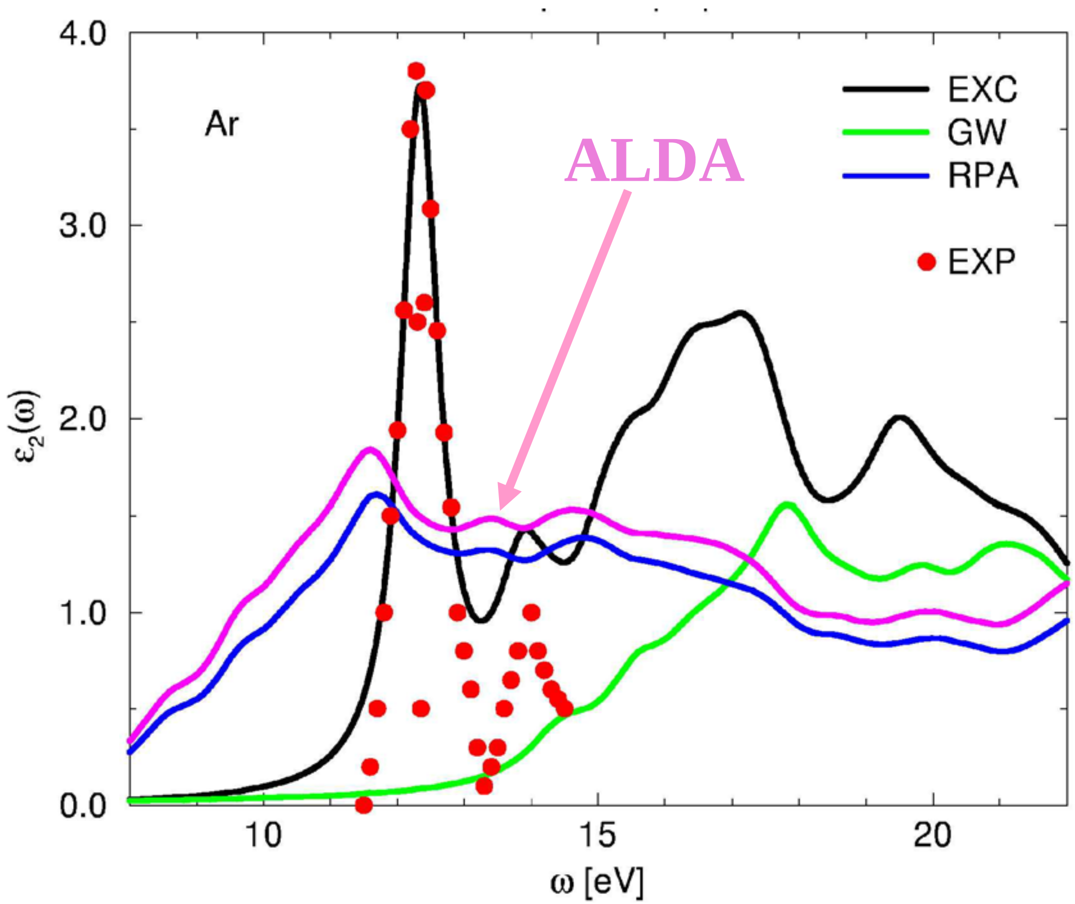
for insulators, $f_{\mathbf{xc}}^{\mathbf{exact}} \xrightarrow[q\to 0]{} 1/q^2$ **divergent.**

- **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 $q \to 0$, 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 $q \to 0$ limit.

CONCLUSION:

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

Excitons in TDDFT

TDDFT response equation (a matrix equation)

$$\boxed{\varepsilon^{-1}(\mathbf{q},\omega)=1+\chi_0(\mathbf{q},\omega)v(\mathbf{q})\left[1-\left(v(\mathbf{q})+f_{\mathrm{xc}}(\mathbf{q},\omega)\right)\chi_0(\mathbf{q},\omega)\right]^{-1}}$$

exact equation

$$f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\mathrm{t}-\mathrm{t}')\equiv\delta v_{\mathrm{xc}}(\mathbf{r},\mathrm{t})/\delta\rho(\mathbf{r}',\mathrm{t}')$$ xc kernel

$$\chi_0(\mathbf{q},\omega)$$ Kohn-Sham response function

RPA is $f_{\mathrm{xc}}=0$

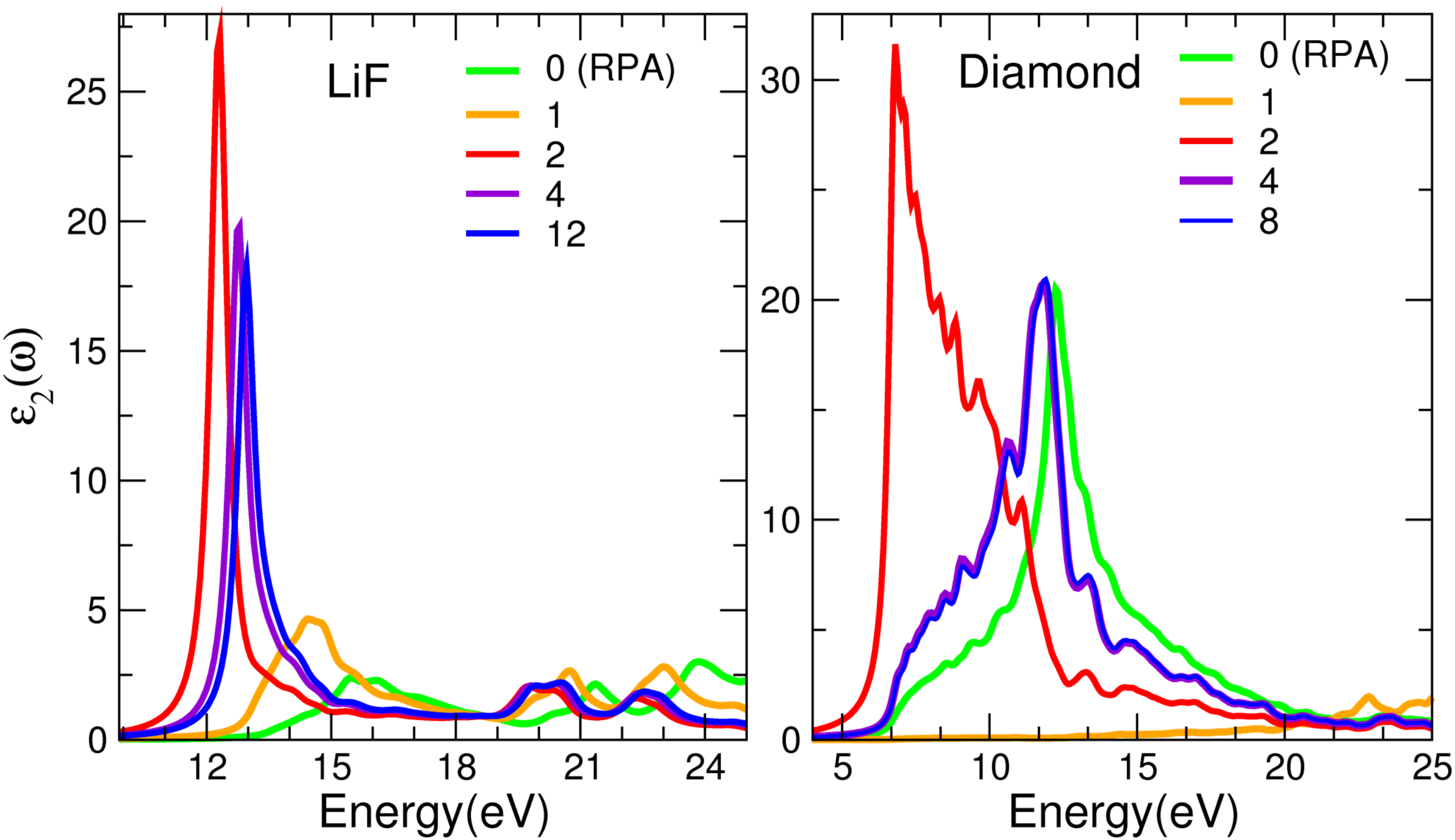
$$\boxed{\varepsilon_0^{-1}(\mathbf{q},\omega)=1+\chi_0(\mathbf{q},\omega)v(\mathbf{q})\left[1-v(\mathbf{q})\chi_0(\mathbf{q},\omega)\right]^{-1}}$$

Bootstrap kernel

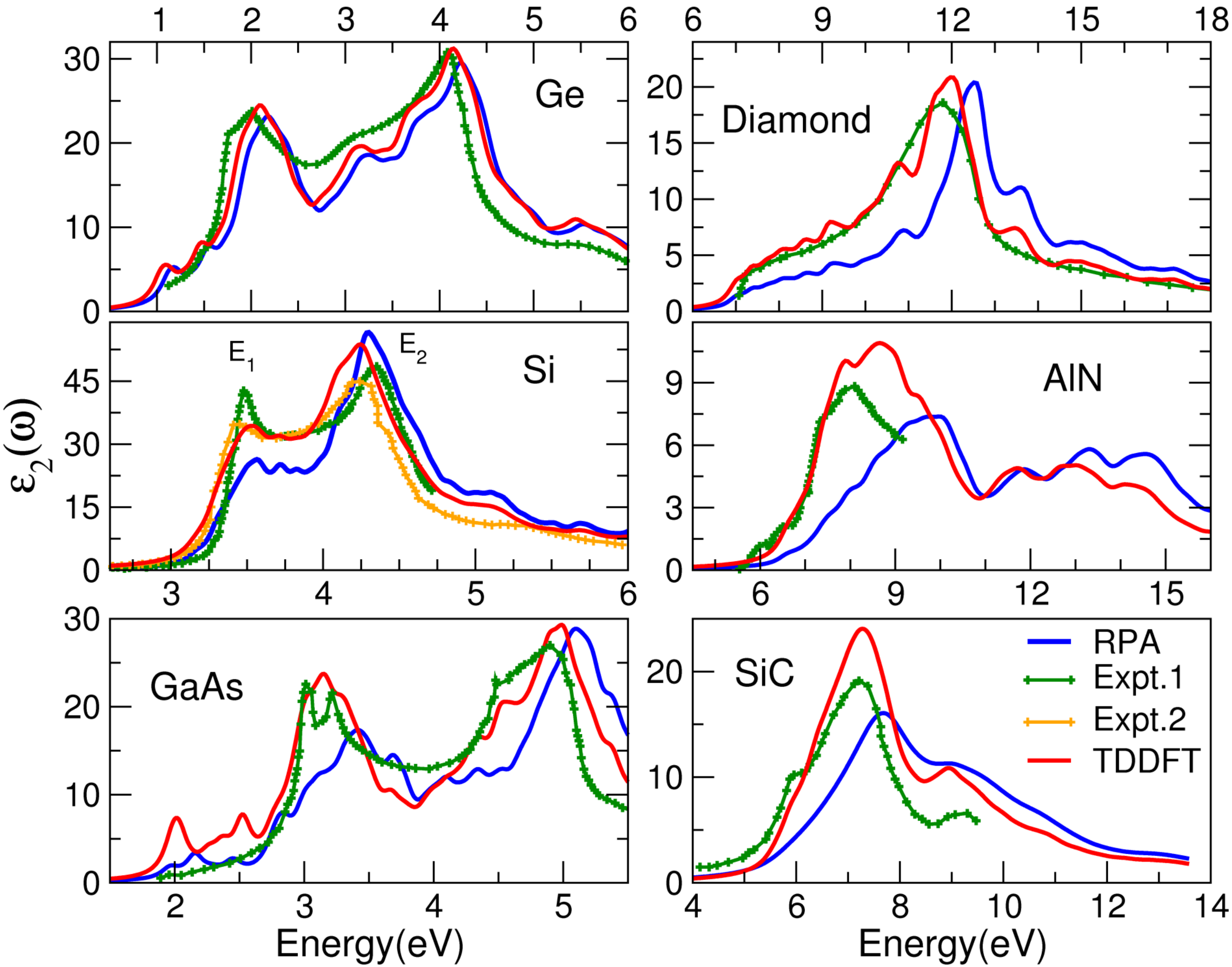
$$\boxed{f_{xc}^{\text{boot}}(\mathbf{q},\omega) = -\frac{\varepsilon^{-1}(\mathbf{q},\omega=0)\,v(\mathbf{q})}{\varepsilon_0^{00}(\mathbf{q},\omega=0)-1} = \frac{\varepsilon^{-1}(\mathbf{q},\omega=0)}{\chi_0^{00}(\mathbf{q},\omega=0)}}$$

$$\varepsilon^{-1}(\mathbf{q},\omega) = 1+\chi_0(\mathbf{q},\omega)\,v(\mathbf{q})\left[1-\left(v(\mathbf{q})+f_{xc}(\mathbf{q},\omega)\right)\chi_0(\mathbf{q},\omega)\right]^{-1}$$

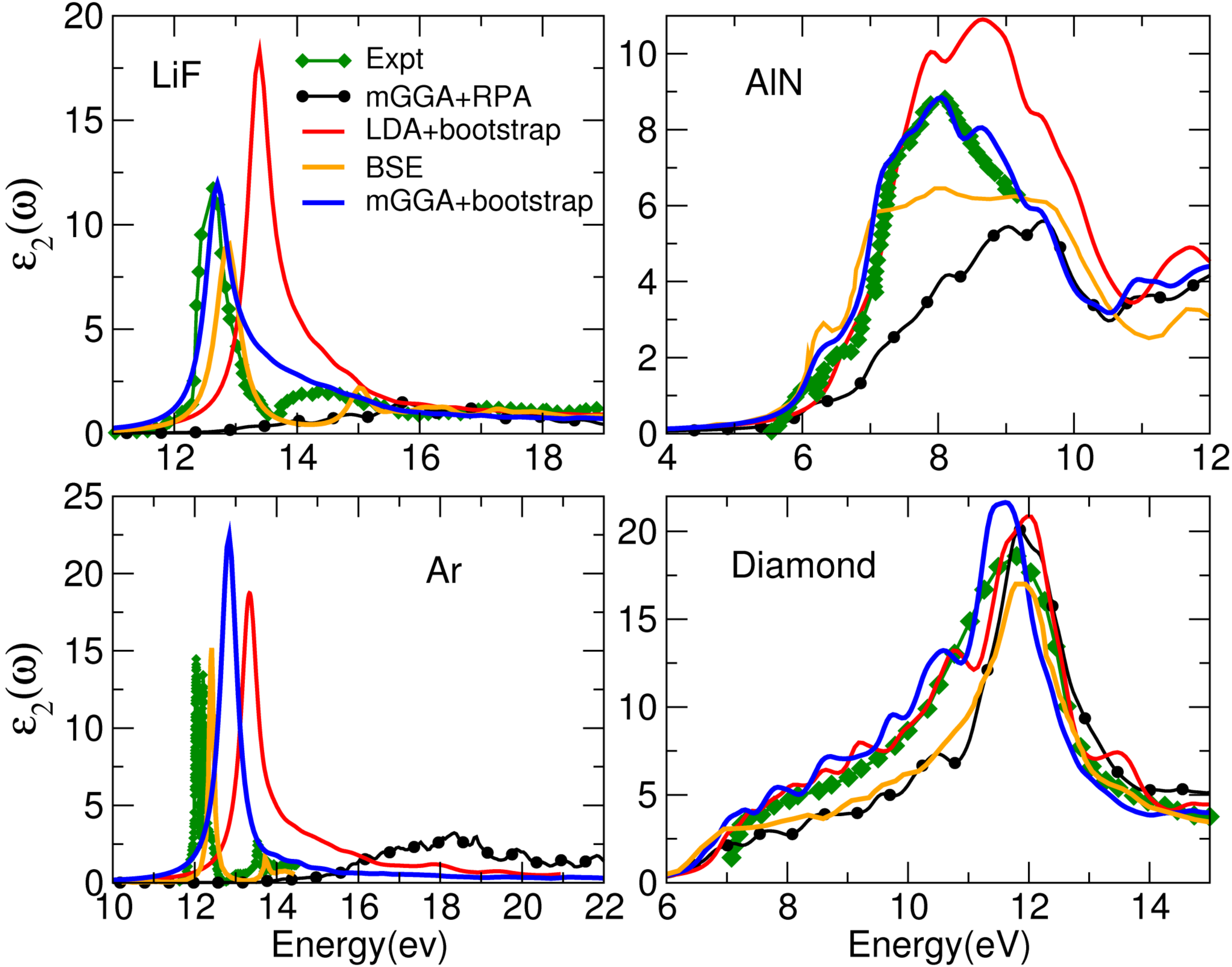
Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011)



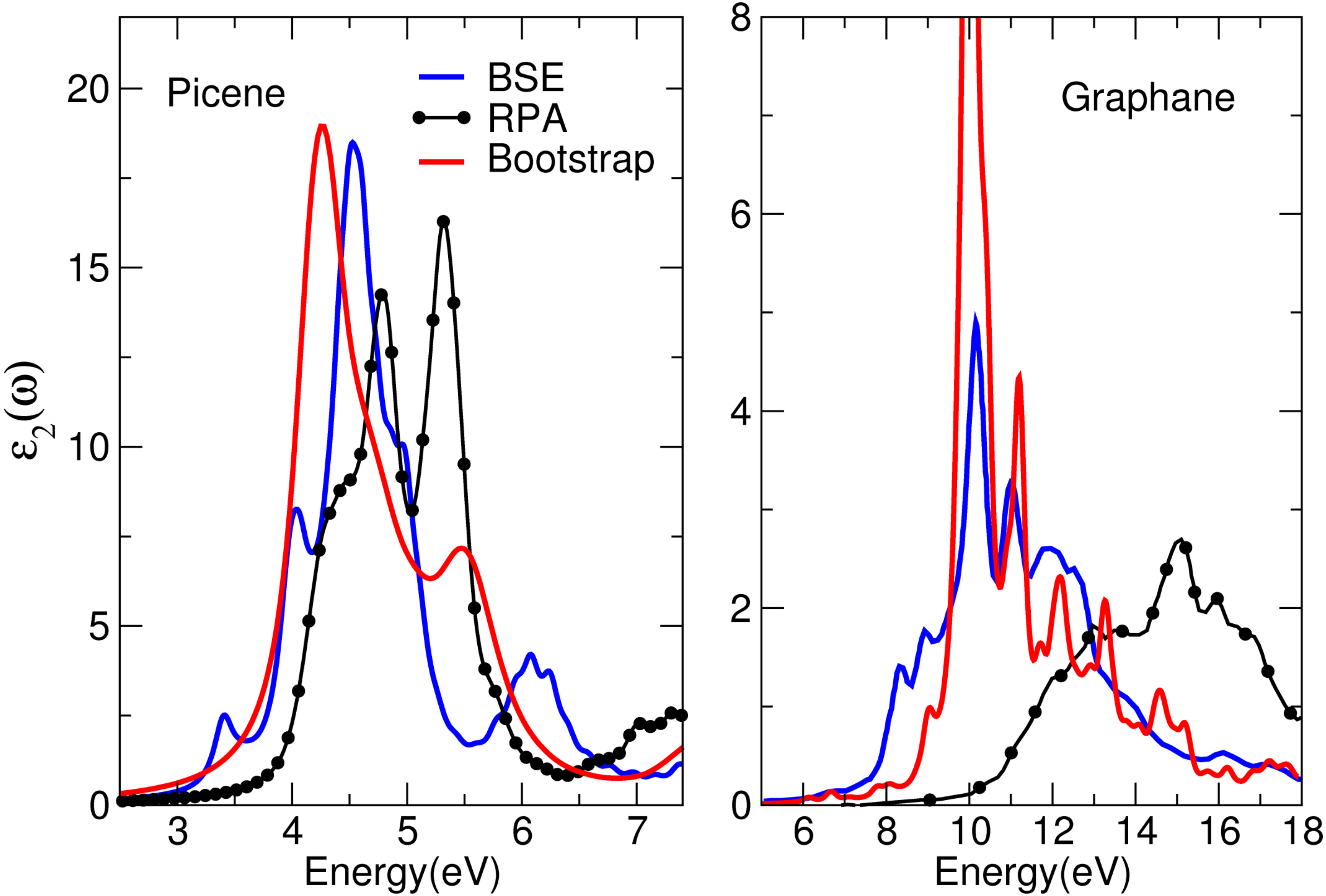
LiF
0 (RPA)
1
2
4
12
Diamond
0 (RPA)
1
2
4
8
$\varepsilon_2(\omega)$
Energy(eV)
Energy(eV)
0
5
10
15
20
25
12
15
18
21
24
0
10
20
30
5
10
15
20
25



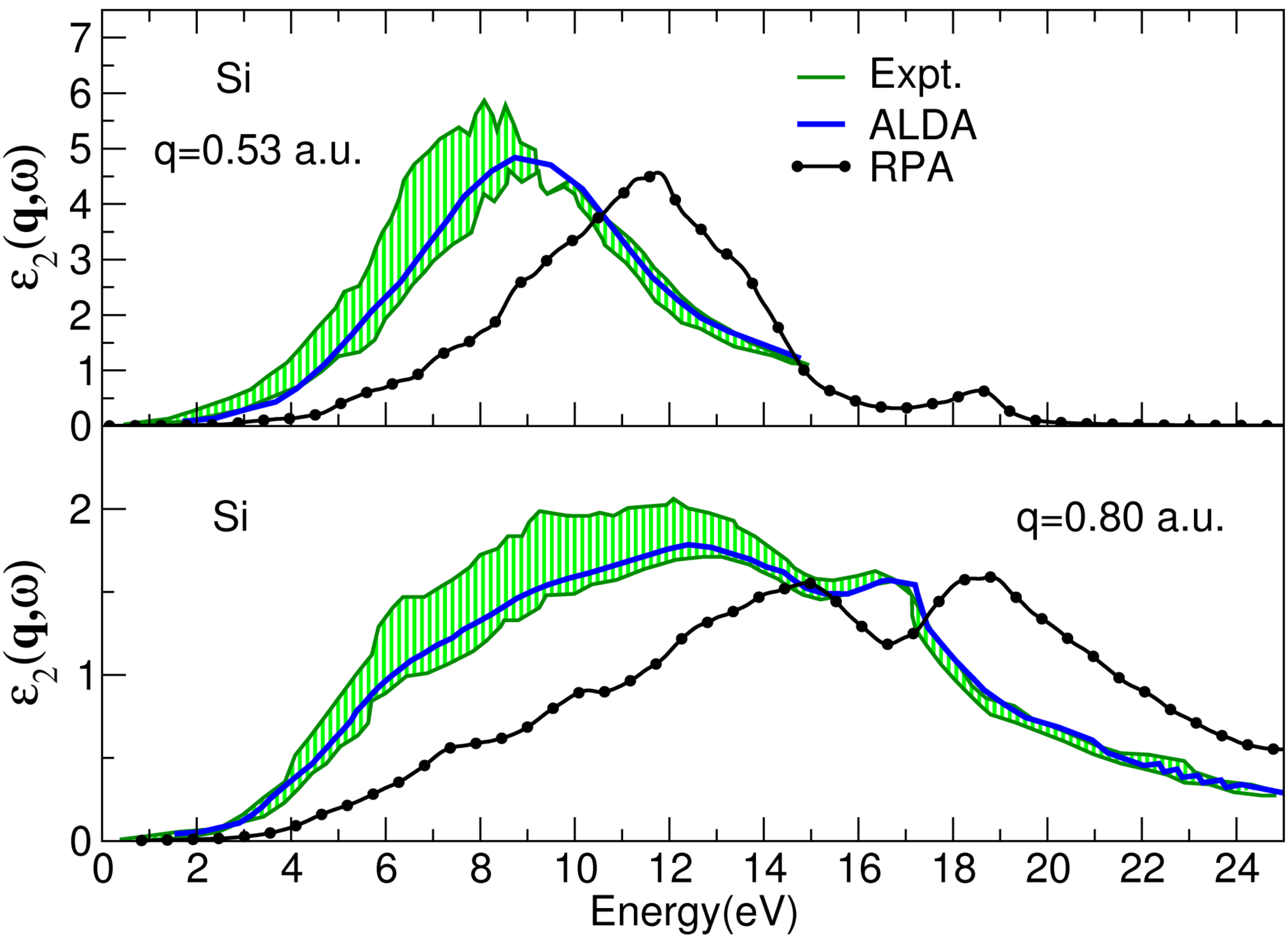
Ge
Diamond
Si
AlN
GaAs
SiC
E1
E2
ε2(ω)
Energy(eV)
Energy(eV)
RPA
Expt.1
Expt.2
TDDFT



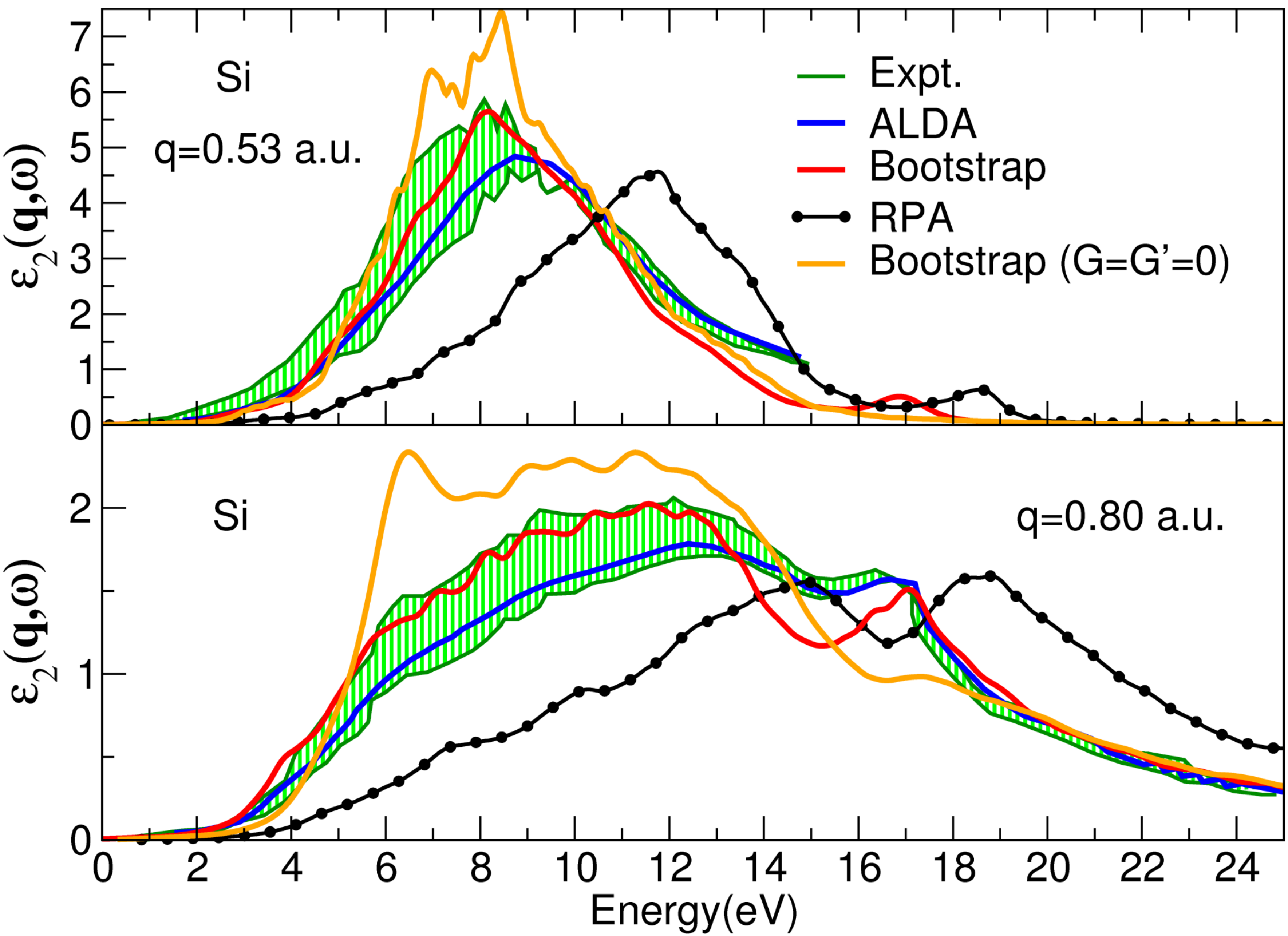
LiF
Expt
mGGA+RPA
LDA+bootstrap
BSE
mGGA+bootstrap
AlN
Ar
Diamond
$\varepsilon_2(\omega)$
$\varepsilon_2(\omega)$
Energy(ev)
Energy(eV)



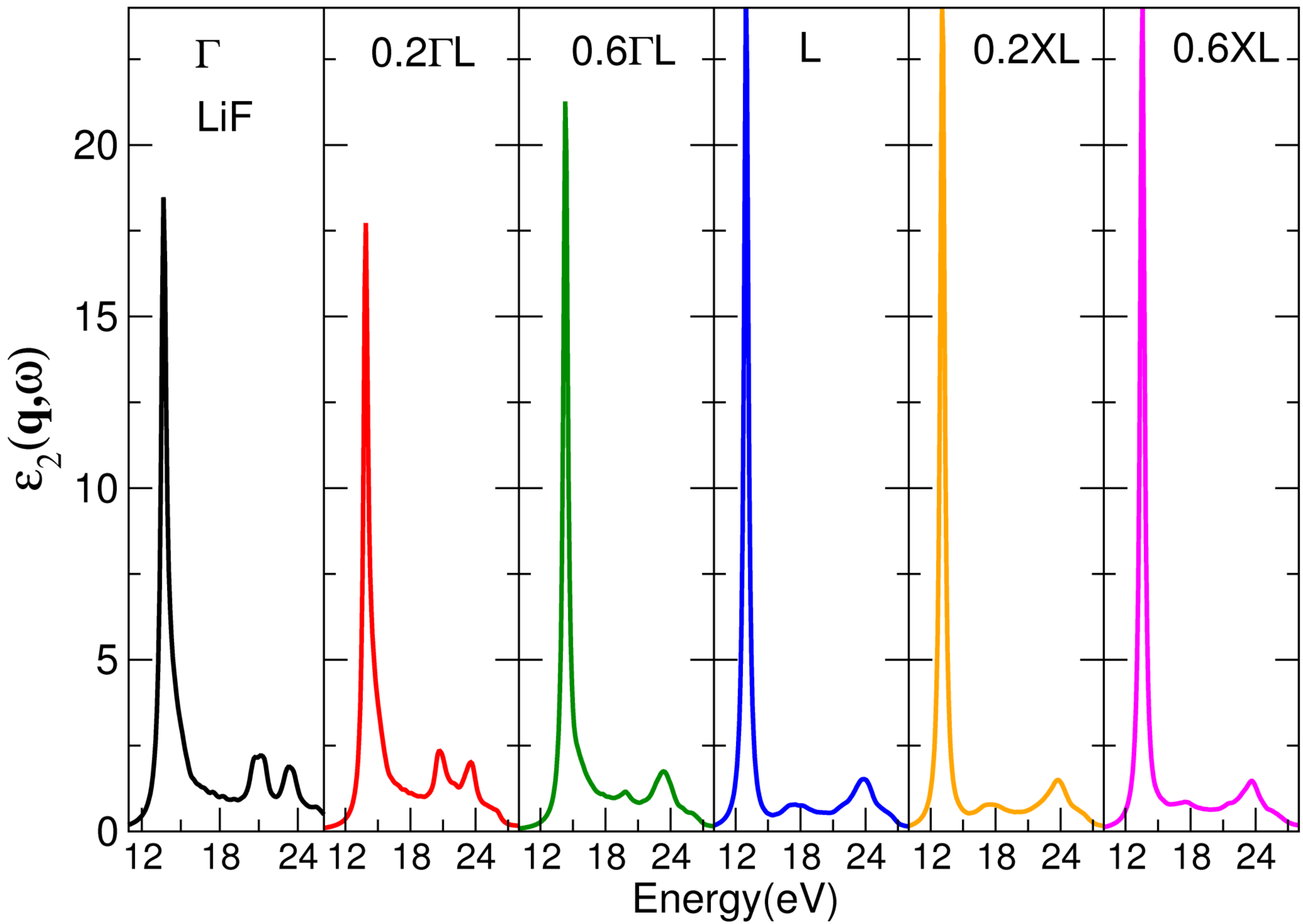
Picene
BSE
RPA
Bootstrap
Graphane
$\varepsilon_2(\omega)$
Energy(eV)
Energy(eV)
0
5
10
15
20
3
4
5
6
7
0
2
4
6
8
6
8
10
12
14
16
18



Si
q=0.53 a.u.
Expt.
ALDA
RPA
Si
q=0.80 a.u.
$\varepsilon_2(\mathbf{q},\omega)$
Energy(eV)

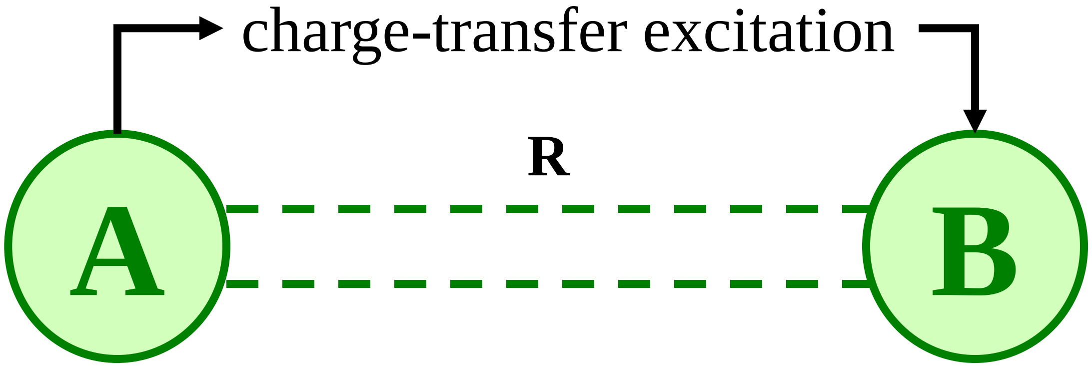


Si
q=0.53 a.u.
Expt.
ALDA
Bootstrap
RPA
Bootstrap (G=G'=0)
Si
q=0.80 a.u.
$\varepsilon_2(\mathbf{q},\omega)$
Energy(eV)



Γ
LiF
0.2ΓL
0.6ΓL
L
0.2XL
0.6XL
ε2(q,ω)
0
5
10
15
20
12
18
24
Energy(eV)

Charge transfer excitations and the discontinuity of f_{xc}



CT excitation energy

$$\Omega_{CT} \approx IP^{(A)} - EA^{(B)} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}$$

Infinite R | **Finite (but large) R**

In exact DFT $\quad IP^{(A)} = -\varepsilon^{(A)}_{HOMO} \qquad = -\varepsilon^{(A)}_{MOL}$

$EA^{(B)} = -\varepsilon^{(B)}_{LUMO} - \Delta^{(B)}_{xc} \qquad = -\varepsilon^{(B)}_{MOL}$

derivative discontinuity

$$\Omega_{CT} \approx \varepsilon^{(B)}_{MOL} - \varepsilon^{(A)}_{MOL} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}$$

$$\boxed{\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 \, |\varphi_B(r')|^2}{|r - r'|}}$$

$$\underbrace{\int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 \, |\varphi_B(r')|^2}{|r - r'|}}_{\sim 1/R}$$

$$\boxed{\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}$$

$$\underbrace{\int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}_{\sim 1/R}$$

In TDDFT (single-pole approximation)

$$\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \varphi_A^*(r')\varphi_B(r') f_{xc}(r, r', \Omega_{CT})\varphi_A(r)\varphi_B^*(r)$$

$$\boxed{\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}$$

$$\underbrace{\int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}_{\sim 1/R}$$

In TDDFT (single-pole approximation)

$$\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \underbrace{\varphi_A^*(r')\varphi_B(r')}_{\text{Exponentially small}} f_{xc}(r, r', \Omega_{CT}) \underbrace{\varphi_A(r)\varphi_B^*(r)}_{\text{Exponentially small}}$$

$$\boxed{\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}$$

$$\underbrace{\int d^3r \int d^3r' \frac{|\varphi_A(r)|^2 |\varphi_B(r')|^2}{|r - r'|}}_{\sim 1/R}$$

In TDDFT (single-pole approximation)

$$\Omega_{CT} \approx \varepsilon_{MOL}^{(B)} - \varepsilon_{MOL}^{(A)} - \int d^3r \int d^3r' \underbrace{\varphi_A^*(r')\varphi_B(r')}_{\text{Exponentially small}} f_{xc}(r, r', \Omega_{CT}) \underbrace{\varphi_A(r)\varphi_B^*(r)}_{\text{Exponentially small}}$$

CONCLUSIONS: To describe CT excitations correctly

- **v_{xc} must have proper derivative discontinuities**
- **$f_{xc}(r,r')$ must increase exponentially as function of r and of r' for $\omega \to \Omega_{CT}$**

Discontinuity of $v_{xc}(r)$:

$$v_{xc}^{+}(\mathbf{r}) = v_{xc}^{-}(\mathbf{r}) + \Delta_{xc}$$

Δ_{xc} is constant throughout space

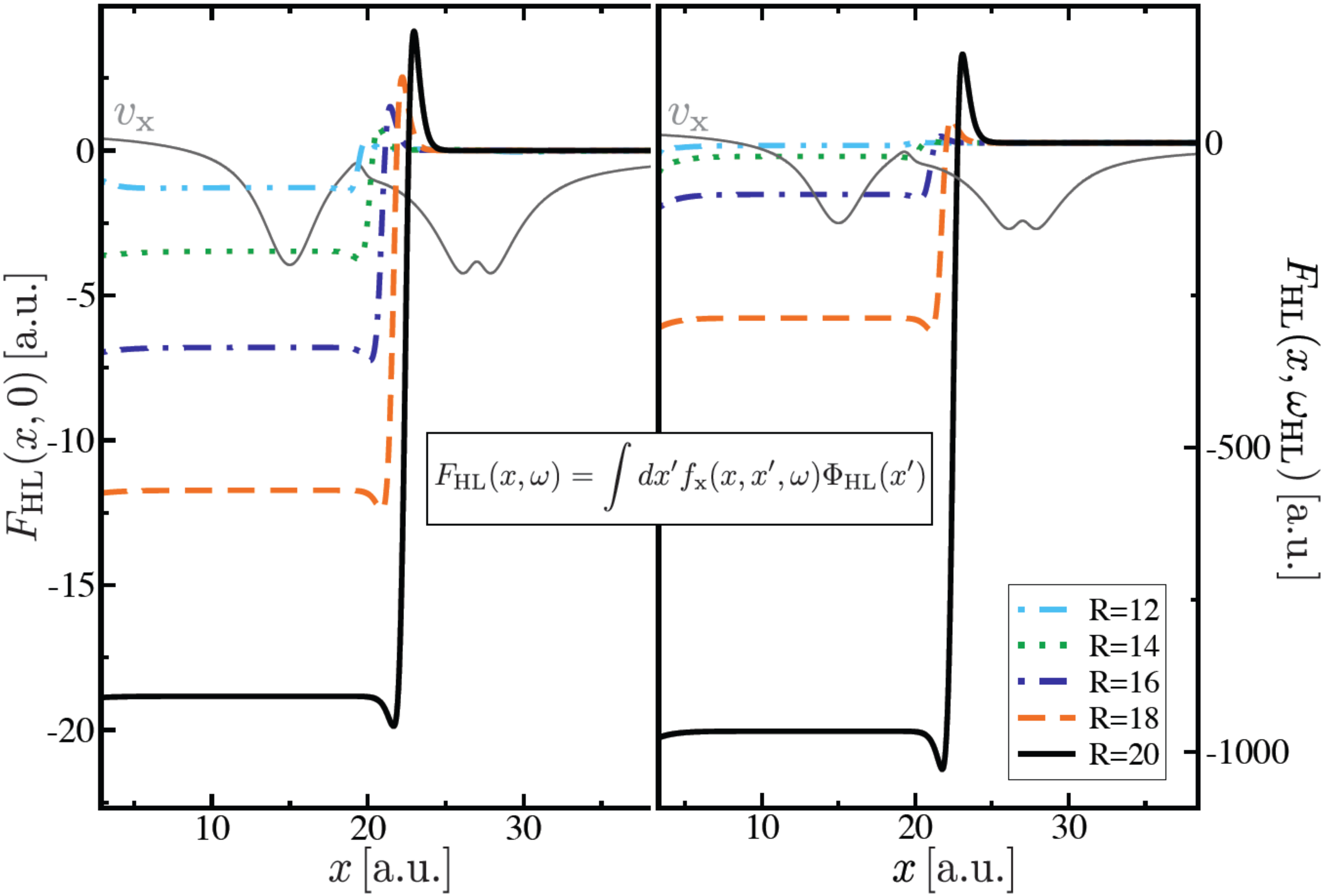
Discontinuity of $f_{xc}(r,r')$:

$$f_{xc}^{+}(\mathbf{r},\mathbf{r}') = f_{xc}^{-}(\mathbf{r},\mathbf{r}') + g_{xc}(\mathbf{r}) + g_{xc}(\mathbf{r}')$$

This exponentially increasing behaviour is achieved by the discontinuity:

$$g_{xc}(\mathbf{r}) \sim \frac{\left|\varphi_L(\mathbf{r})\right|}{n(\mathbf{r})} \sim e^{-2\left(\sqrt{2A_s}-\sqrt{I}\right)r} \qquad r \to \infty$$

He-Be neutral diatomic in 1D



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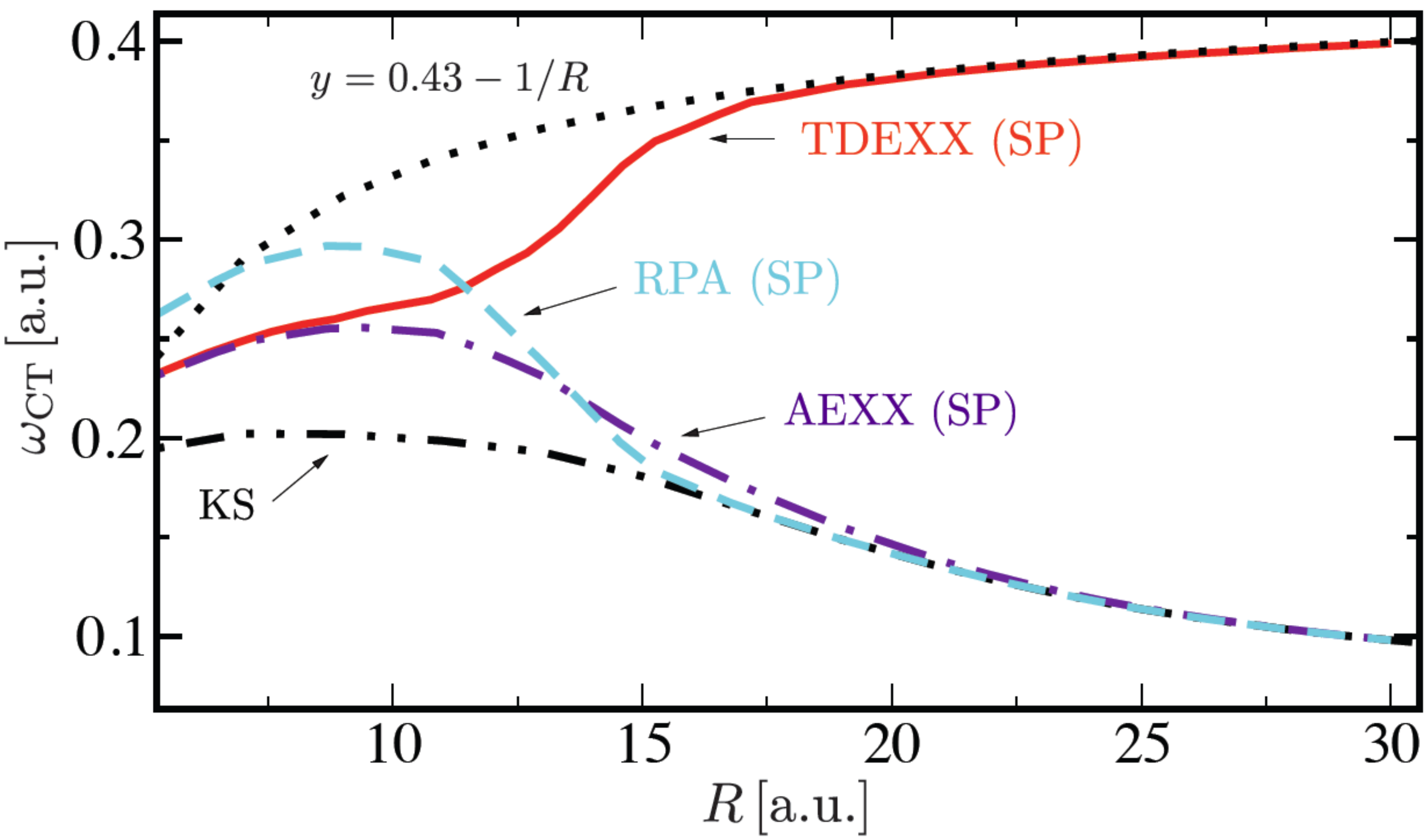
He-Be neutral diatomic in 1D



$$\omega_{CT} = \omega_q + 2\left\langle q \middle| v + f_x(\omega_q) \middle| q \right\rangle \rightarrow \omega_q + \Delta_x - 1/R$$

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Thanks !