Lecture 2

Nonadiabatic electron dynamics in TDDFT

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Benasque, September 2006

Overview

Lecture 1

Part I: Basics and formalism

- Beyond the adiabatic approximation: why and how?
- Current-TDDFT
- The VK functional: technical details

Part II: Applications in the linear response regime

- polarizabilities of polymers
- atomic excitation energies
- intersubband plasmons in quantum wells
- Spin-Current-TDDFT

Lecture 2

Part III: Nonlinear regime

- TDKS equation with memory
- Dissipation: where does the energy go?
- C-TDDFT versus L-TDDFT
- TDOEP

Ultranonlocality in DFT: “upgrades”

- Band insulators:

$$f_{xc}(\vec{k},\vec{k},0) \xrightarrow[k\to 0]{} \frac{\alpha}{k^2} \Longrightarrow$$

Polarization DFT

Gonze, Ghosez, and Godby, PRL **74**, 4035 (1995)

- TDDFT:

$$f_{xc}(\vec{k},\vec{k}',\omega) \xrightarrow[k\to 0]{} \alpha(\omega)\frac{\vec{k}\cdot\vec{k}'}{k^2} \Longrightarrow$$

C-TDDFT

Vignale and Kohn, PRL **77**, 2037 (1996)

- Spin-TDDFT:

$$f^{unif}_{xc,\sigma\sigma'}(\vec{k},\omega) \xrightarrow[k\to 0]{} \frac{A(\omega)}{k^2}\frac{\sigma\sigma' n^2}{4n_\sigma n_{\sigma'}} + B_{\sigma\sigma'}(\omega) \Longrightarrow$$

SC-TDDFT

Situation even worse: ultranonlocality appears in the homogeneous case!

Qian, Constantinescu, Vignale, PRL **90**, 066402 (2003)

Excitation energies from SC-TDDFT

$$\vec{j}_{1\sigma}(\vec{r},\omega) = \int d^3r' \, \vec{\vec{\chi}}_{\sigma}(\vec{r},\vec{r}',\omega)\left\{ \vec{A}_{H,1\sigma}(\vec{r},\omega) + \vec{A}_{xc,1\sigma}(\vec{r},\omega)\right\}$$

KS current-current response tensor:

$$\chi_{\mu\nu\sigma}(\vec{r},\vec{r}',\omega) = n_{0\sigma}(\vec{r})\delta(\vec{r}-\vec{r}')\delta_{\mu\nu} + \frac{1}{2}\sum_{j,k}^{\infty} \frac{f_{k\sigma} - f_{j\sigma}}{\varepsilon_{k\sigma} - \varepsilon_{j\sigma} + \omega + i\eta} P_{\mu}^{kj\sigma}(\vec{r}) P_{\nu}^{jk\sigma}(\vec{r}')$$

where $P_{\mu}^{kj\sigma} = \varphi_{k\sigma}^{*}(\vec{r})\nabla_{\mu}\varphi_{j\sigma}(\vec{r}) - \varphi_{j\sigma}(\vec{r})\nabla_{\mu}\varphi_{k\sigma}^{*}(\vec{r})$

effective vector potential in ALDA:

$$\vec{A}_{H,1\sigma} + \vec{A}_{xc,1\sigma}^{ALDA} = \sum_{\sigma'} \frac{\vec{\nabla}}{(i\omega)^2} \int d^3r' \left[\frac{1}{|\vec{r}-\vec{r}'|} + f_{xc,\sigma\sigma'}^{ALDA}(\vec{r},\vec{r}') \right] \vec{\nabla}' \cdot \vec{j}_{\sigma'}(\vec{r}',\omega)$$

SC-TDDFT beyond the ALDA

Qian, Constantinescu, Vignale,
PRL **90**, 066402 (2003)

- spin-dependent generalization of the xc viscoelastic stress tensor
- depends on velocity gradients

$$\vec{A}_{xc,1\sigma}(\vec{r},\omega) = \vec{A}^{ALDA}_{xc,1\sigma}(\vec{r},\omega) - \frac{1}{i\omega n_\sigma(\vec{r})}\sum_{\sigma'}\vec{\nabla}\cdot\vec{\vec{\sigma}}_{xc,\sigma\sigma'}(\vec{r},\omega)$$
$$-\frac{n^2(\vec{r})\mathrm{A}(\vec{r};\omega)}{4\omega^2}\sum_{\sigma'}\frac{\sigma\sigma'}{n_\sigma(\vec{r})n_{\sigma'}(\vec{r})}\vec{j}_{\sigma'}(\vec{r},\omega)$$

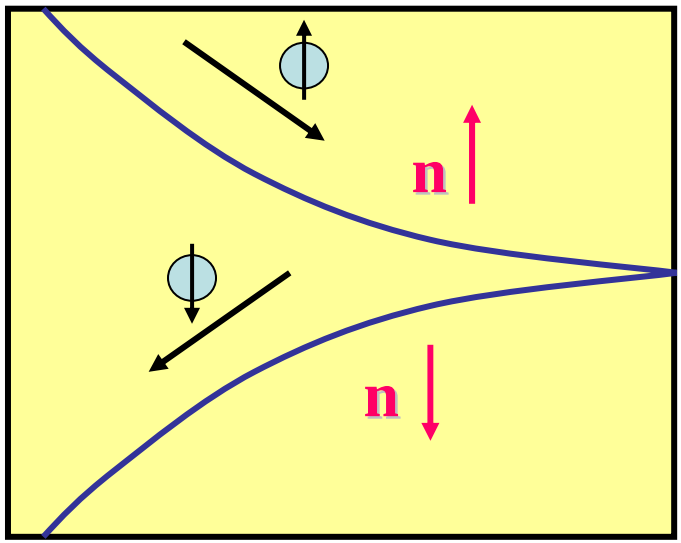
spin-transresistivity:

$$\rho_{\uparrow\downarrow}(\omega) = -i\frac{n^2\mathrm{A}(\omega)}{4\omega n_\uparrow n_\downarrow}$$

- new term, depends on the velocities themselves
- disappears in the static limit (A~ω^2)
- real part: spin mass
- imaginary part: spin Coulomb drag

The spin Coulomb drag effect

Even in the purest material (no spin-flip), spin currents decay due to Coulomb interaction between different spin populations.



SCD counteracts spin diffusion in opposite directions.

⇨ **Spin-transresistivity** $\rho_{\uparrow\downarrow}$

$$D_s = D_{ni}\frac{S}{S_{ni}}\frac{1}{1+\left|\rho_{\uparrow\downarrow}\right|/\rho_{Drude}}$$

spin diffusion constant

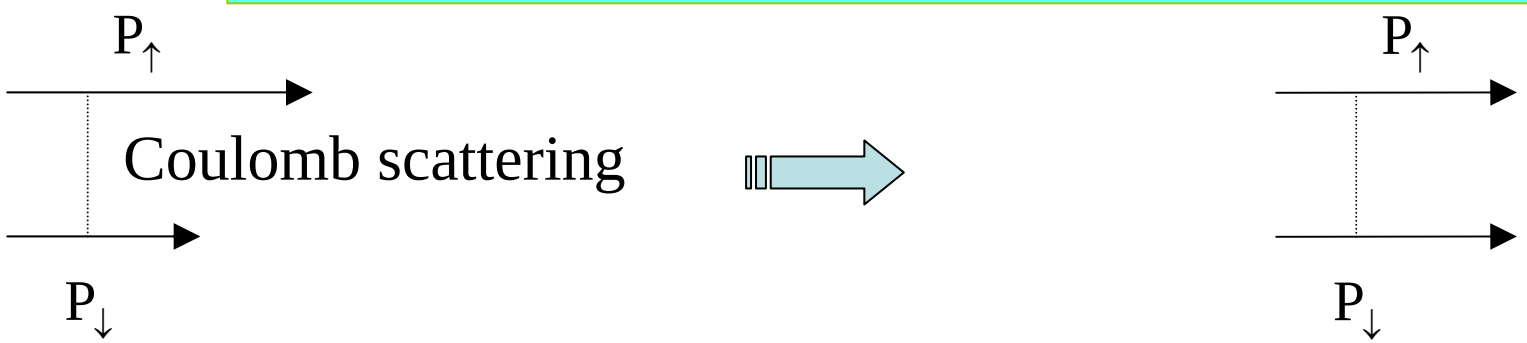
spin stiffness

Theory: I. D'Amico and G. Vignale, EPL **55**, 566 (2001), PRB **65**, 85109 (2002) PRB **68**, 045307 (2003)

Experiment: C.P. Weber, N. Gedik, J.E. Moore, J. Orenstein, J. Stephens, and D. D. Awschalom, Nature **437**, 1330 (2005)

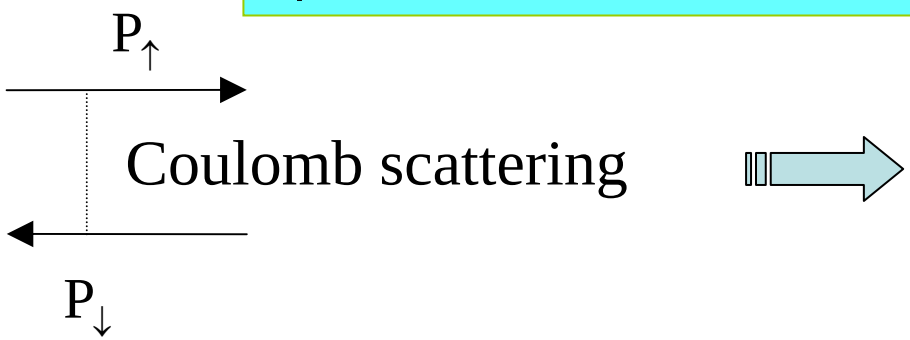
The spin Coulomb drag effect

Spin+ Charge mode → Charge mode



SCD 'pumps' momentum from faster to slower population

Spin mode → complete damping

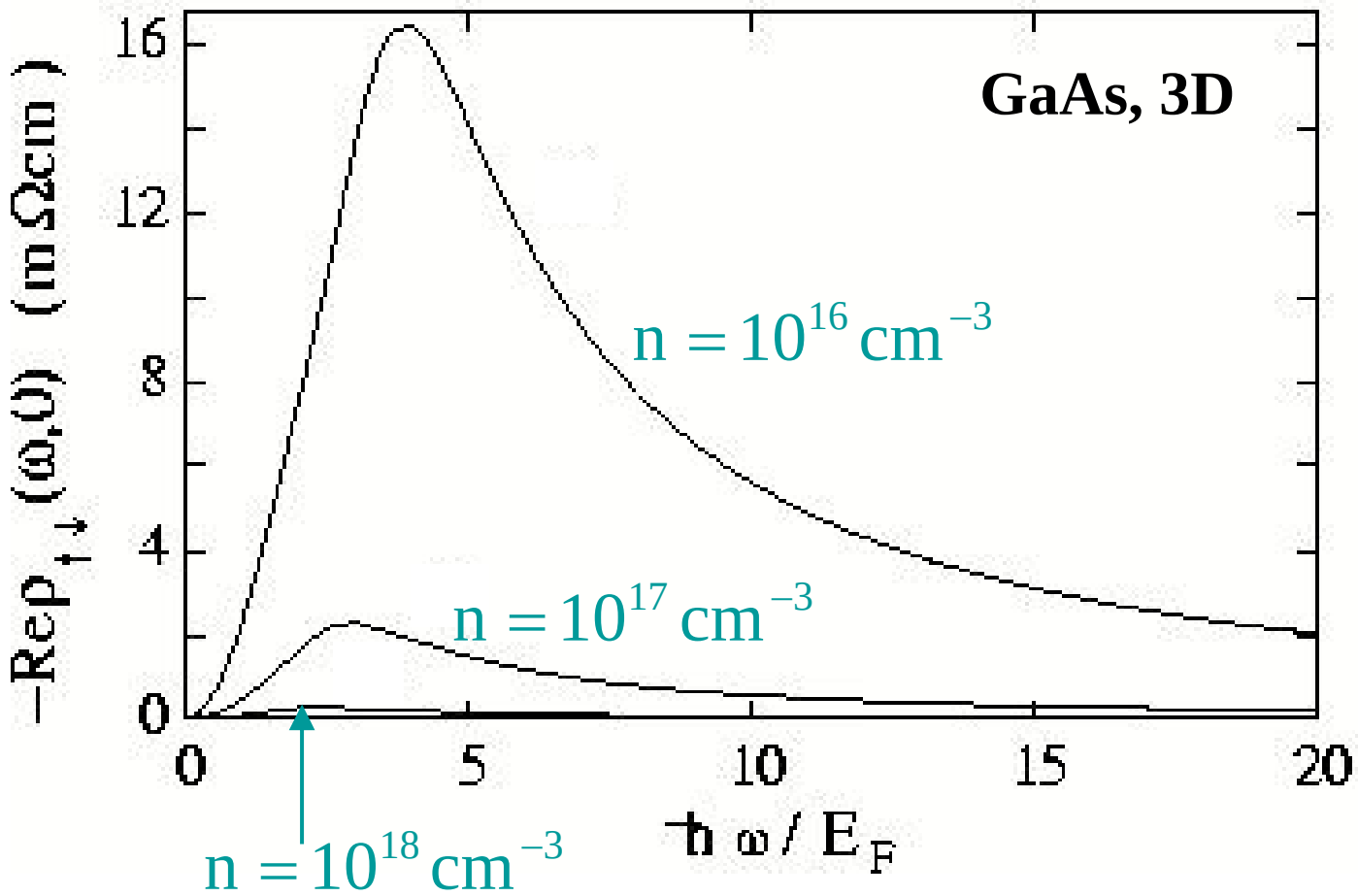


$P_\uparrow = 0, \quad P_\downarrow = 0$

SCD damps *both* spin populations

P_{tot} conserved, $P_{\uparrow,\downarrow}$ *not* conserved

Spin-transresistivity: frequency dependence



I. D'Amico and C.A.U., PRB Rapids (2006), in press

Small-matrix approximation in SC-TDDFT

for an excitation between levels p and q:

$$\chi_{ij\sigma}(\vec{r},\vec{r}',\omega) \approx \frac{(i\omega)^2}{4\omega_{pq\sigma}^2}\left(\frac{1}{\omega+\omega_{pq\sigma}}-\frac{1}{\omega-\omega_{pq\sigma}}\right)P_{i\sigma}^{pq}(\vec{r})P_{j\sigma}^{pq}(\vec{r}')$$

(complex) excitation energy

$$\Omega_{\pm\sigma}^2 = \omega_{pq\sigma}^2 + 2\omega_{pq\sigma}S_{\pm\sigma}$$

linewidth

$$\Gamma_{\pm} = \mathrm{Im}\, S_{\pm\sigma}$$

$$S_{\pm\sigma} = \underbrace{\left(S_{\sigma\bar{\sigma}}^{H+ALDA} \pm S_{\sigma\bar{\sigma}}^{H+ALDA}\right)}_{\text{Hartree + ALDA: real (no dissipation)}} + \underbrace{\left(S_{\sigma\bar{\sigma}}^{VE} \pm S_{\sigma\bar{\sigma}}^{VE}\right) + \left(S_{\sigma\bar{\sigma}}^{SCD} \pm S_{\sigma\bar{\sigma}}^{SCD}\right)}_{\text{Viscoelastic + SCD: complex (dissipative)}}$$

Total linewidth: $\Gamma_{\pm} = \Gamma_{\pm}^{disorder} + \Gamma_{\pm}^{VE} + \Gamma_{\pm}^{SCD}$

SC-TDDFT energy shift for excitation energies

$$S_{\sigma\sigma'}^{H+ALDA} = \int d^3r \int d^3r' \left[\frac{1}{|\vec{r} - \vec{r}'|} + f_{xc,\sigma\sigma'}^{ALDA}(\vec{r}, \vec{r}') \right] \varphi_{p\sigma}(\vec{r}) \varphi_{q\sigma}(\vec{r}) \varphi_{p\sigma'}(\vec{r}') \varphi_{q\sigma'}(\vec{r}')$$

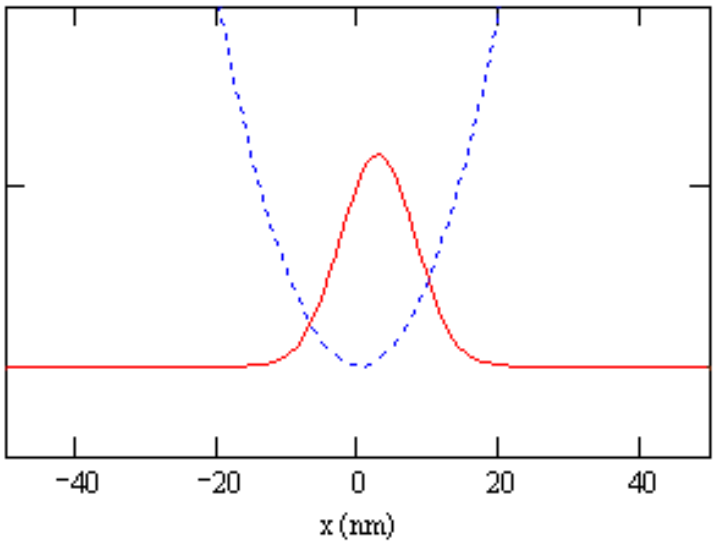
$$S_{\sigma\sigma'}^{VE} = \frac{i\omega}{\omega_{pq\sigma}^2} \int d^3r \, \vec{\vec{\sigma}}_{\sigma\sigma'}^{xc,pq}(\vec{r}, \omega) \vec{\nabla} \left[\frac{\vec{j}_{pq\sigma}(\vec{r})}{n_\sigma(\vec{r})} \right]$$

$$\left(S_{\sigma\bar{\sigma}}^{SCD} \pm S_{\sigma\bar{\sigma}}^{SCD} \right) = \frac{ie^2\omega}{\omega_{pq\sigma}^2} \int d^3r \left[\frac{n_{\bar{\sigma}}}{n_\sigma} \left| \vec{j}_{pq\sigma} \right|^2 \mp \vec{j}_{pq\bar{\sigma}} \cdot \vec{j}_{pq\sigma} \right] \rho_{\uparrow\downarrow}(\omega; n_\uparrow, n_\downarrow)$$

structure of a (complex) power loss term in an AC spintronics circuit

Is there a system in which the SCD power loss channel dominates?

Parabolic quantum wells



Charge-density excitation (CDE) in a parabolic well: **Kohn's mode**

$$\Gamma_{CDE}^{VE} = 0$$

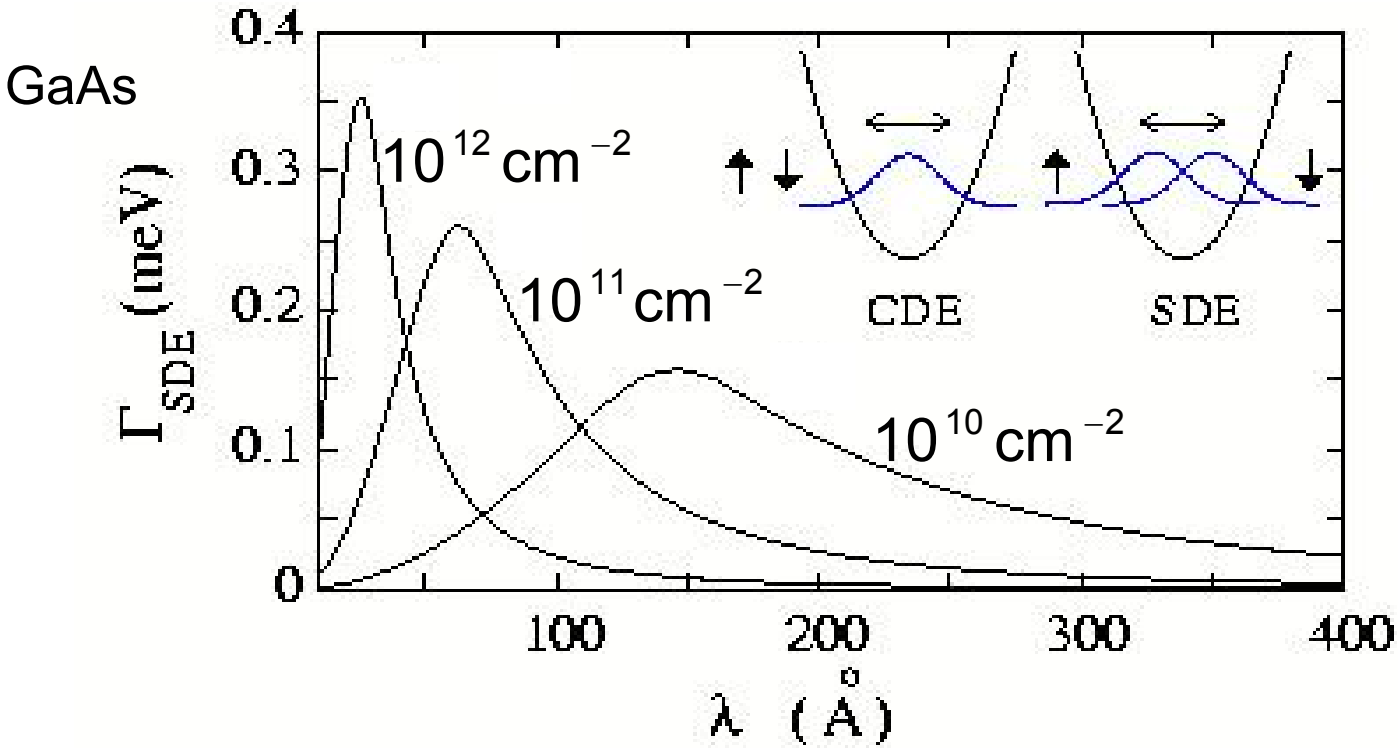
Spin-density excitation (SDE) in a parabolic well:

$$\Gamma_{SDE}^{VE} \quad \text{small}$$

$$\Gamma_{SDE} - \Gamma_{CDE} \approx \left(\Gamma_{SDE}^{disorder} + \Gamma_{SDE}^{SCD}\right) - \Gamma_{CDE}^{disorder} \approx \Gamma_{SDE}^{SCD}$$

impurity scattering affects CDE & SDE similarly

Spin plasmon linewidth vs. parabolic well curvature



proposed experiment:

1) measure linewidth of CDE and SDE collective modes in the same parabolic well (inelastic light scattering)
2) Difference of linewidths due (mostly) to SCD effect

I. D'Amico and C.A.U., PRB Rapids (2006), in press

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TDKS equation in C-TDDFT

$$\left[\frac{1}{2}\left(\frac{\vec{\nabla}}{i}+\frac{1}{c}\vec{A}_{ext}(\vec{r},t)+\frac{1}{c}\vec{A}_{xc}(\vec{r},t)\right)^2+V_{ext}(\vec{r},t)+V_H(\vec{r},t)-i\frac{\partial}{\partial t}\right]\varphi_j(\vec{r},t)=0$$

- A rigorous extension of the LDA into the nonlinear dynamical regime has recently been formulated (L-TDDFT, see later)
- However, the viscoelastic expression of linear-response C-TDDFT can be easily extended into the dynamical regime:

$$\frac{1}{c}\frac{\partial\vec{A}_{xc}}{\partial t}=-\vec{\nabla}V_{xc}^{ALDA}+\frac{\vec{\nabla}\cdot\vec{\vec{\sigma}}_{xc}}{n(\vec{r},t)}$$

G. Vignale, C.A.U., and S. Conti, PRL **79**, 4878 (1997)

- Valid up to second order in the spatial derivatives
- The gradients need to be small, but the velocities themselves can be large

Nonlinear C-TDDFT: xc stress tensor

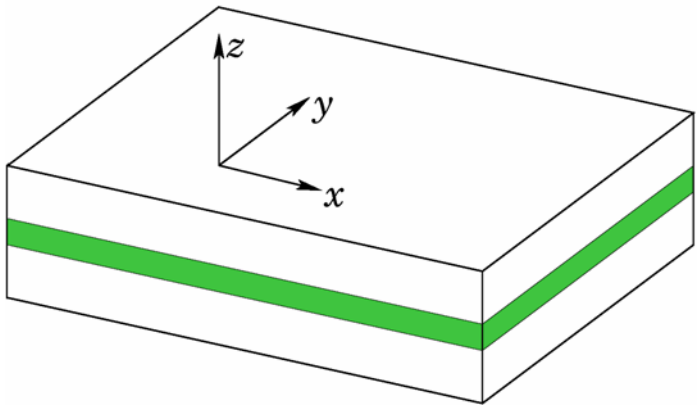
time-dependent velocity field: $\vec{v}(\vec{r},t) = \vec{j}(\vec{r},t)/n(\vec{r},t)$

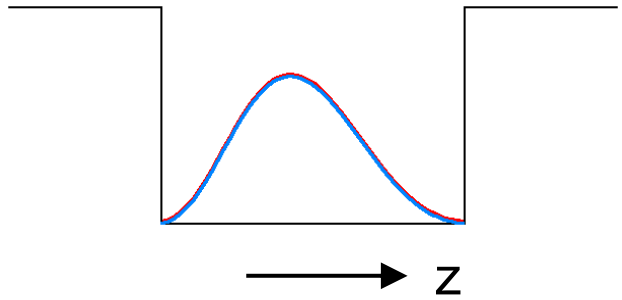
$$\sigma_{xc,ij}(\vec{r},t) = \int_{-\infty}^{t} dt'\, \eta_{xc}(\vec{r},t,t')\left[\nabla_i v_j(\vec{r},t') + \nabla_j v_i(\vec{r},t') - \frac{2}{3}\vec{\nabla}\cdot\vec{v}(\vec{r},t')\delta_{ij}\right]$$
$$+ \int_{-\infty}^{t} dt'\, \zeta_{xc}(\vec{r},t,t')\vec{\nabla}\cdot\vec{v}(\vec{r},t')\delta_{ij}$$

where the viscosity coefficients are defined as Fourier transforms:

$$\eta_{xc}(\vec{r},t,t') = \int \frac{d\omega}{2\pi}\tilde{\eta}(\bar{n},\omega)e^{-i\omega(t-t')}\Big|_{\bar{n}=n(\vec{r},t)}$$

Nonlinear C-TDDFT: “1D” systems





Consider a 3D system which is uniform along two directions

⇒ can transform xc vector potential into scalar potential:

$$V_{xc}(z,t) = V_{xc}^{\mathrm{ALDA}}(z,t) + V_{xc}^{M}(z,t)$$

with the memory-dependent xc potential

$$V_{xc}^{M}(z,t) = -\int_{-\infty}^{z} dz' \frac{\nabla_{z'}\sigma_{xc,zz}(z',t)}{n(z',t)}$$

The xc memory kernel

Assuming that the system has been in the ground state (with zero velocity) for t<0, the zz component of the xc stress tensor is

$$\sigma_{xc,zz}(z',t) = \int_0^t dt' Y\big(n(z',t), t-t'\big) \nabla_{z'} v_{z'}(z',t')$$

where the memory kernel is given by

$$Y(n,t-t') = \frac{4}{3}\eta(n,t-t') + \zeta(n,t-t')$$

Remember the definition of the viscosity coefficients:

$$\tilde{\eta}_{xc}(n,\omega) = -\frac{n^2}{i\omega} f_{xc}^{T}(n,\omega)$$

$$\tilde{\zeta}_{xc}(n,\omega) = -\frac{n^2}{i\omega}\left(f_{xc}^{L}(n,\omega) - \frac{4}{3} f_{xc}^{T}(n,\omega) - \frac{d^2 e_{xc}^{unif}}{dn^2} \right)$$

The xc memory kernel

$$Y(n,t-t') = \int \frac{d\omega}{2\pi}\left[\frac{4}{3}\tilde{\eta}(n,\omega)+\tilde{\zeta}(n,\omega)\right]e^{-i\omega(t-t')}$$

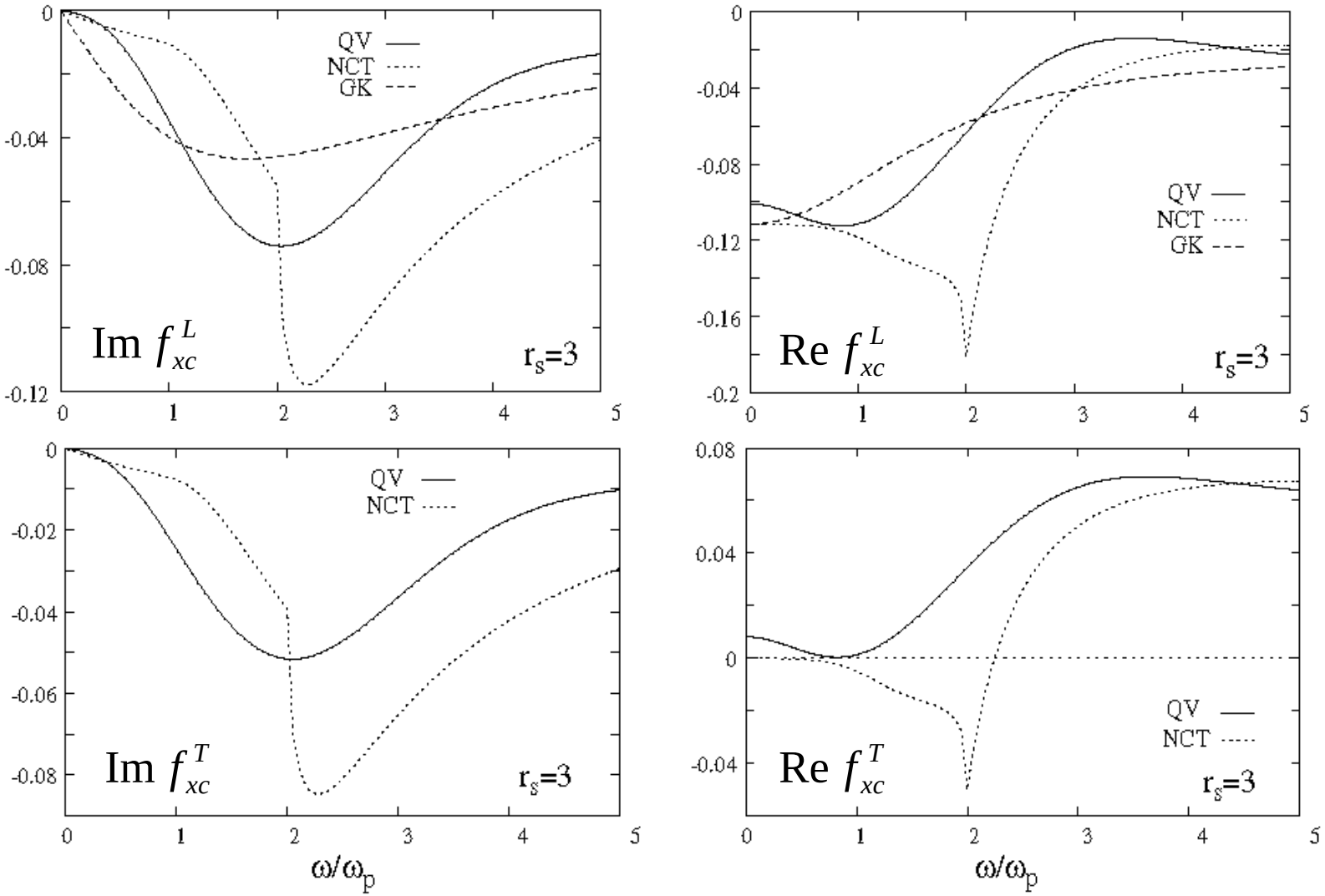
$$= \int \frac{d\omega}{2\pi}\left[f_{xc}^{L}(n,\omega) - \left(e_{xc}^{unif}\right)''\right]e^{-i\omega(t-t')}$$

Using contour integration and Kramers-Kronig, we find

$$Y(n,t-t') = \frac{4}{3}S_{xc}(0) - \frac{n^2}{\pi}\int \frac{d\omega}{\omega}\,\mathrm{Im}\, f_{xc}^{L}(\omega)\cos[\omega(t-t')]$$

static xc shear modulus: $S_{xc}(0) = \frac{3n^2}{4}\left[\mathrm{Re}\, f_{xc}^{L}(0) - \left(e_{xc}^{unif}\right)''\right]$

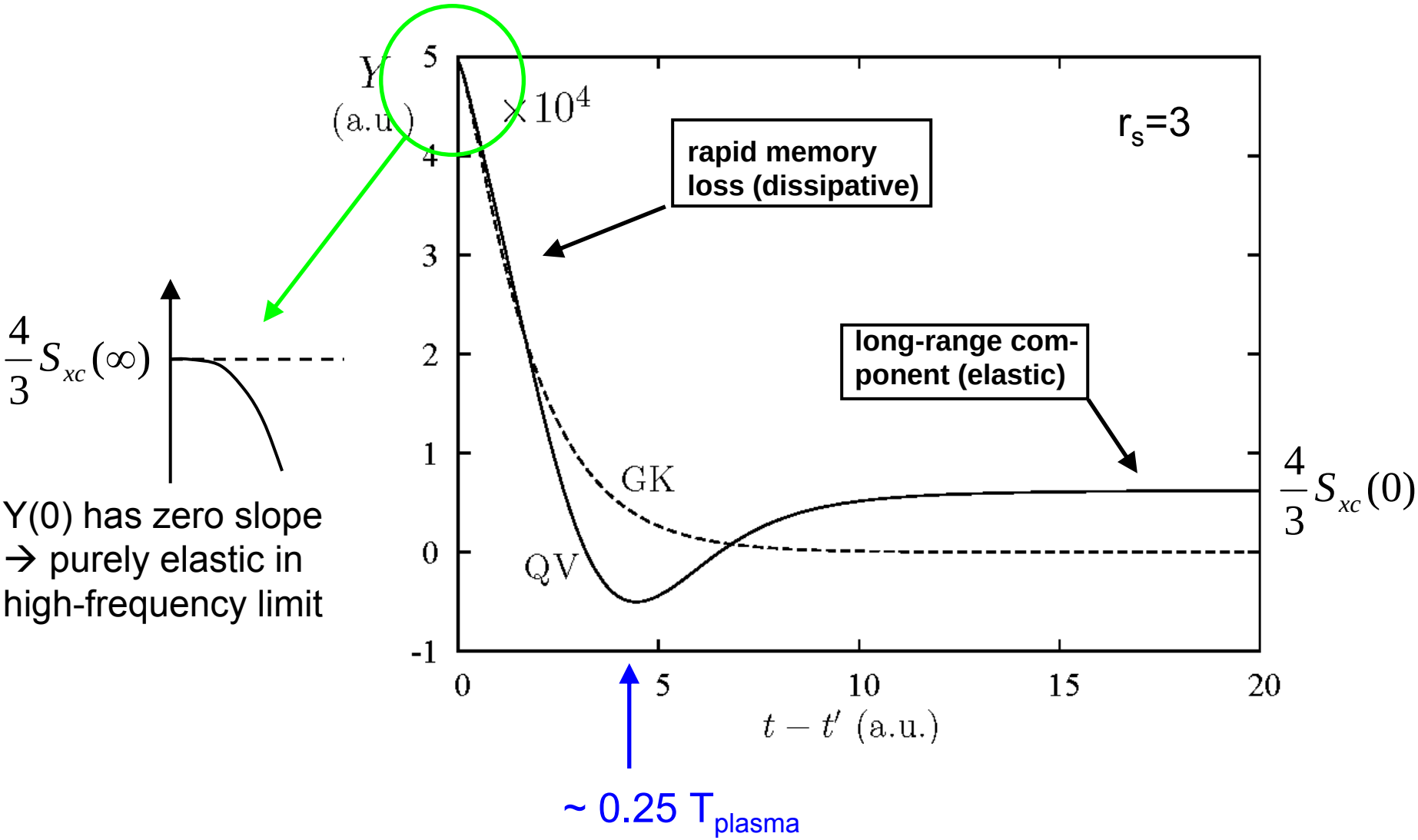
xc kernels of the homogeneous electron gas



GK: E.K.U. Gross and W. Kohn, PRL **55**, 2850 (1985)
NCT: R. Nifosi, S. Conti, and M.P. Tosi, PRB **58**, 12758 (1998)
QV: X. Qian and G. Vignale, PRB **65**, 235121 (2002)

The xc memory kernel

H.O. Wijewardane and C.A.U., PRL **95**, 086401 (2005)



Y(0) has zero slope → purely elastic in high-frequency limit

xc potential with memory: simple model

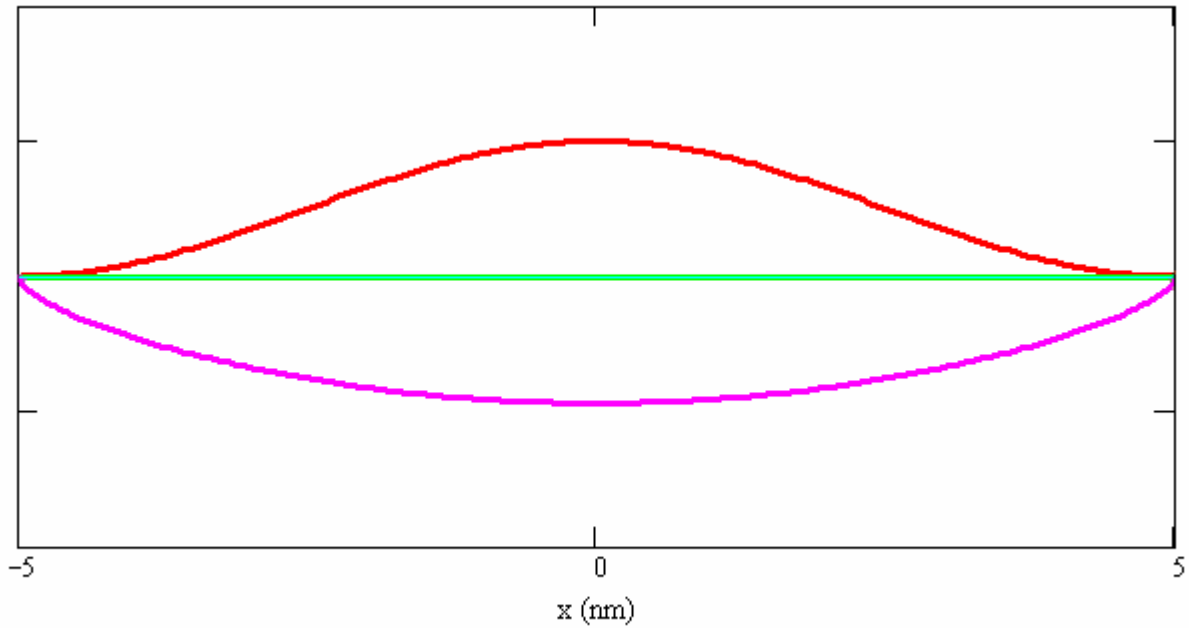
$$n(z,t) = \frac{2N_s}{L}\cos^2\left(\frac{z\pi}{L}\right)\left[1 + A\sin\omega t\ \sin\left(\frac{z\pi}{L}\right)\right]$$

$n(z,t)$

$V_{xc}^{M,GK}(z,t)$

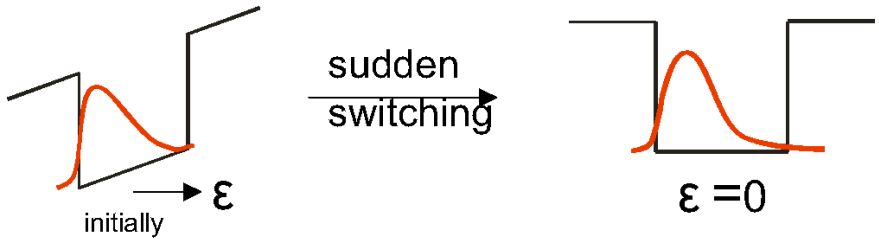
$V_{xc}^{M,QV}(z,t)$

$V_{xc}^{\mathrm{ALDA}}(z,t)$



XC Memory ⇒ Phase Lag ⇒ Retardation Force

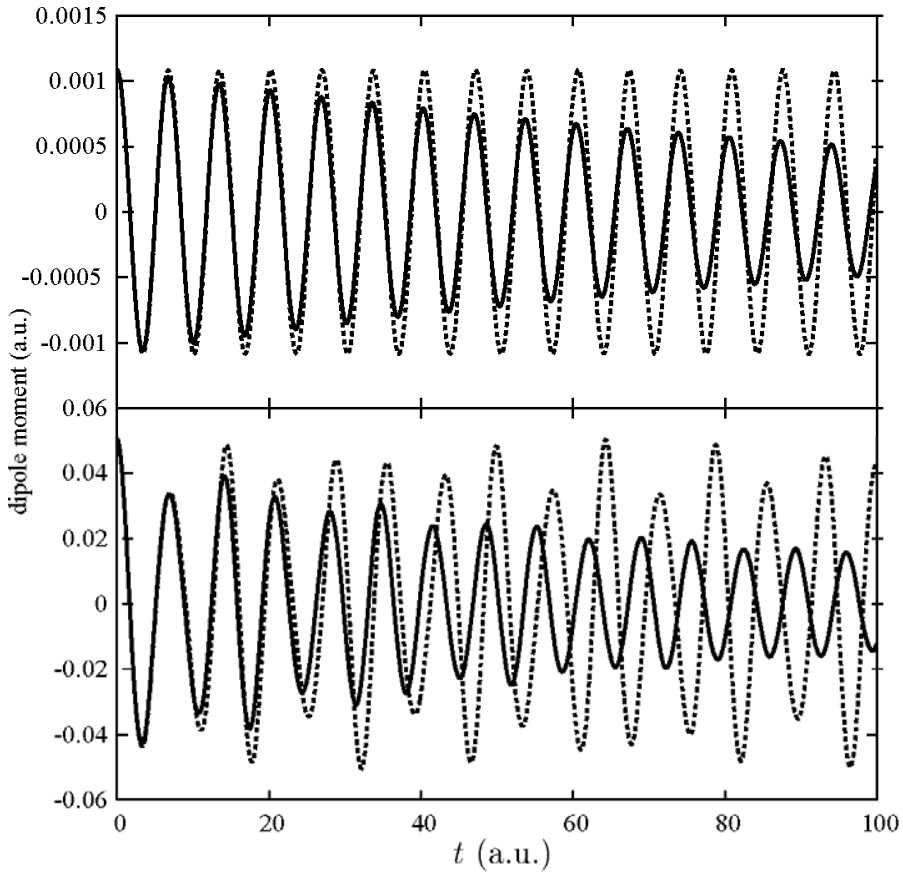
xc potential with memory: full TDKS calculation



40 nm
GaAs/AlGaAs

Weak excitation
(initial field 0.01)

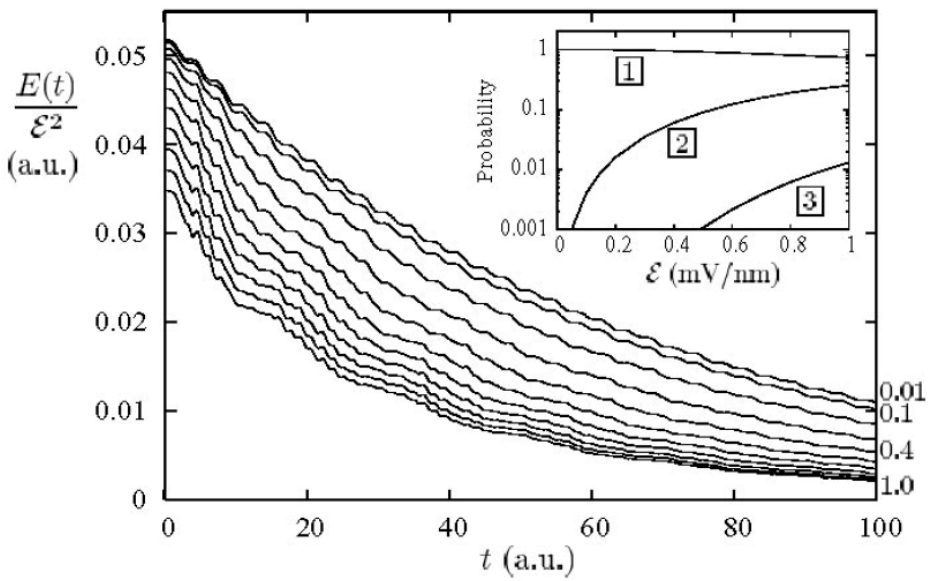
Strong excitation
(initial field 0.5)



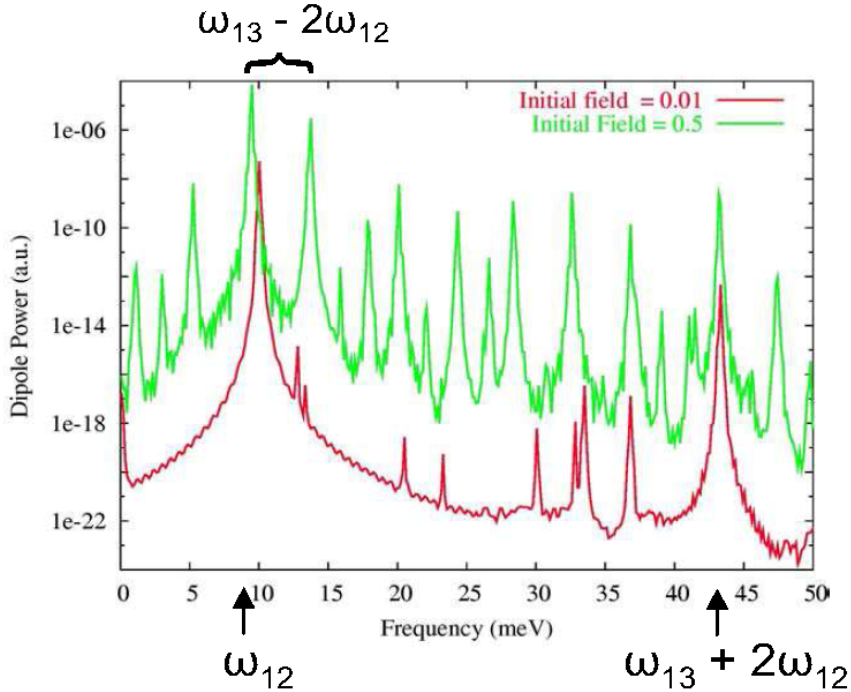
ALDA
ALDA+M

xc potential with memory: energy dissipation

Gradual loss of excitation energy



dipole power spectrum



Weak excitation: $E(t) \sim E_0 e^{-t/T_s}$

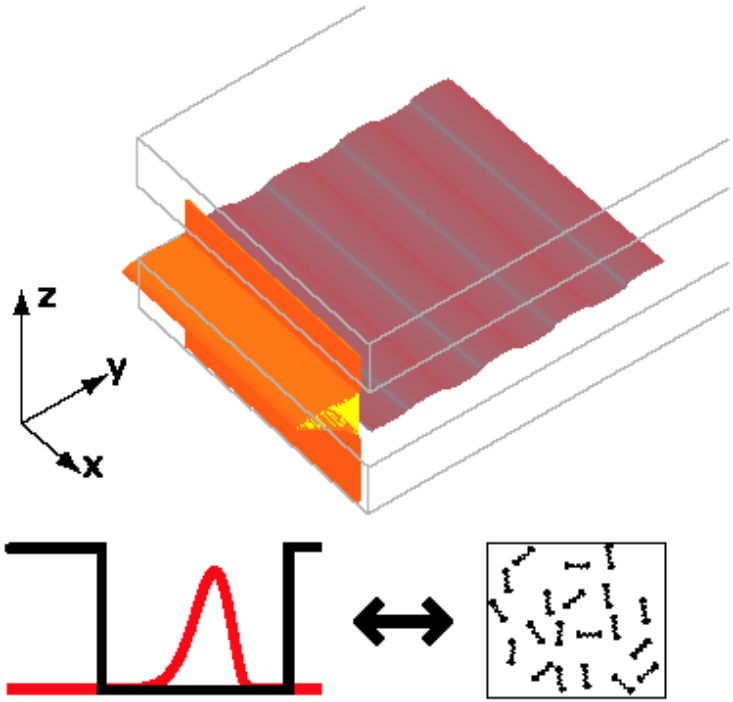
Strong excitation: $E(t) \sim E_1 e^{-t/T_s} + E_2 e^{-t/T_f}$

+ sideband modulation

T_s, T_f: slow and fast ISB relaxation times (hot electrons)

...but where does the energy go?

- The system is not driven by external fields, so the energy should be conserved.
- In linear response calculations of atomic excitation energies, the VK functional gives a finite linewidth, which is unphysical.

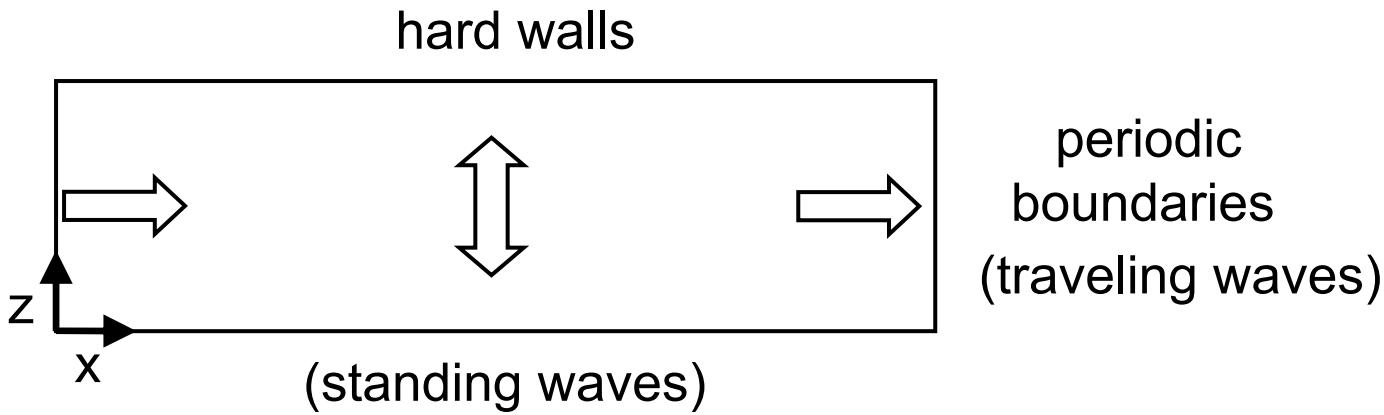


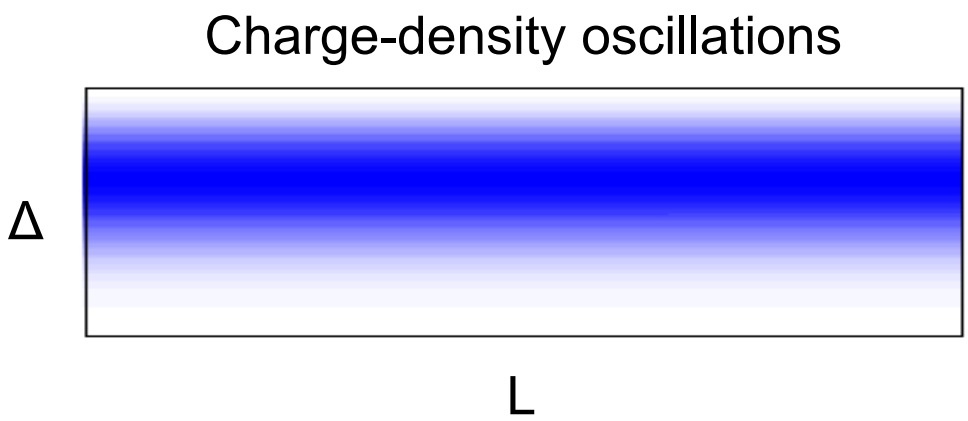
R. D'Agosta and G. Vignale, PRL **96**, 016405 (2006)

- collective motion along z is coupled to the in-plane degrees of freedom
- the x-y degrees of freedom act like a reservoir
- decay into multiple particle-hole excitations

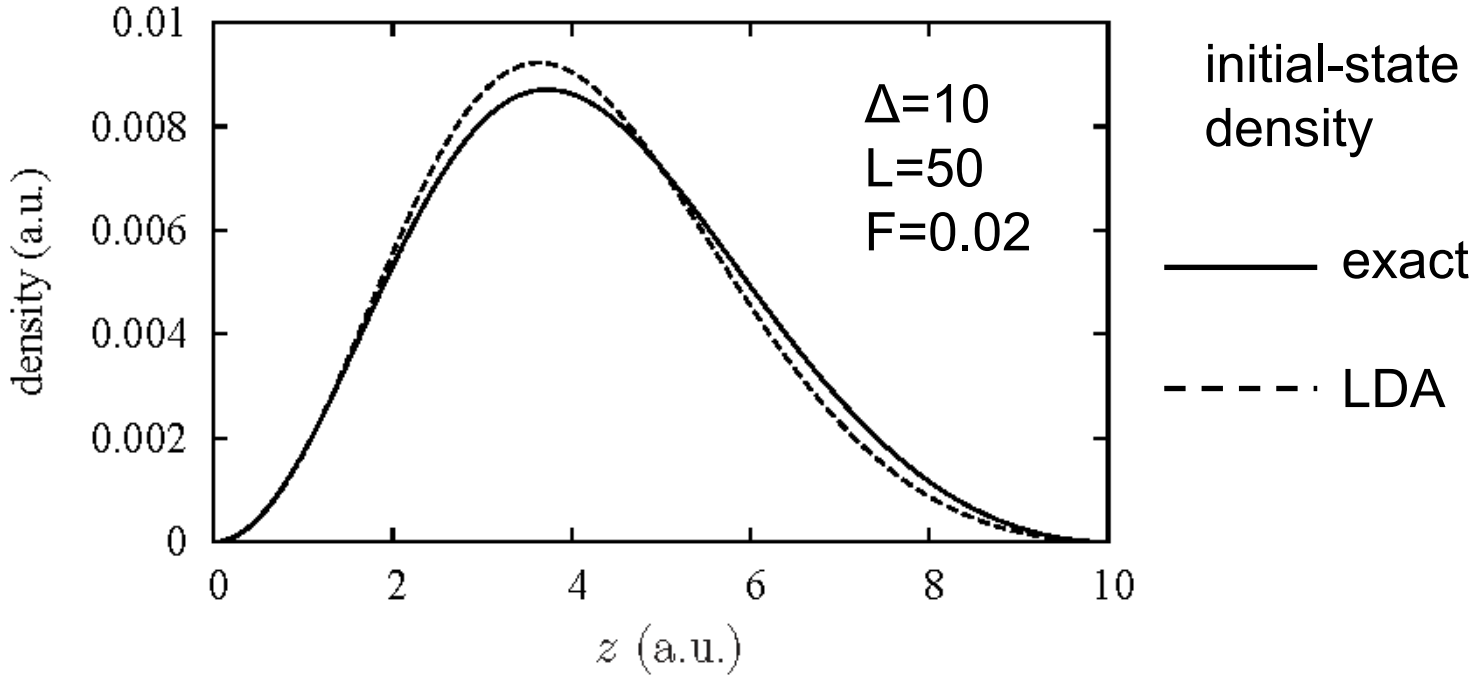
This is the situation for infinite systems. But what about finite systems?

Example: two electrons on a 2D quantum strip



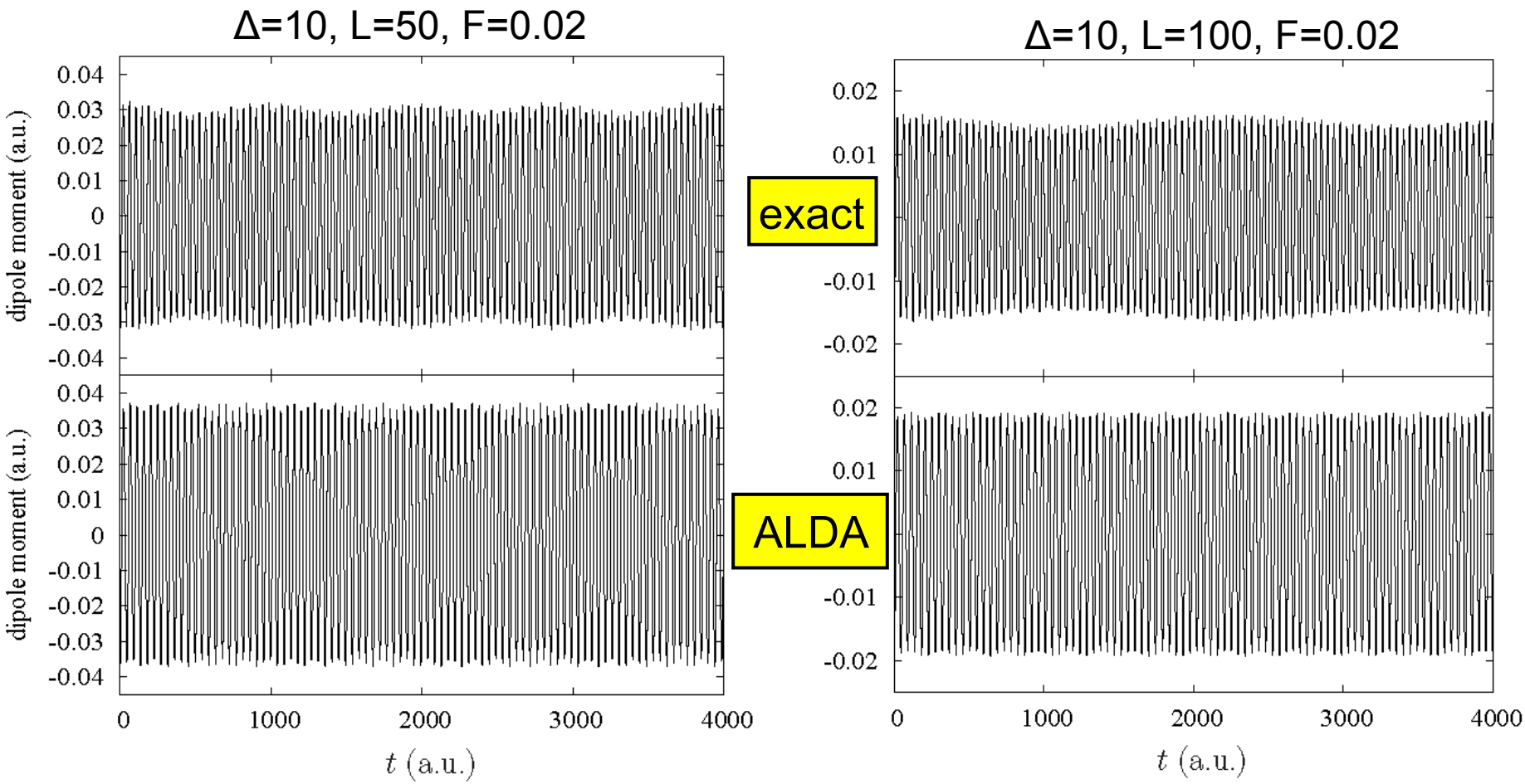


Example: two electrons on a 2D quantum strip



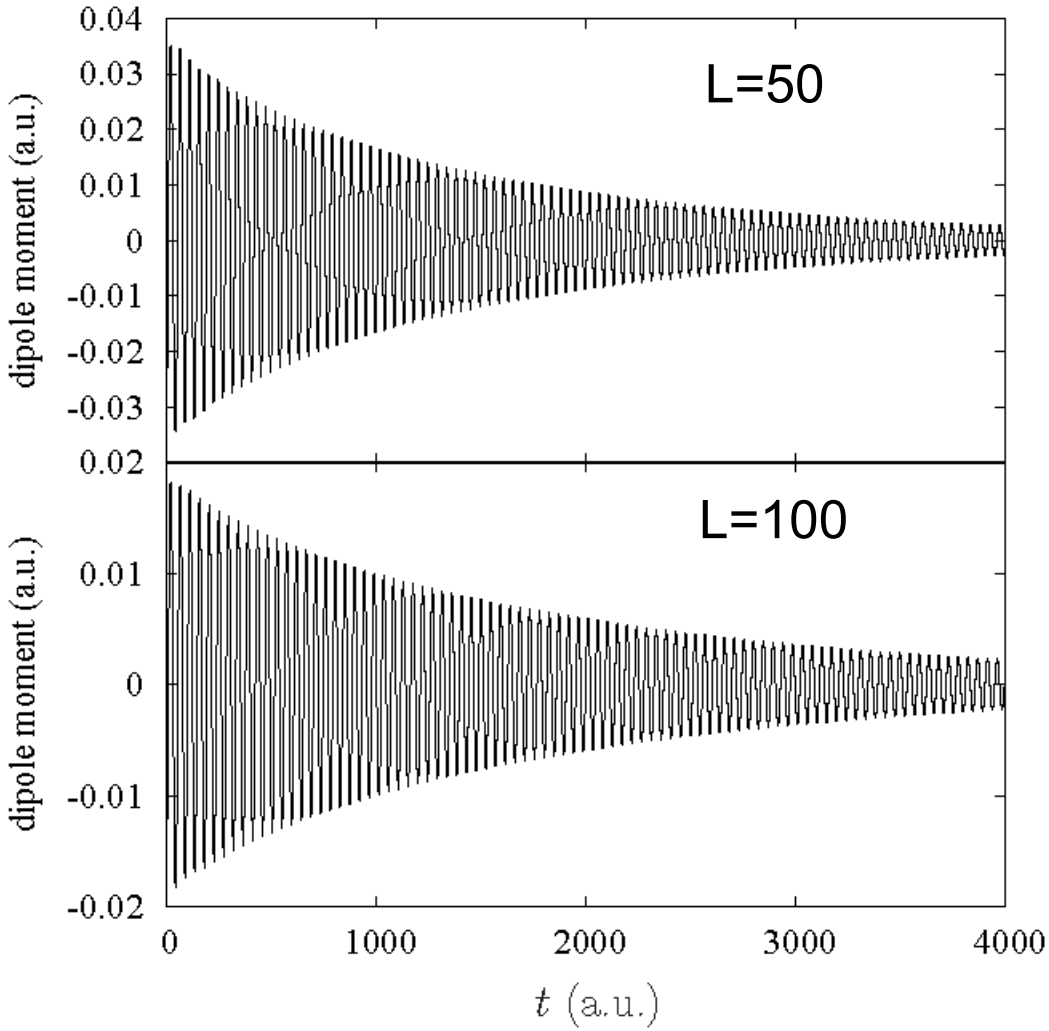
- Compare exact calculation (time-dependent CI) with TDKS
- Initial state: constant electric field, which is suddenly switched off
- After switch-off, free propagation of the charge-density oscillations

2D quantum strip: time-dependent dipole moment



- Exact calculations give a beating pattern of d(t), due to a superposition of dipole oscillations involving single and double excitations
- Recurrence time increases with length of the strip
- ALDA misses the beating pattern since it has no multiple excitations

2D quantum strip: ALDA+M



- ALDA+M: d(t) is exponentially damped
- The VK functional cannot tell that the system is finite. It treats the system locally like a homogeneous electron gas.
- infinite recurrence time emerges in the thermo-dynamic limit of the system
- damping of d(t) is due to decoherence, involving many excitations with a continuous spectrum

2-electron system: TDKS energy

R. D'Agosta and G. Vignale, PRL **96**, 016405 (2006)

$$E_{KS}(t) = 2\int d\vec{r}\,\varphi^*(\vec{r},t)\left[\frac{1}{2}\left(\frac{\vec{\nabla}}{i} + \vec{A}_{xc}(\vec{r},t)\right)^2 + V(\vec{r},t)\right]\varphi(\vec{r},t)$$
$$+ E_H[n(t)] + E_{xc}[n(t)]$$

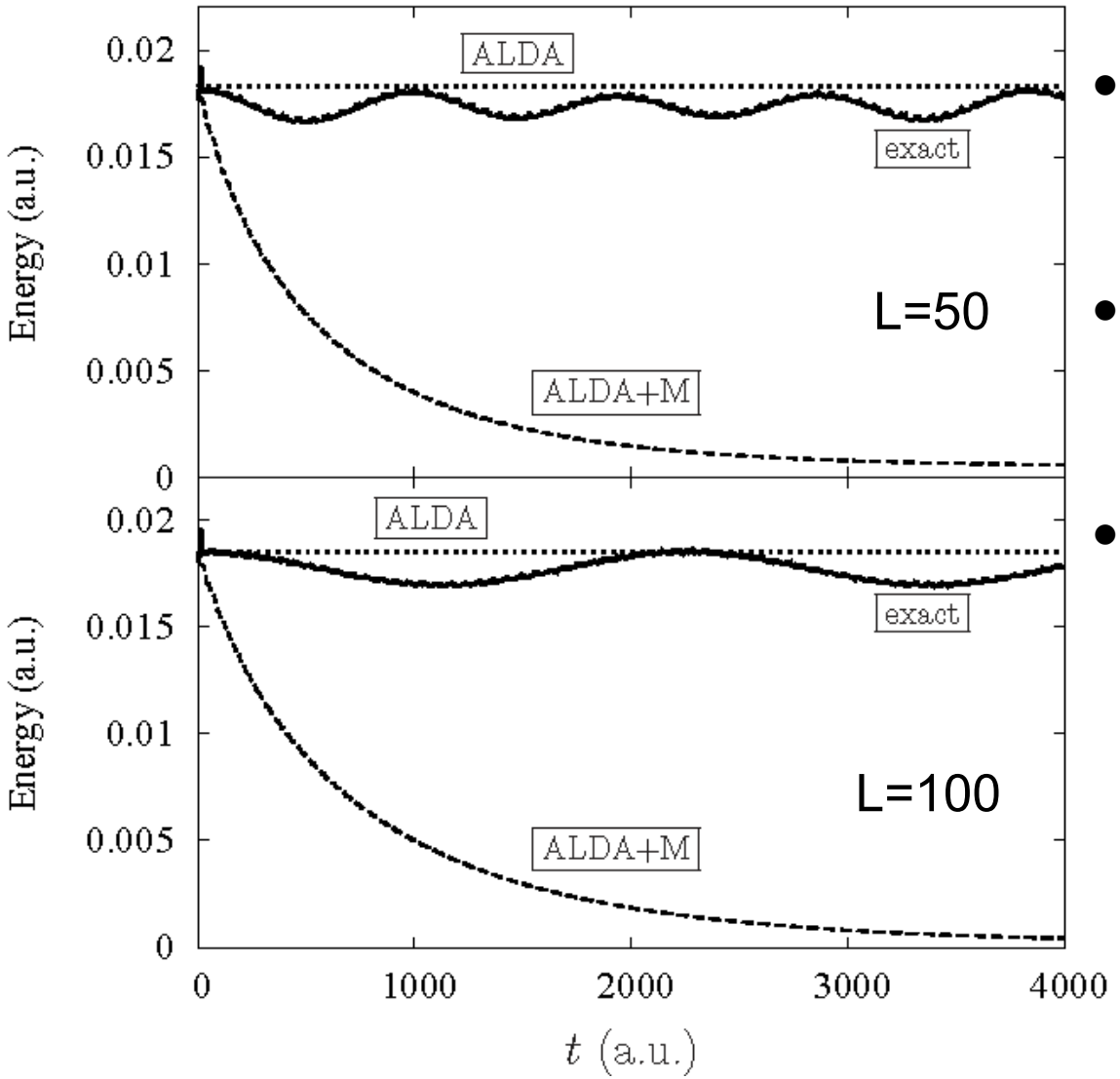
From the exact calculation, we have the exact density, but not the exact functionals. We determine the energy by integrating its rate of change:

$$\dot{E}_{KS}(t) = \int d\vec{r}\;\; \vec{j}(\vec{r},t)\cdot\dot{\vec{A}}_{xc}(\vec{r},t)$$

$$= -L\int_0^{\Delta} dz\;\; j_z(z,t)\frac{d}{dz}V_{xc}^{dyn}(z,t)$$

where $V_{xc}^{dyn}(\vec{r},t) = -\dot{\alpha}(\vec{r},t) - \frac{1}{2}|\vec{\nabla}\alpha(\vec{r},t)|^2$ (see lecture 1)

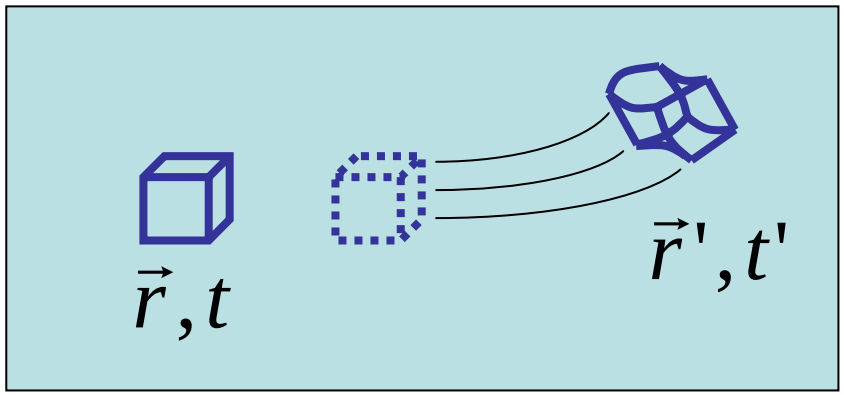
2-electron system: TDKS energy



- ALDA gives constant energy, ALDA+M dissipates energy exponentially
- The energy of the exact TDKS system is **not** constant but oscillates
- In order to reproduce the modulations of the dipole amplitude, the exact xc potential acts like an external force which alternatingly damps and drives the system.

TDDFT in the Lagrangian frame (L-TDDFT)

I.V. Tokatly, PRB **71**, 165104 and 165105 (2005), and TDDFT book (Ch. 8)
C.A.U. and I.V. Tokatly, PRB **73**, 235102 (2006)



- use a reference frame that moves with the fluid.
- basic variables: positions of fluid elements and their deformations
- nonlinear coordinate transformation $\vec{r} = \vec{r}\left(\vec{\xi}, t\right)$

$$\frac{\partial \vec{r}\left(\vec{\xi},t\right)}{\partial t} = \vec{v}\left(\vec{r}(\vec{\xi},t),t\right), \qquad \vec{r}(\vec{\xi},0) = \vec{\xi}$$

Lagrangian coordinate

$$\bar{g}_{ij}(\vec{r},t) = \frac{\partial \xi_k(\vec{r},t)}{\partial r_i}\frac{\partial \xi_k(\vec{r},t)}{\partial r_j}$$

Cauchy's deformation tensor in the laboratory frame

$$n(\vec{r},t) = \sqrt{\bar{g}(\vec{r},t)}\; n_0\left(\vec{\xi}(\vec{r},t)\right)$$

TDDFT in the Lagrangian frame: stress tensor

$$-\frac{\partial A_{xc,i}}{\partial t}+v_j\left(\nabla_i A_{xc,j}-\nabla_j A_{xc,i}\right)=\frac{c}{n}\nabla_j P_{xc,ij}[\bar{g}_{ij}]$$

where $P_{xc,ij}=P_{ij}-T_{ij}^{KS}$ (stress tensor of interacting minus kinetic stress tensor of KS system)

- xc stress tensor is a spatially local functional of $\bar{g}_{ij}$ (which, in turn, is a functional of the velocity)
- in general, it contains both elastic and dissipative effects.
- This is the exact extension of LDA into the dynamical regime
- The interacting stress tensor is only approximately known.

The small deformation approximation

$$P_{xc,ij}(t) = P_{xc}^{ALDA}(t)\delta_{ij}$$
$$+\int_0^t dt'\left[\frac{\delta_{ij}}{2}K_{xc}(t-t')\delta\bar{g}_{kk}(t') + \mu_{xc}(t-t')\left(1-\frac{\delta_{ij}}{3}\right)\delta\bar{g}_{kk}(t')\right]$$

$$\delta\bar{g}_{ij}(\vec{r},t) = -\left(\frac{\partial u_i}{\partial r_j}+\frac{\partial u_j}{\partial r_i}\right) \quad \text{and} \quad \partial_t\vec{u} = \vec{v}$$

in the regime of small deformations, we recover the nonlinear form of C-TDDFT (i.e., ALDA+M), where

$$\mu_{xc} = -i\omega\tilde{\eta}_{xc} \qquad K_{xc} = -i\omega\tilde{\zeta}$$

- This puts nonlinear C-TDDFT on firm grounds
- Remember, the deformations are small, but the velocities can be large.

Nonlinear elastic approximation to L-TDDFT

If we neglect dissipation, a nonlinear local approximation for the stress tensor can be rigorously derived:

$$P_{xc,ij} = \frac{2}{3}\bar{g}_{ij}\sqrt{\bar{g}}\,E_{xc}^{kin}\left(\frac{n}{\sqrt{\bar{g}}}\right) + L_{ij}(\bar{g}_{kl})E_{xc}^{pot}\left(\frac{n}{\sqrt{\bar{g}}}\right)$$

where $E_{xc}^{kin}(n) = 3n^{7/3}\left(\frac{e_{xc}^{unif}}{n^{4/3}}\right)'$ and $E_{xc}^{pot}(n) = -3n^{8/3}\left(\frac{e_{xc}^{unif}}{n^{5/3}}\right)'$

and L_{ij} is a known function.

- Exact in the high-frequency limit, for any deformation
- For small deformations, this reduces to the purely elastic high-frequency limit of C-TDDFT.
- deviations of the deformation tensor g from δ_{ij} can be viewed as a measure of nonadiabaticity.

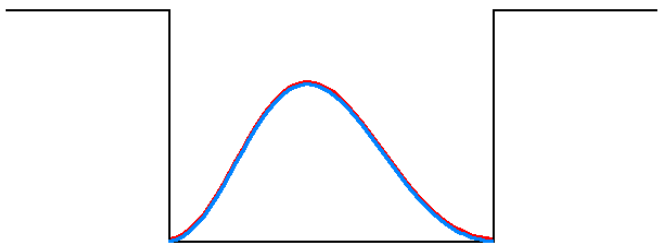
L-TDDFT versus C-TDDFT: simple "1D" models

C.A.U. and I.V. Tokatly, PRB **73**, 235102 (2006)

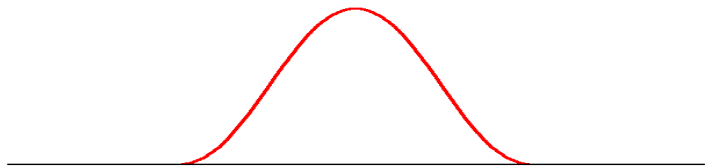
$$n(x,t) = \sqrt{\bar{g}(x,t)}\; n_0(\xi(x,t)) \quad \text{and} \quad \bar{g}(x,t) = \left(\frac{\partial \xi}{\partial t}\right)^2$$

let $$n_0(\xi) = \frac{2N}{L}\cos^2\left(\frac{\pi\xi}{L}\right)$$

and choose analytical expressions for $v(\xi,t)$ and $x(\xi,t)$ which can easily be inverted.

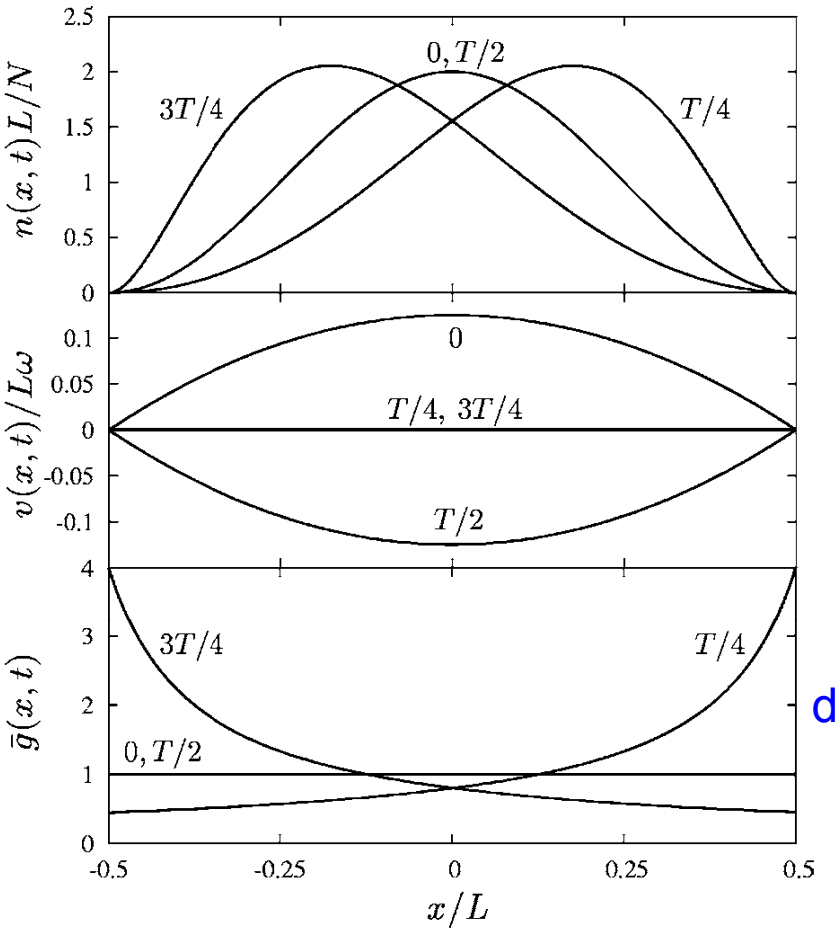


sloshing mode



breathing mode

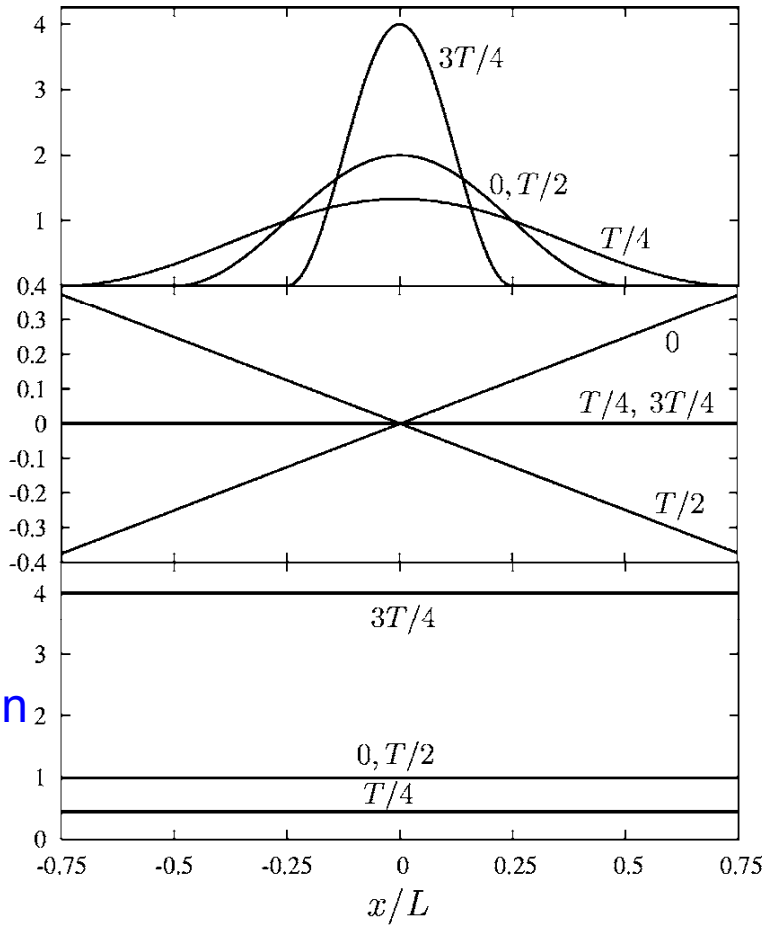
L-TDDFT versus C-TDDFT: simple “1D” models



density

velocity

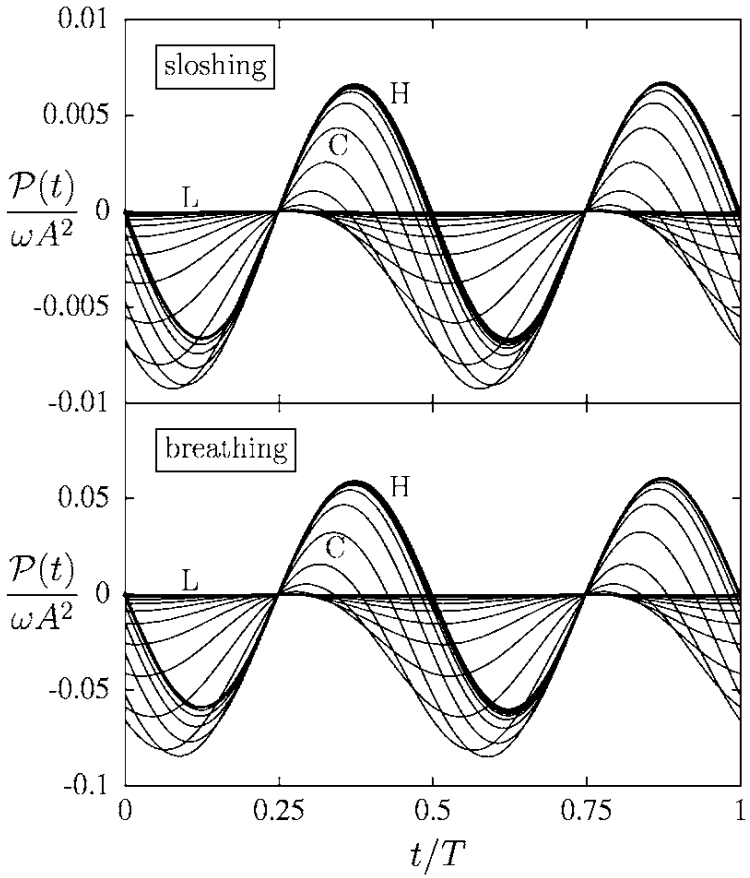
deformation

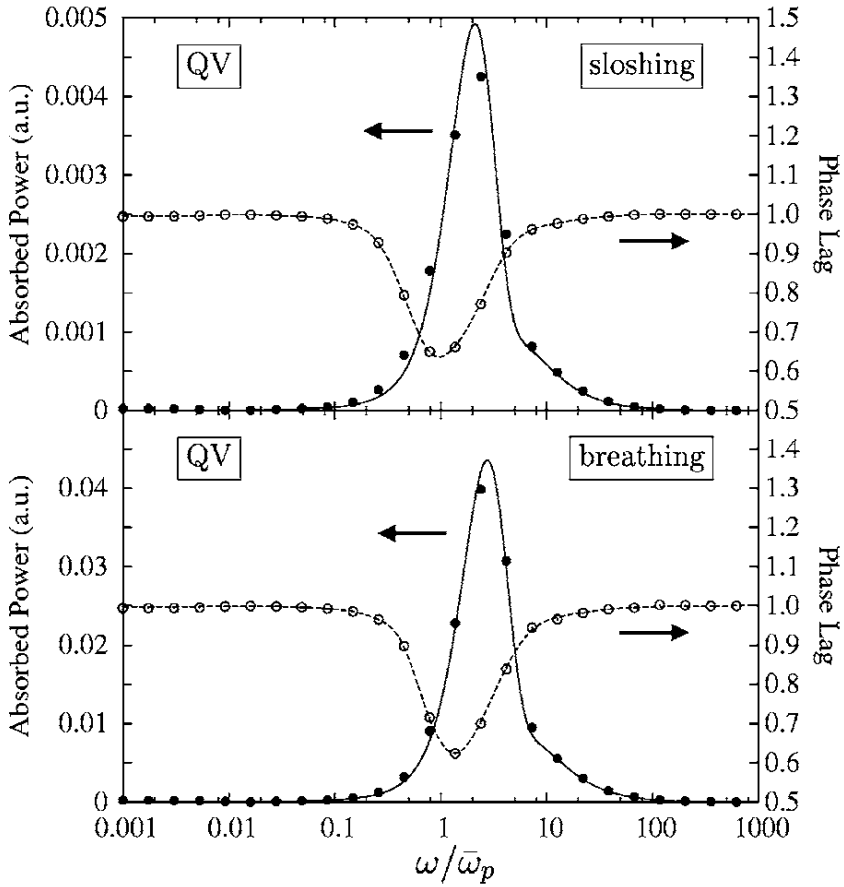


sloshing mode: not too strongly deformed (cousin of Kohn’s mode)

breathing mode: strongly deformed everywhere (very un-hydrodynamic)

Power absorption and phase lag in C-TDDFT





power associated with the modes:

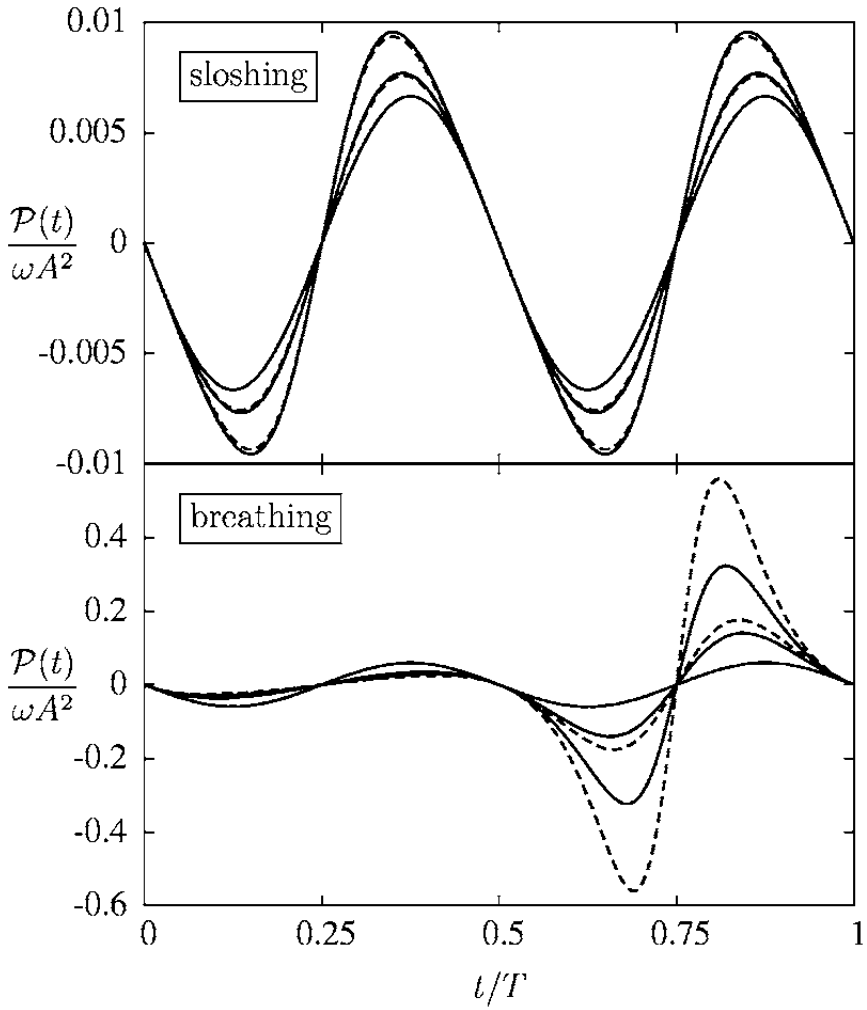
$$P(t) = \int dx\, v(x,t) n(x,t) \frac{\partial}{\partial x} V_{xc}^{M}(x,t)$$

phase lag:

π/2: purely dissipative

π: purely elastic

L-TDDFT versus C-TDDFT: high-frequency limit



C-TDDFT

L-TDDFT (exact)

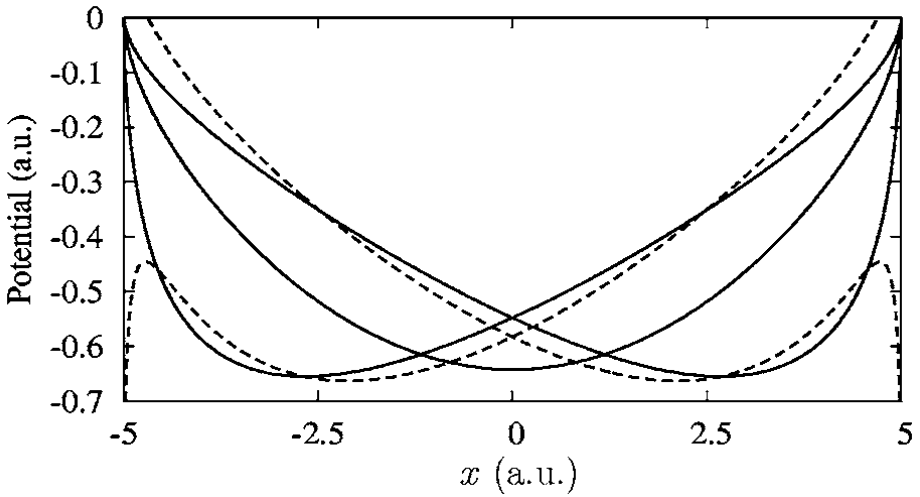
- in the high-frequency limit, the elastic approximation for L-TDDFT becomes the exact dynamical extension of the LDA (for all deformations)
- for small deformations, C-TDDFT becomes exact (for all frequencies)
- for largest amplitudes, C-TDDFT deviates:
  <2.5% for sloshing mode
  ~100% for breathing mode

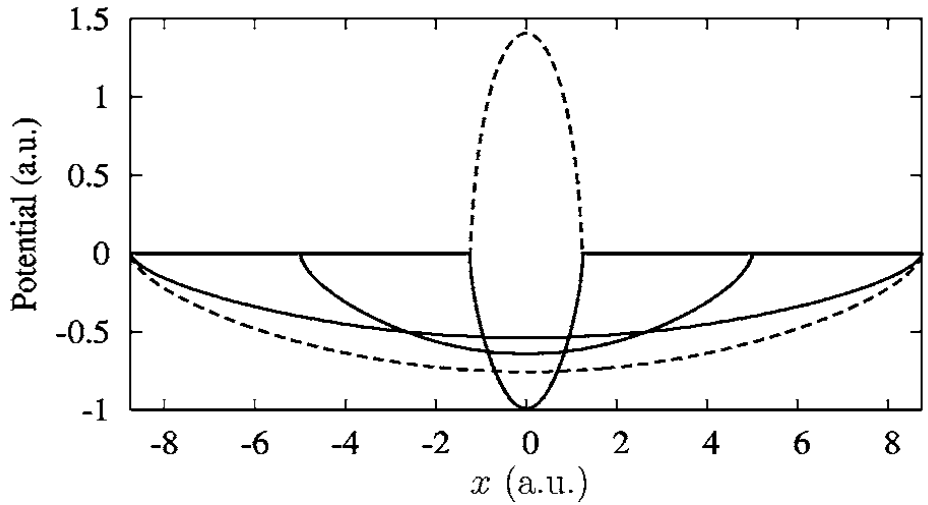
The nonlinear C-TDDFT remains good for moderate deformations!

Breakdown of the ALDA

L-TDDFT in the high-frequency, purely elastic limit ($\omega >> \omega_p$)

——— V_{xc}^{ALDA} ----- $V_{xc}^{L-TDDFT}$ (exact)





Sloshing mode: small deformation, minor corrections to ALDA

Breathing mode: large deformation, ALDA breaks down

Time-dependent optimized effective potential

C.A.U., U.J. Gossmann, E.K.U. Gross, PRL **74**, 872 (1995)

$$\sum_{j=1}^{N} \int_{-\infty}^{t} dt' \int d^3r' \left[V_{xc}(\vec{r}'t') - u_{xcj}(\vec{r}'t') \right] \varphi_j(\vec{r}t) \varphi_j^*(\vec{r}'t') K(\vec{r}t, \vec{r}'t') - c.c. = 0$$

$$K(\vec{r}t, \vec{r}'t') = \sum_{k=1}^{\infty} \varphi_k^*(\vec{r}t) \varphi_k(\vec{r}'t') \qquad u_{xcj}(\vec{r}t) = \frac{1}{\varphi_j^*(\vec{r}t)} \frac{\delta A_{xc}[\{\varphi_i\}]}{\delta \varphi_j(\vec{r}t)}$$

simplified, adiabatic scheme: time-dependent KLI

$$V_{xc}^{KLI}(\vec{r},t) = \sum_j \frac{n_j(\vec{r},t)}{n(\vec{r},t)} \left[u_{xc,j}(\vec{r},t) + \int d^3r' \left| \varphi_j(\vec{r}',t) \right|^2 \left\{ V_{xc}^{KLI}(\vec{r}',t) - u_{xc,j}(\vec{r}',t) \right\} \right]$$

Time-dependent optimized effective potential

Applications of TDOEP in the linear regime [A. Goerling, TDDFT book]:

- Optical spectra of solids
  Kim and Goerling, PRL 89, 096402 (2002)
- Molecular excitation energies and dynamic polarizabilities
  Hirata et al., PRA **71**, 032507 (2005)

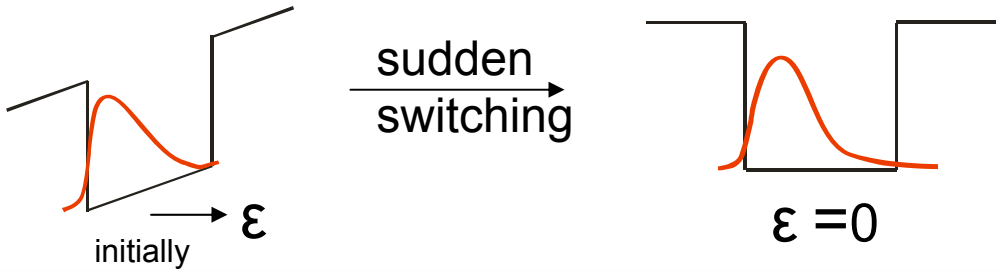
} static (ω=0) kernel

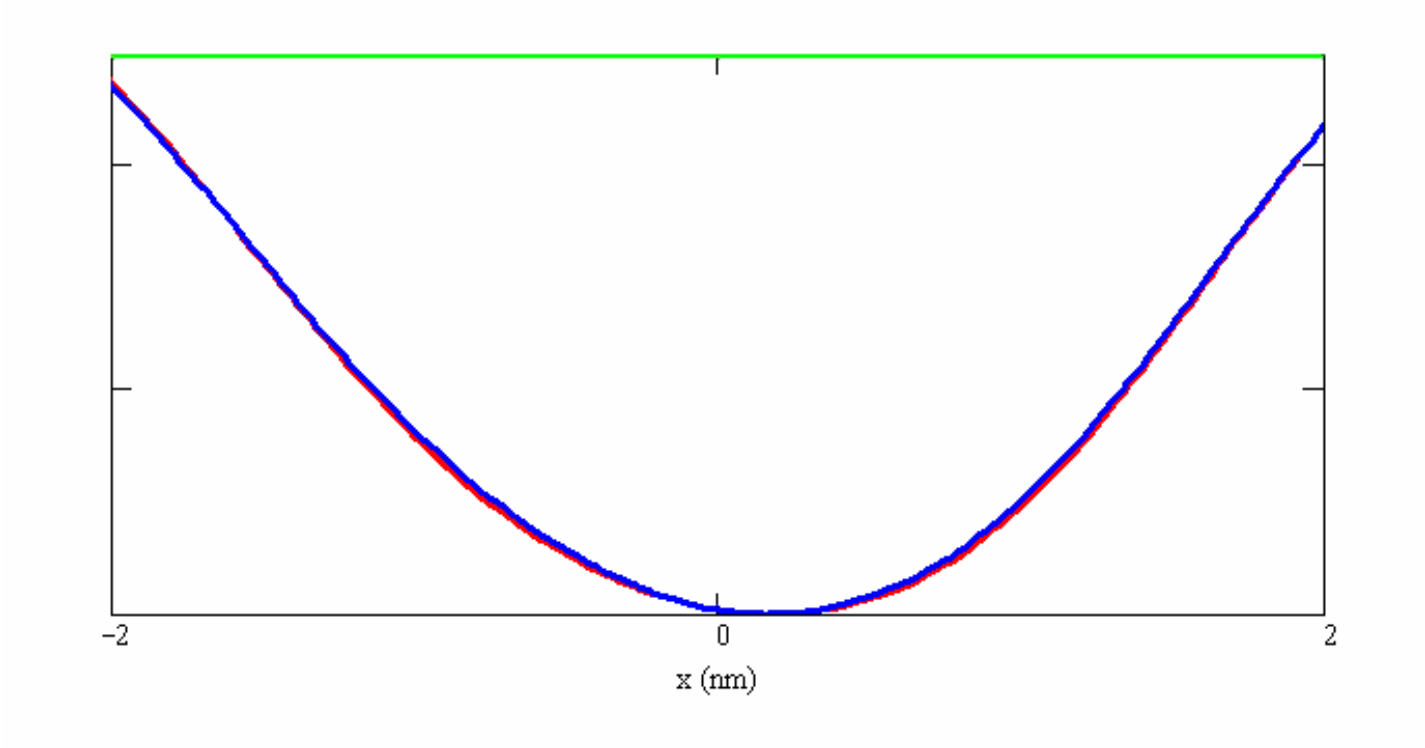
Shigeta, Hirao, Hirata, PRA **73**, 010502 (2006) ω-dependent kernel

Applications of TDKLI in the nonlinear regime:

- Atoms in strong fields
  C.A.U. and E.K.U. Gross, Comments At. Mol. Phys. **33**, 211 (1997)
  M. Mundt and S. Kuemmel, PRL **95**, 203004 (2005)
- Metallic clusters
  C.A.U., P.-G. Reinhard, E. Suraud, PRA **62**, 053202 (2000),
  H.S. Nguyen, A.D. Bandrauk, C.A.U, PRA **69**, 063415 (2004)

Full TDOEP versus TDKLI: exact exchange

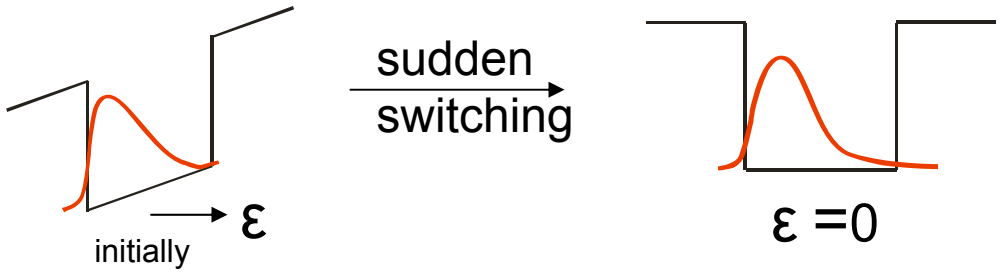


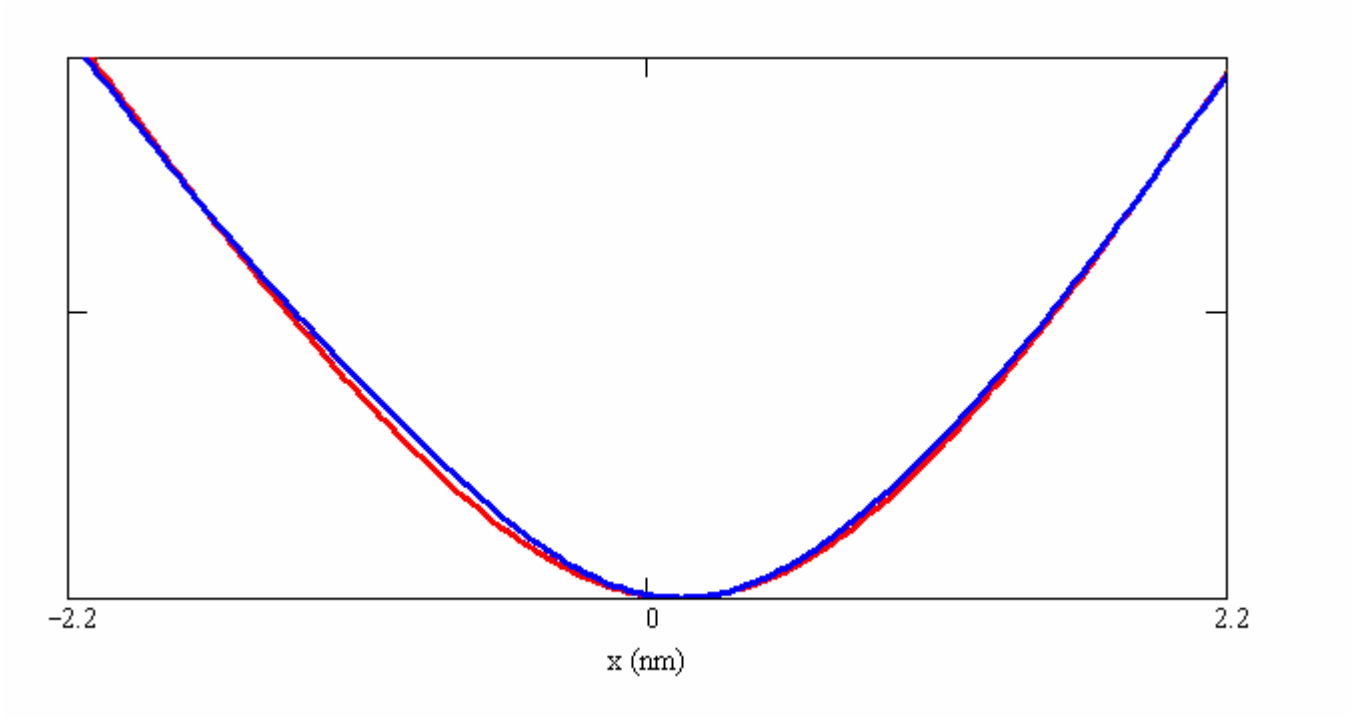


full TDOEP-XX TDKLI-XX (no memory)

(correct asymptotics, discontinuous as a new level is filled)

Full TDOEP versus TDKLI: LDA-SIC





full TDOEP-SIC

TDKLI-SIC (no memory)

Summary

- A rigorous formulation of local time-dependent xc effects is established by L-TDDFT.
- C-TDDFT emerges as small-deformation approximation.
- Nonadiabatic effects are both elastic and dissipative. It depends on the frequency which effect is more important.
- The ALDA breaks down when the electronic density rapidly undergoes large deformations.
- Orbital-based TDOEP seems the way to go for finite systems. First applications are underway.

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