Lecture 3

TDCDFT: Nonlinear regime

Carsten A. Ullrich
University of Missouri

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Overview

Lecture I: Basic formalism of TDCDFT

Lecture II: Applications of TDCDFT in linear response

Lecture III: TDCDFT in the nonlinear regime

- ►Time-dependent Kohn-Sham with memory
- ►Energy dissipation
- ►TDDFT in the Lagrangian frame
- ►Another way to treat memory in TDDFT: time-dependent OEP (TDOEP)

TDKS equation in TDCDFT

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

- A rigorous extension of the LDA into the nonlinear dynamical regime has recently been formulated (Lagrangian TDDFT, see later)
- However, the viscoelastic expression of linear-response TDCDFT can be easily (but somewhat ad hoc) extended into the dynamical regime:

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

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 VK-TDCDFT: xc stress tensor

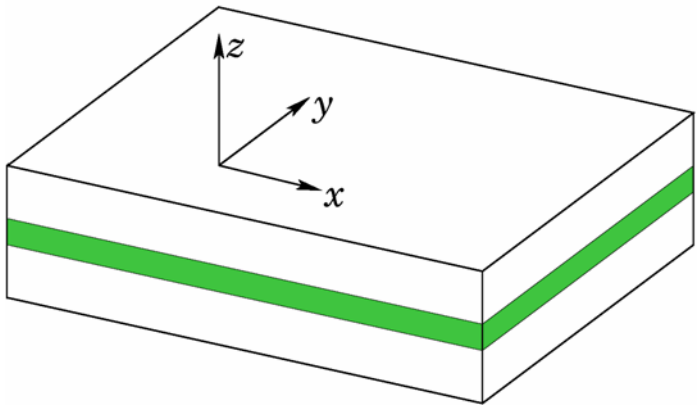
time-dependent velocity field: $\mathbf{v}(\mathbf{r},t) = \mathbf{j}(\mathbf{r},t)/n(\mathbf{r},t)$

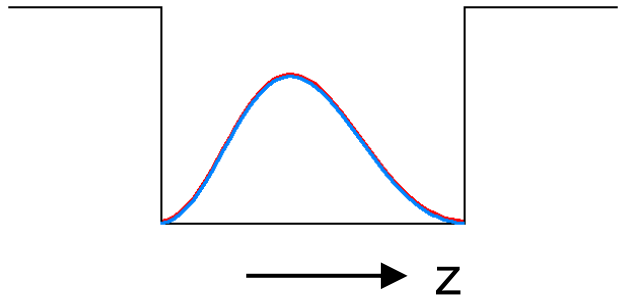
$$\sigma_{xc,ij}(\mathbf{r},t) = \int_{-\infty}^{t} dt'\, \eta_{xc}(\mathbf{r},t,t')\left[\nabla_i \mathrm{v}_j(\mathbf{r},t') + \nabla_j \mathrm{v}_i(\mathbf{r},t') - \frac{2}{3}\nabla\cdot\mathrm{v}(\mathbf{r},t')\delta_{ij}\right]$$
$$+ \int_{-\infty}^{t} dt'\, \zeta_{xc}(\mathbf{r},t,t')\nabla\cdot\mathrm{v}(\mathbf{r},t')\delta_{ij}$$

where the viscosity coefficients are defined as Fourier transforms:

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

Nonlinear TDCDFT: “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

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

where the memory kernel is given by

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

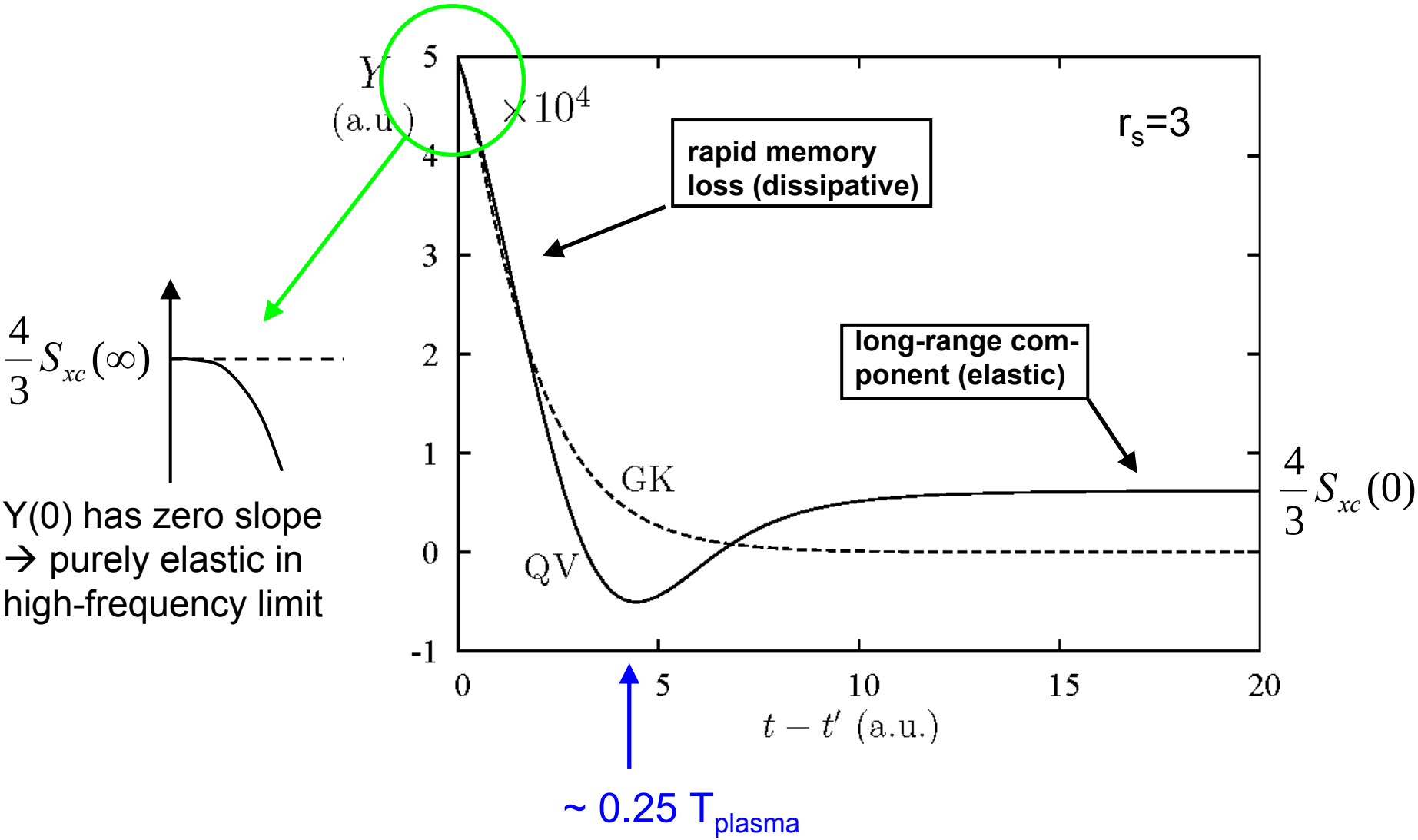
Using the definition of the viscosity coefficients, one finds explicitly

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

static xc shear modulus

The xc memory kernel

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



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

~ 0.25 T_{plasma}

xc potential with memory: simple model

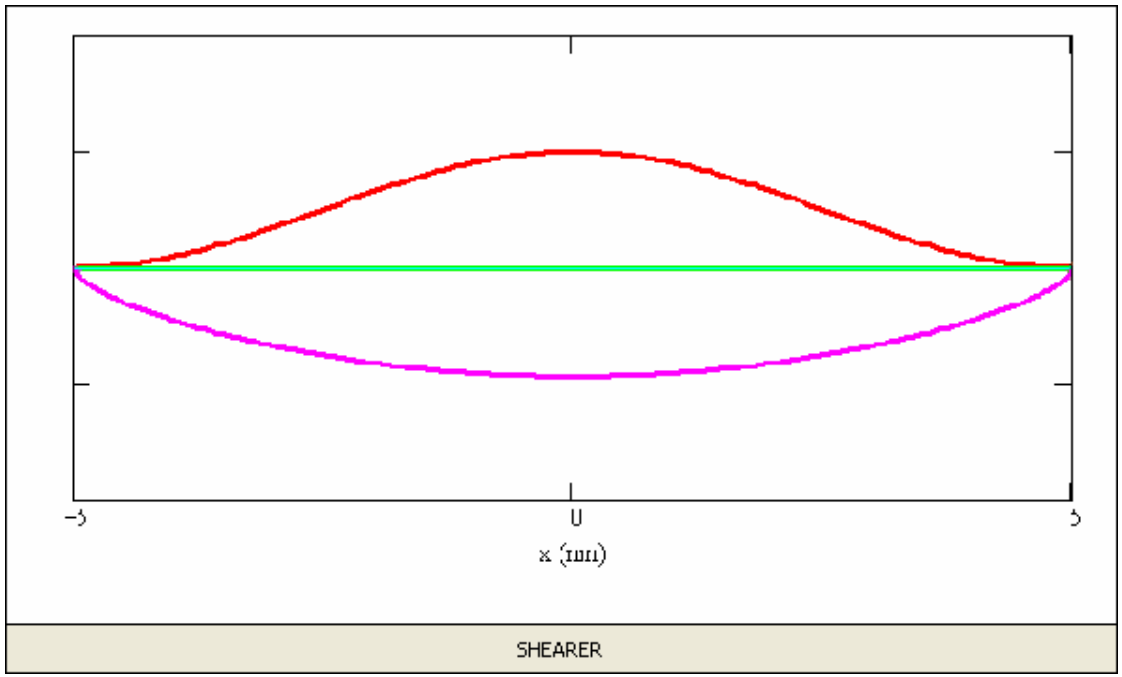
$$n(z,t) = \frac{2N_s}{L}\cos^2\left(\frac{z\pi}{L}\right)\left[1 + A\sin\omega t\ \sin\left(\frac{z\pi}{L}\right)\right]$$

$n(z,t)$

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

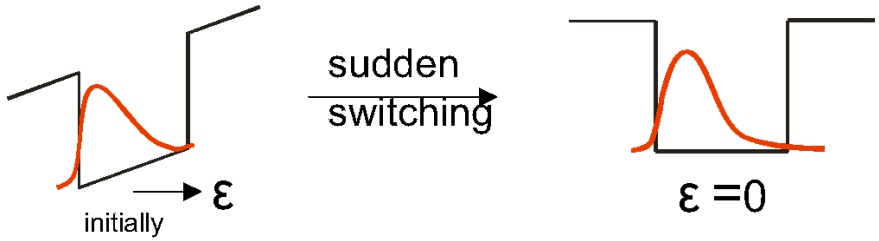
$V_{xc}^{M,QV}(z,t)$

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



XC Memory ⇒ Phase Lag ⇒ Retardation Force

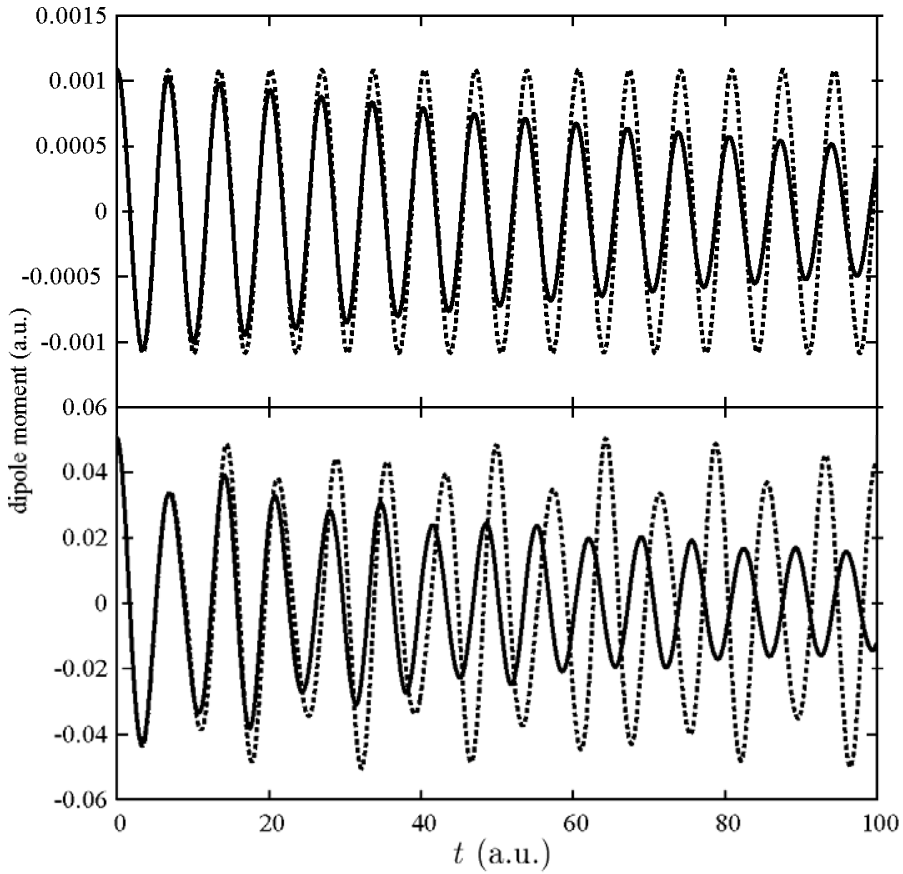
xc potential with memory: full TDKS calculation



40 nm
GaAs/AlGaAs

Weak excitation
(initial field 0.01)

Strong excitation
(initial field 0.5)

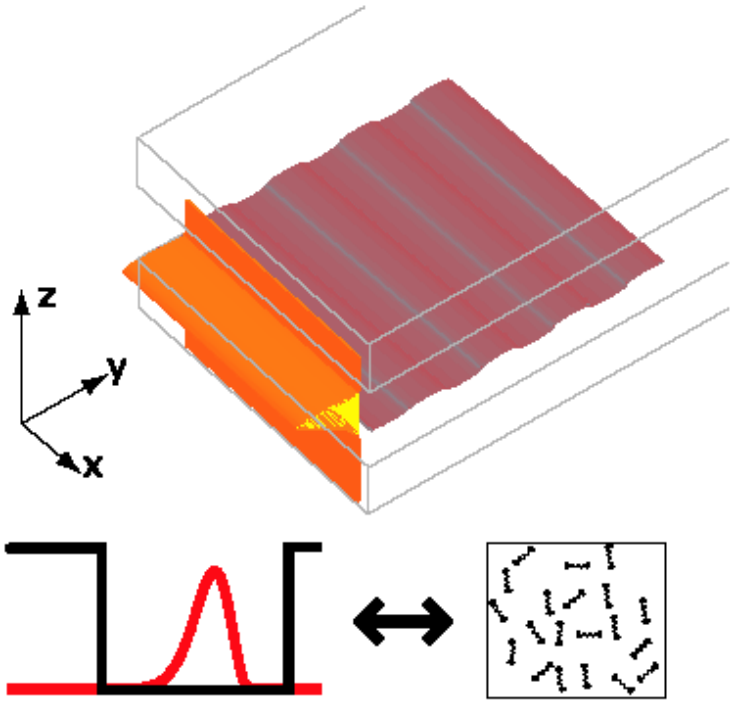


ALDA
ALDA+M

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

...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.

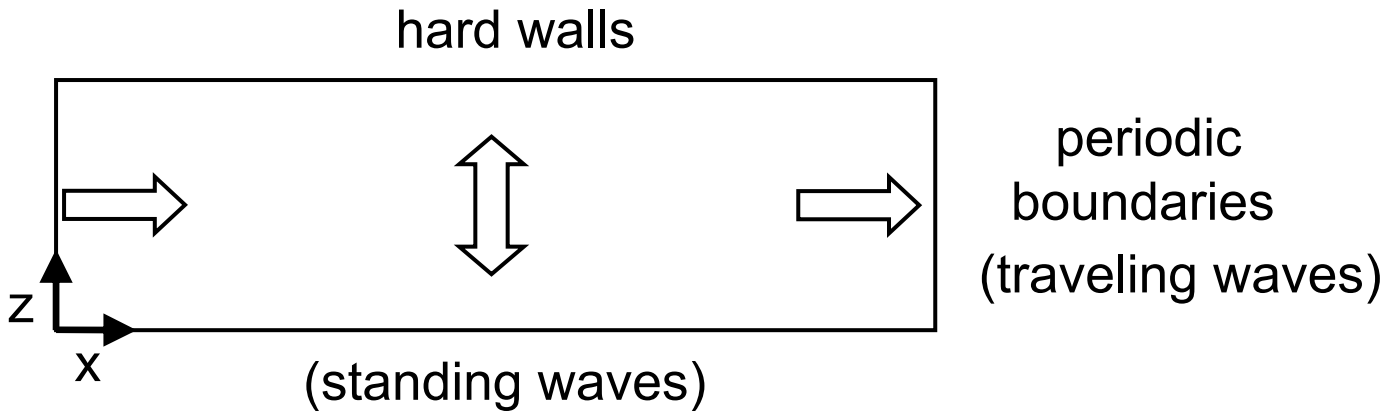


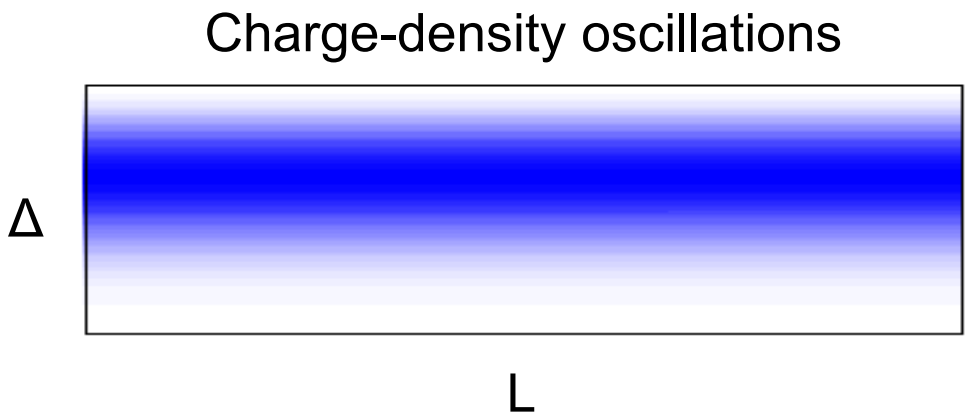
R. D'Agosta and G. Vignale, PRL **96**, 016405 (2006)

- 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?

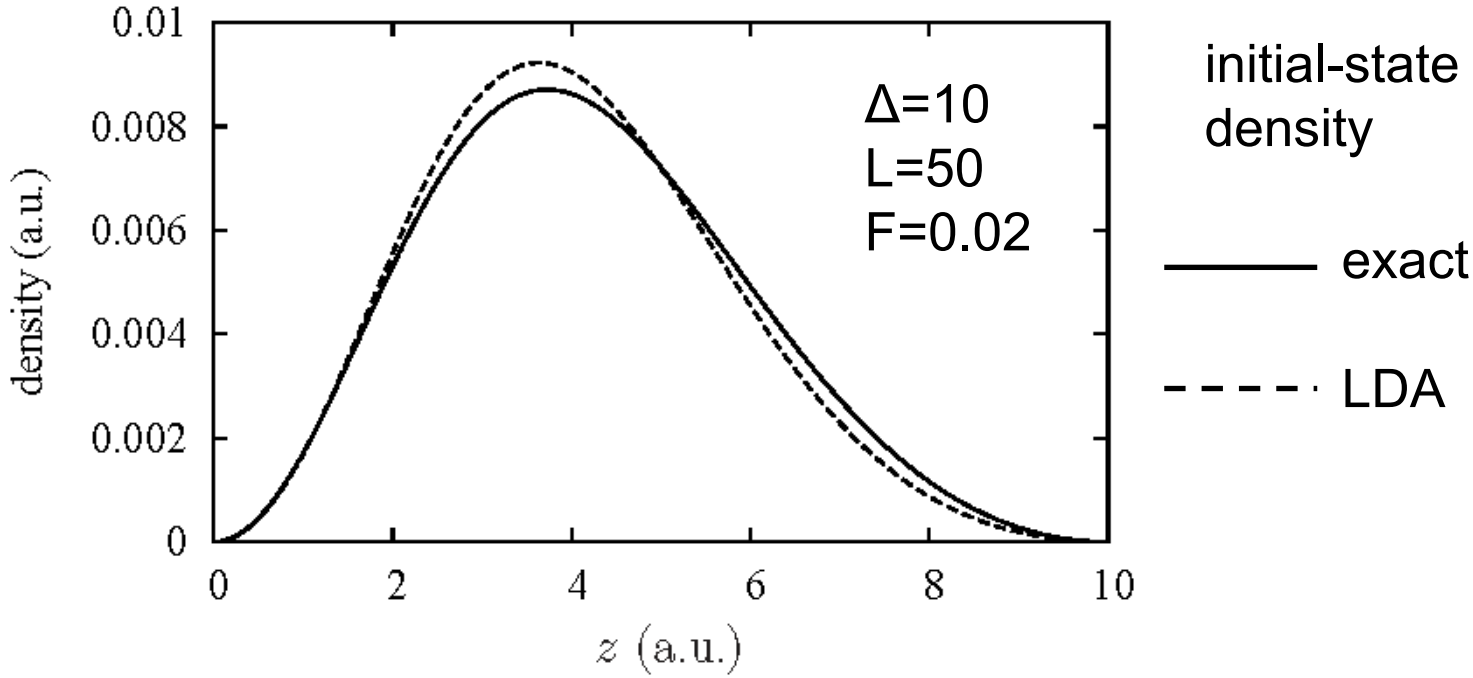
Example: two electrons on a 2D quantum strip





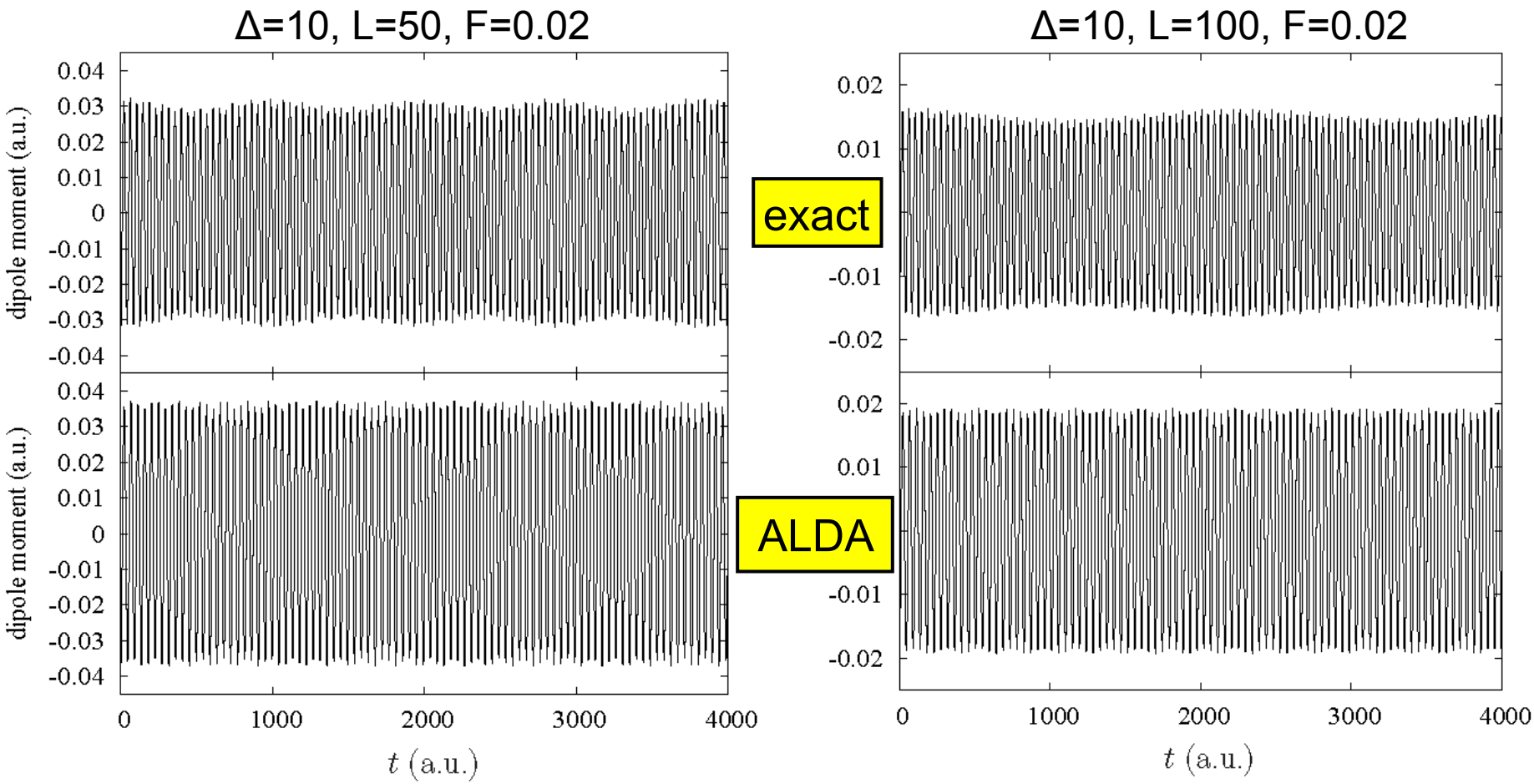
C.A. Ullrich, JCP **125**, 234108 (2006)

Example: two electrons on a 2D quantum strip



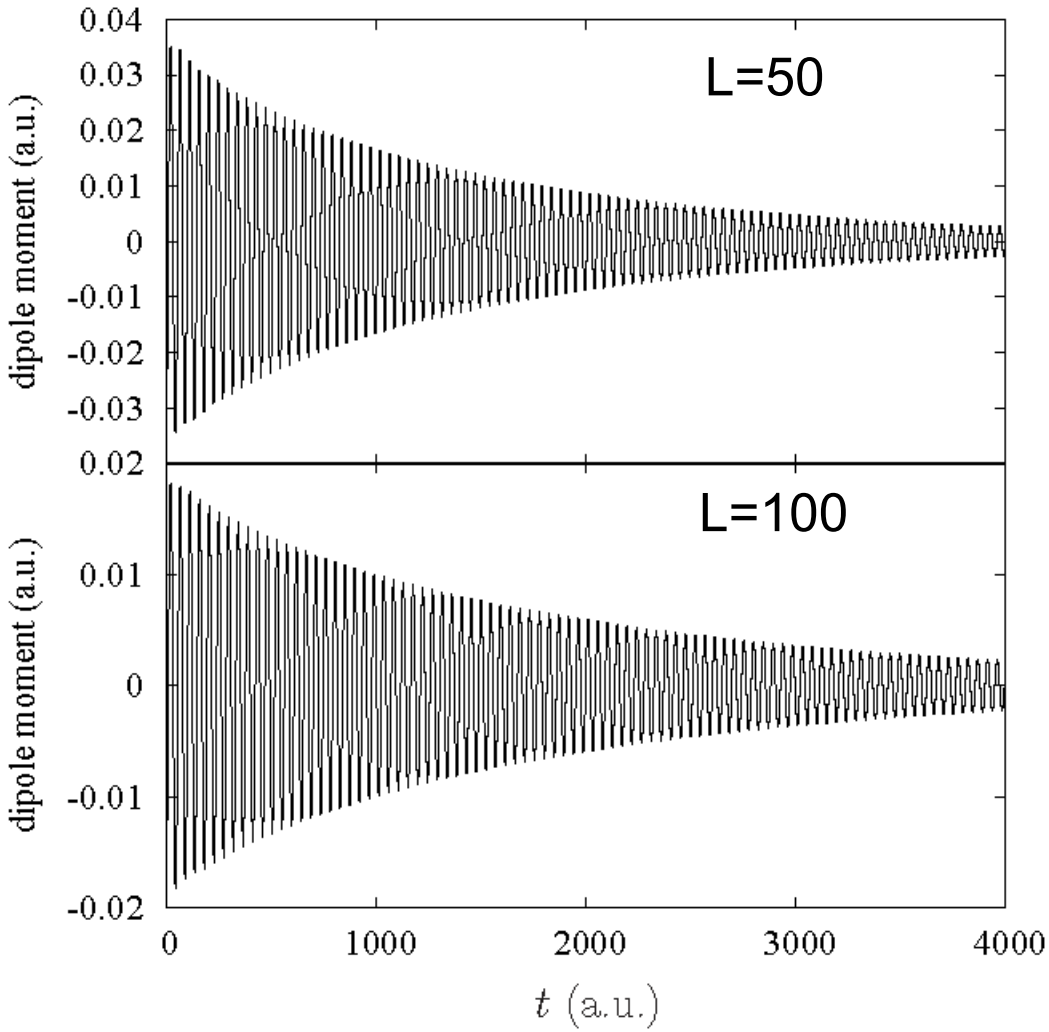
- Compare exact calculation (time-dependent CI) with TDKS
- Initial state: constant electric field, which is suddenly switched off
- After switch-off, free propagation of the charge-density oscillations

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
- To modulate d(t), the exact $V_{xc}(t)$ alternately damps and drives the system
- ALDA misses the beating pattern since it has no multiple excitations

2D quantum strip: ALDA+M



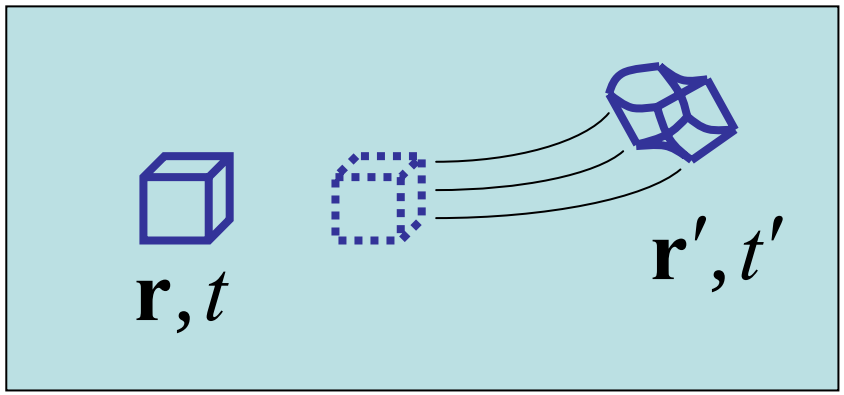
- d(t) is exponentially damped
- Unlike the exact $V_{xc}(t)$, the VK functional only damps, but does not drive back (only accounts for retardation)
- The VK functional cannot tell that the system is finite. It treats the system locally like a homogeneous electron gas.
- infinite recurrence time emerges in the thermo-dynamic limit of the system
- damping of d(t) is due to decoherence, involving many excitations with a continuous spectrum

Summary first part

- In the nonlinear, real-time domain, the frequency-dependence of the XC stress tensor translates into memory dependence
- We solved TDKS equations with memory for charge-density oscillations in quantum well
- The VK functional causes dissipation, where energy gets transferred into incoherent multiple particle-hole excitations
- Model calculations for 2D quantum strip show how the exact TDKS xc potential causes multiple excitations by its nonadiabatic behavior (driving and damping).
- The VK functional misses this behavior, but becomes correct in the thermodynamic limit (infinite system size and particle number).

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); I.V. Tokatly, PRB **75**, 125105 (2007)



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

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

Lagrangian coordinate

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

Cauchy's deformation tensor in the laboratory frame (a functional of the velocity)

$$n(\mathbf{r},t) = \sqrt{\bar{g}(\mathbf{r},t)}\, n_0\big(\xi(\mathbf{r},t)\big)$$

TDDFT in the Lagrangian frame: stress tensor

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

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

- This is a **formally exact** time-dependent many-body theory. The interacting stress tensor is of course only approximately known.

- For **small gradients of** $\bar{g}_{ij}$, the xc stress tensor is a **spatially local** functional of $\bar{g}_{ij}$ (but a nonlocal functional in time).

This is the exact extension of LDA into the dynamical regime. In general, it contains both elastic and dissipative effects.

The small deformation approximation

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

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

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

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

- **This puts nonlinear VK-TDCDFT on firm grounds.**
- Remember, the deformations are small, but the velocities can be large.

Nonlinear elastic approximation

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

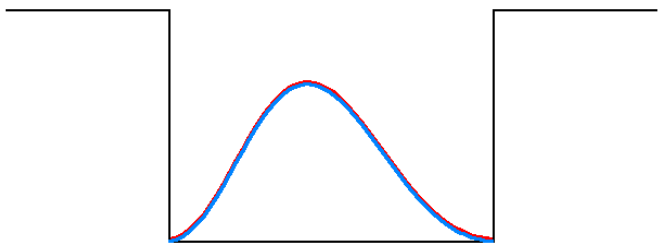
L-TDDFT versus VK-TDCDFT: simple "1D" models

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

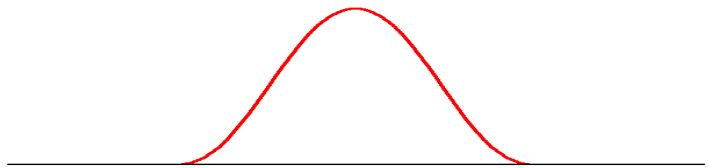
$$n(x,t) = \sqrt{\bar{g}(x,t)}\; n_0(\xi(x,t)) \quad \text{and} \quad \bar{g}(x,t) = \left(\frac{\partial \xi}{\partial t}\right)^2$$

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.

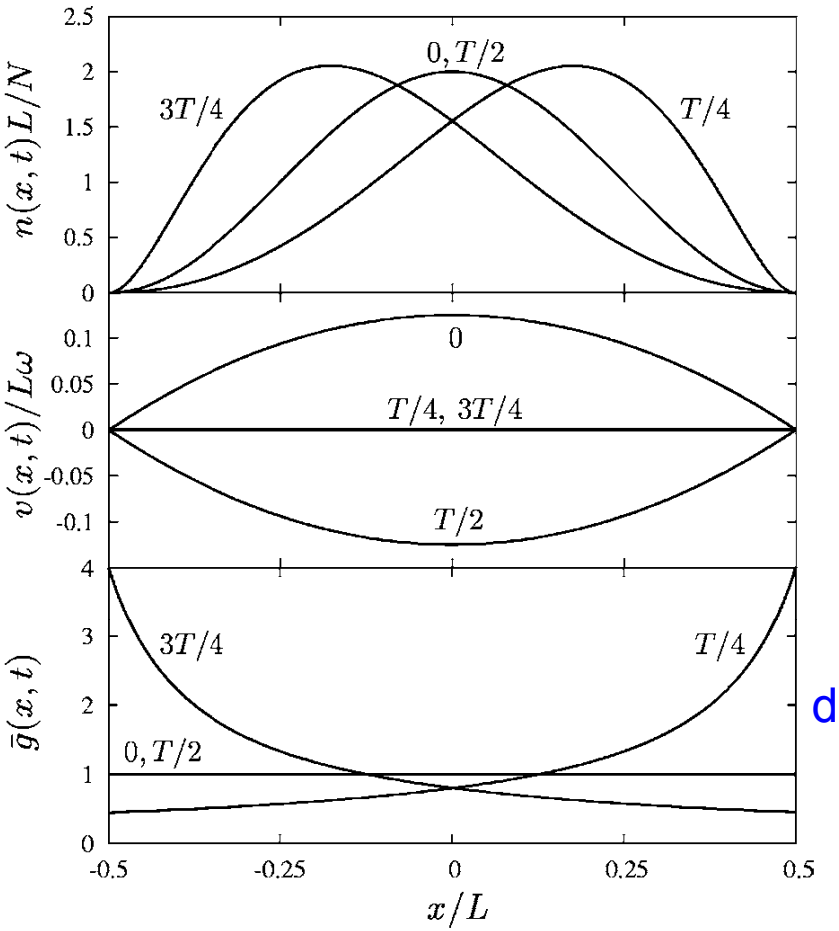


sloshing mode



breathing mode

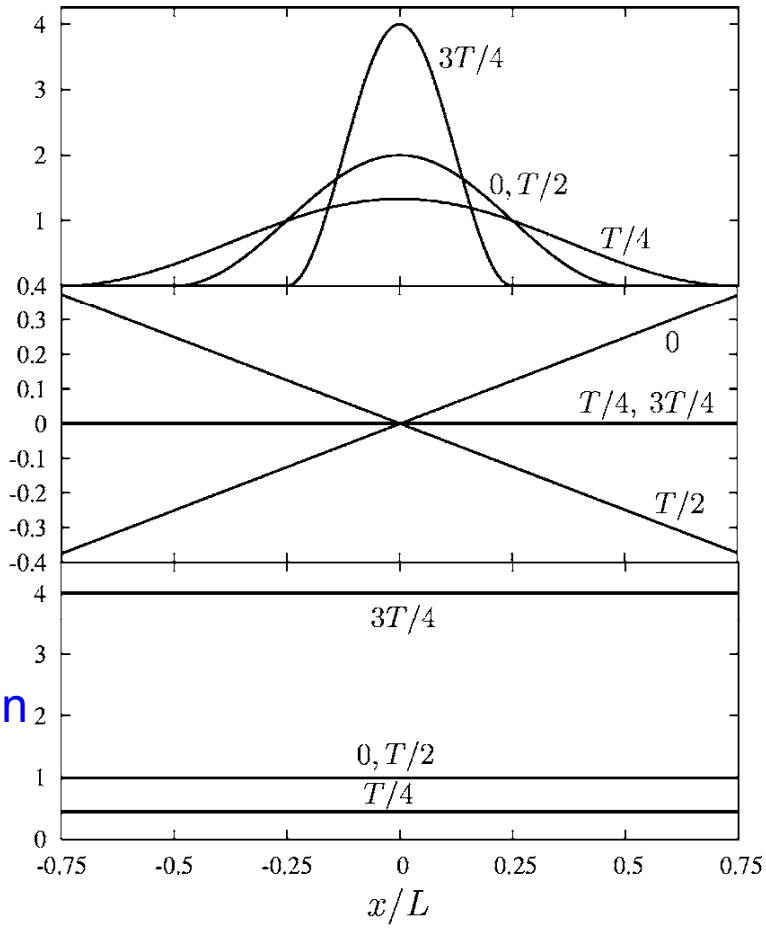
L-TDDFT versus TDCDFT: simple “1D” models



density

velocity

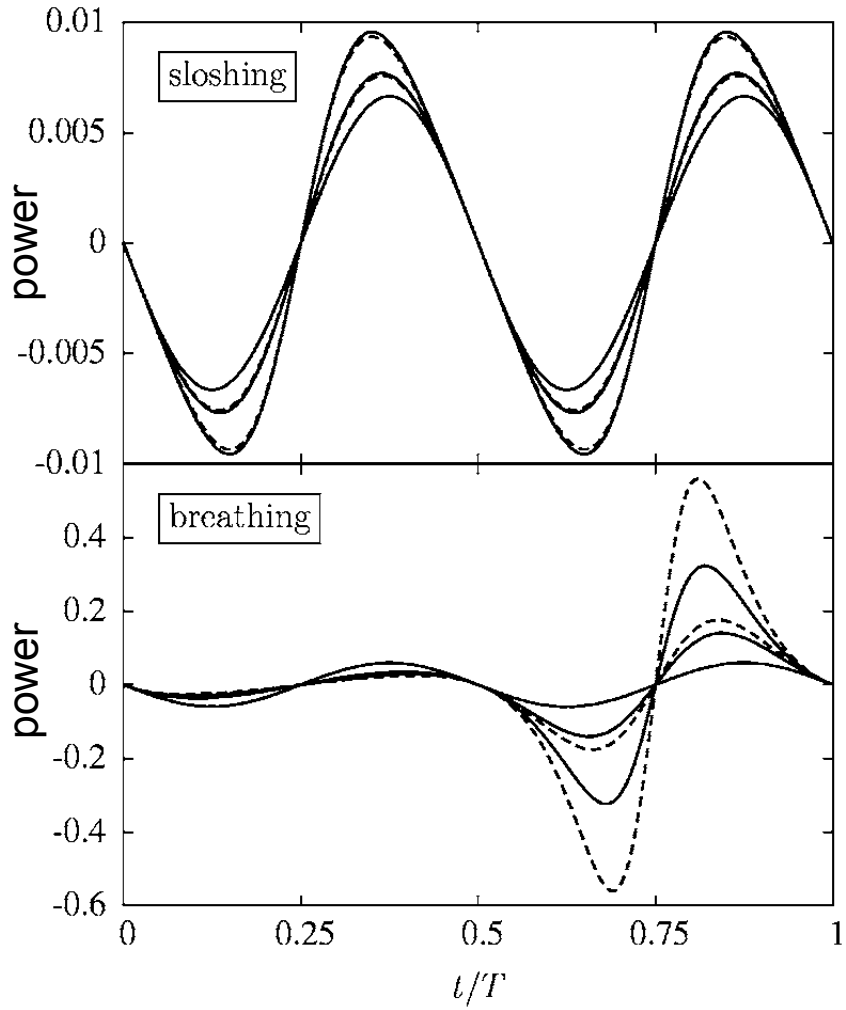
deformation



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

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

L-TDDFT versus TDCDFT: high-frequency limit



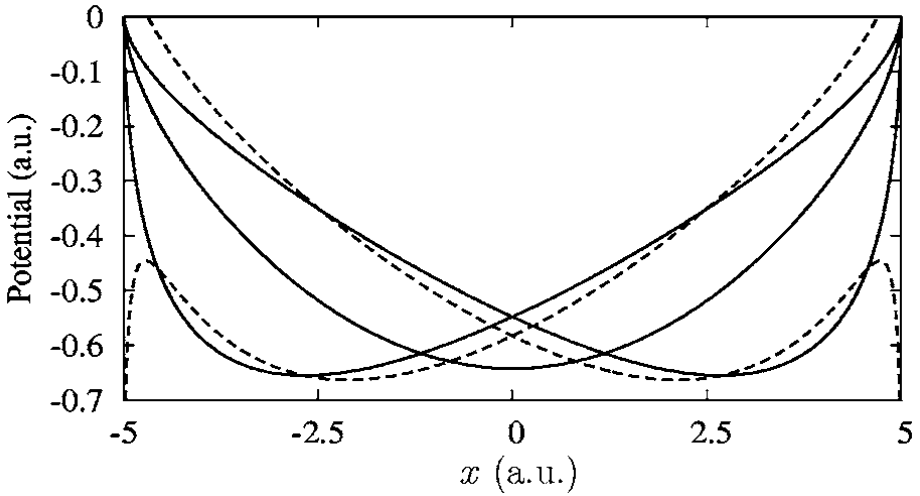
- in the high-frequency limit, the elastic approximation for L-TDDFT becomes the exact dynamical extension of the LDA (for all deformations)
- for small deformations, TDCDFT becomes exact (for all frequencies)
- for largest amplitudes, TDCDFT deviates:
  <2.5% for sloshing mode
  ~100% for breathing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

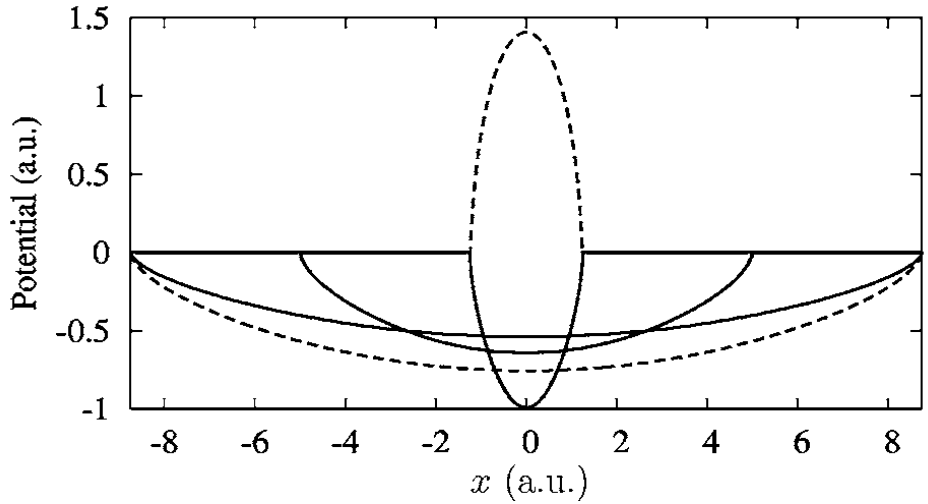
The nonlinear TDCDFT remains good for moderate deformations!

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

Summary second part

- A rigorous formulation of local time-dependent xc effects is established by TDDFT in the Lagrangian frame
- VK-TDCDFT 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.
- A more general formulation of Lagrangian TDDFT has recently become available: TDDefFT (TD deformation functional theory), including vector potentials (Tokatly 2007).

Time-dependent optimized effective potential

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

$$0 = i\sum_{j=1}^{N_\sigma}\int_{-\infty}^{t} dt' \int d^3r' \left[V_{xc\sigma}(\mathbf{r}',t') - u_{xcj\sigma}(\mathbf{r}',t')\right]$$

$$\times \sum_{k=1}^{\infty} \varphi_{k\sigma}(\mathbf{r}',t')\varphi^*_{k\sigma}(\mathbf{r},t)\varphi_{j\sigma}(\mathbf{r},t)\varphi^*_{j\sigma}(\mathbf{r}',t') \; + \; c.c.$$

where $u_{xcj\sigma}(\mathbf{r},t) = \dfrac{1}{\varphi^*_{j\sigma}(\mathbf{r},t)} \dfrac{\delta A_{xc}\left[\{\varphi_{i\sigma}\}\right]}{\delta\varphi_{j\sigma}(\mathbf{r},t)}$

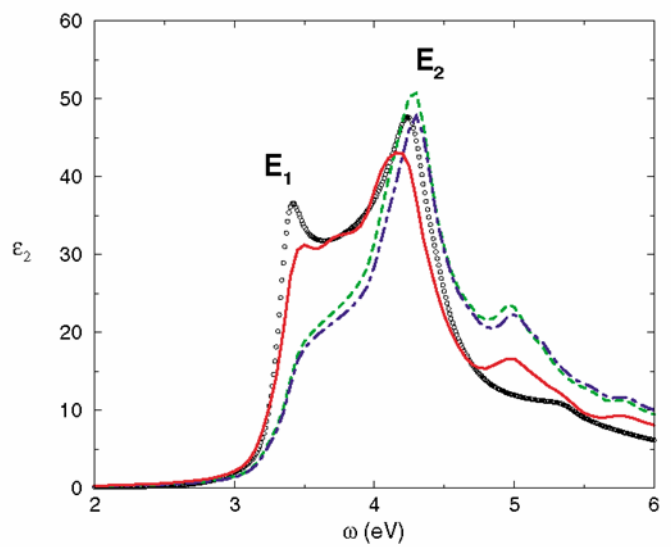
exact exchange: $u_{xj\sigma}(\mathbf{r},t) = -\dfrac{1}{\varphi^*_{j\sigma}(\mathbf{r},t)} \sum_{k=1}^{N_\sigma} \int d^3r' \dfrac{\varphi^*_{j\sigma}(\mathbf{r}',t)\varphi_{k\sigma}(\mathbf{r}',t)\varphi^*_{k\sigma}(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|}$

Applications of TDOEP in the linear regime

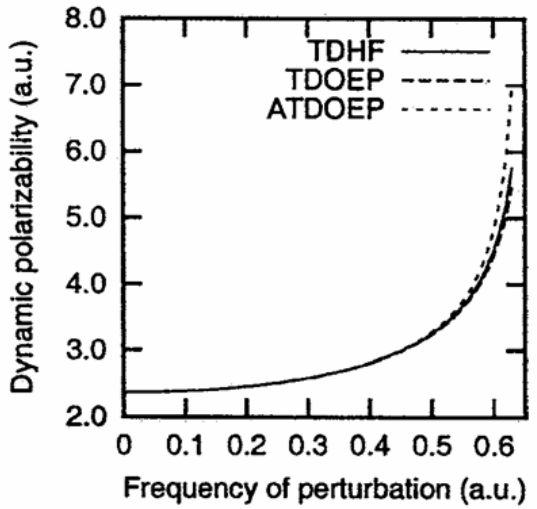
- Optical spectra of solids
  Kim and Goerling, PRL **89**, 096402 (2002)
- Molecular excitation energies and dynamic polarizabilities
  Hirata et al., PRA **71**, 032507 (2005)
  Shigeta, Hirao, Hirata, PRA **73**, 010502 (2006)

} static (ω=0) kernel

ω-dependent kernel



Kim and Goerling (Silicon)



Shigeta et al. (Neon)

Time-dependent KLI

$$V_{xc\sigma}^{KLI}(\mathbf{r},t) = \sum_j \frac{n_{j\sigma}(\mathbf{r},t)}{n_\sigma(\mathbf{r},t)} u_{xcj\sigma}(\mathbf{r},t) \quad \left.\right\} \text{Slater potential}$$

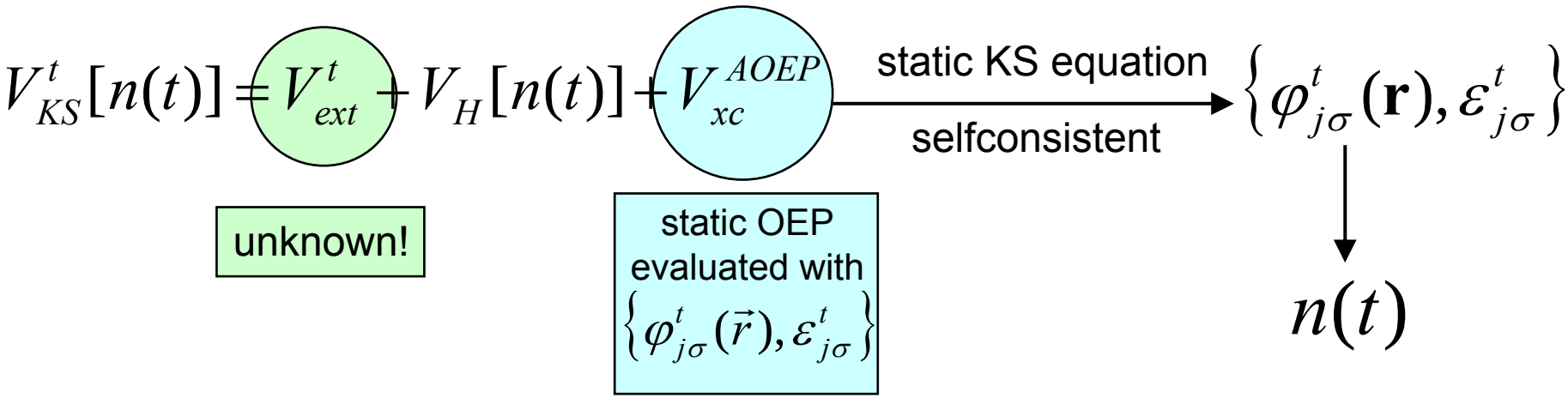
$$+ \sum_j \frac{n_{j\sigma}(\mathbf{r},t)}{n_\sigma(\mathbf{r},t)} \int d^3r'\, n_{j\sigma}(\mathbf{r}',t) \left\{ V_{xc\sigma}^{KLI}(\mathbf{r}',t) - u_{xcj\sigma}(\mathbf{r}',t) \right\} \Bigg]$$

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)
- No zero-force theorem for TDKLI
  Mundt, Kuemmel, van Leeuwen, Reinhard, PRA **75**, 050501 (2007)

Adiabatic approximation to TDOEP

AOEP: static OEP which produces $n(t)$ as selfconsistent ground-state density



Step 1: invert static KS equation: $n(t) \longrightarrow V_{KS}^{t}, \left\{\varphi_{j\sigma}^{t}(\mathbf{r}), \varepsilon_{j\sigma}^{t}\right\}$

Step 2: construct V_{xc}^{AOEP} from $\left\{\varphi_{j\sigma}^{t}(\mathbf{r}), \varepsilon_{j\sigma}^{t}\right\}$

see also M. Thiele, E.K.U. Gross, S. Kümmel, PRL **100**, 153004 (2008)

Numerical solution of TDOEP: step-by-step?

$$0 = i\sum_{j=1}^{N_\sigma}\int_{-\infty}^{t} dt' \int d^3r' \left[V_{xc\sigma}(\mathbf{r}',t') - u_{xcj\sigma}(\mathbf{r}',t')\right]$$

$$\times \sum_{k=1}^{\infty} \varphi_{k\sigma}(\mathbf{r}',t')\varphi^*_{k\sigma}(\mathbf{r},t)\varphi_{j\sigma}(\mathbf{r},t)\varphi^*_{j\sigma}(\mathbf{r}',t') \; + \; c.c.$$

- Integrand vanishes at upper limit *(t'=t)*
- $V_{xc\sigma}(t')$ only determined for $t'<t$
- Step-by-step time propagation fails

Mundt and Kümmel, PRA **74**, 022511 (2006): numerical instabilities??

Numerical solution of TDOEP: global iteration

$\varphi_j(0)$ — **global selfconsistency** — $\varphi_j(T)$

$t=0$ $\qquad$ $t=T$ $\qquad$ t

n^{th} iteration:

$$i\frac{\partial \varphi_j^{(n)}}{\partial t} = \left(-\frac{\nabla^2}{2} + \overbrace{V^{(n-1)}(t)}^{\text{given}}\right)\varphi_j^{(n)}, \quad t=[0,T]$$

$$\left\{\varphi_j^{(n)}(t)\right\} \xrightarrow{\text{TDOEP}} V^{(n)}(t), \quad t=[0,T]$$

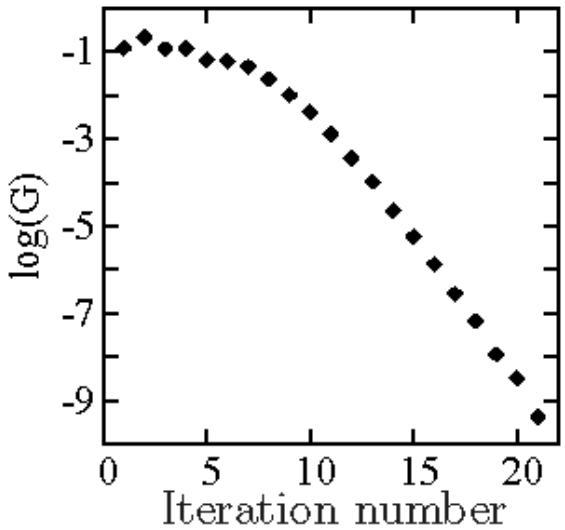
$(n+1)^{\text{st}}$ iteration:

$$i\frac{\partial \varphi_j^{(n+1)}}{\partial t} = \left(-\frac{\nabla^2}{2} + V^{(n)}(t)\right)\varphi_j^{(n+1)}$$

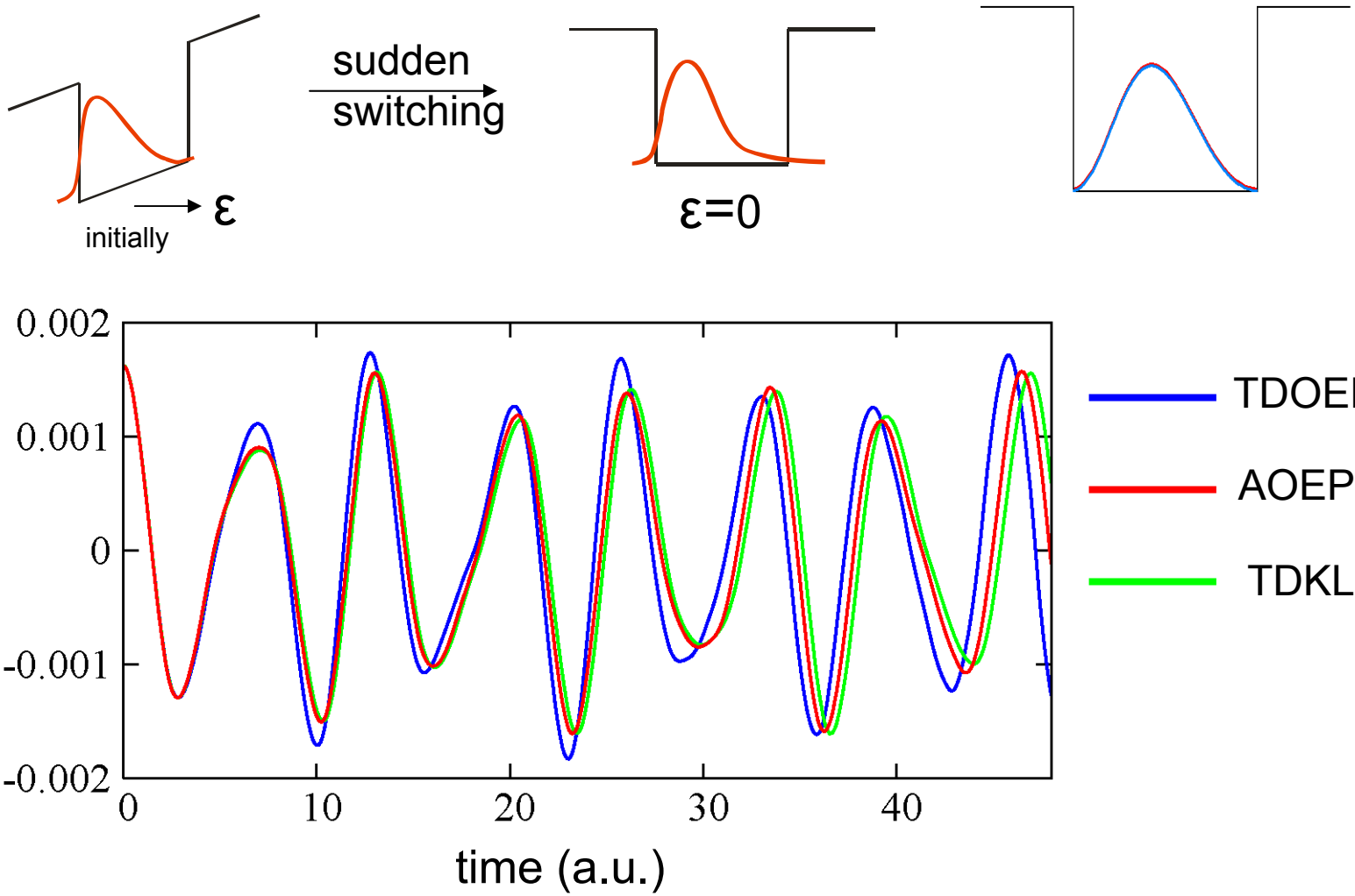
$\vdots$

Convergence index:

$$G = \frac{\int_0^T \left|d_{\text{old}}(t) - d_{\text{new}}(t)\right| dt}{\int_0^T \left|d_{\text{new}}(t)\right| dt}$$



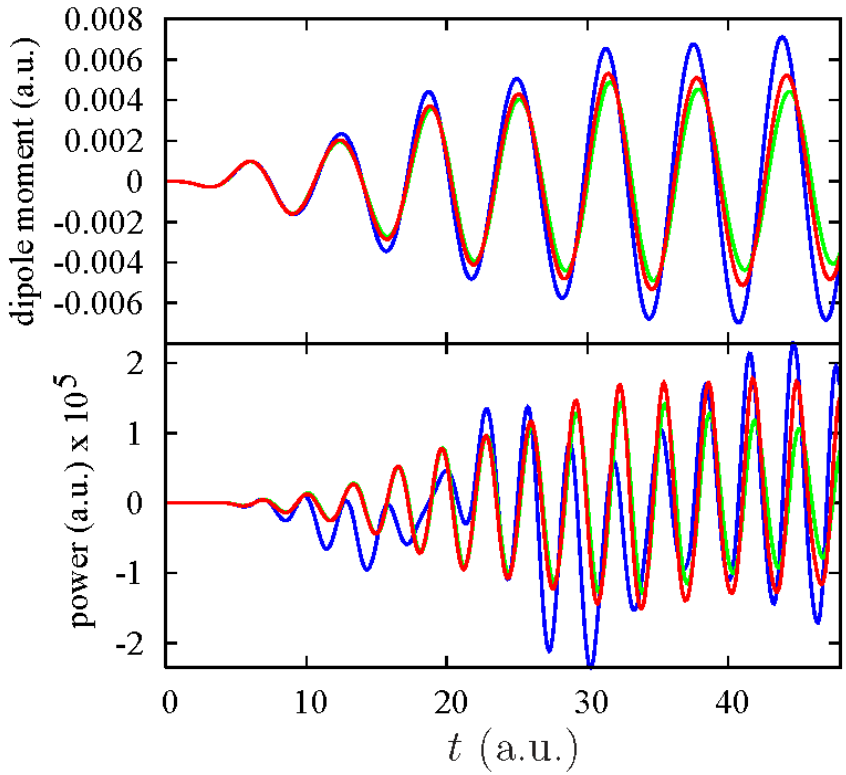
Free charge-density oscillations



- TDOEP slightly blueshifted: memory gives rise to elastic contribution (x-only)

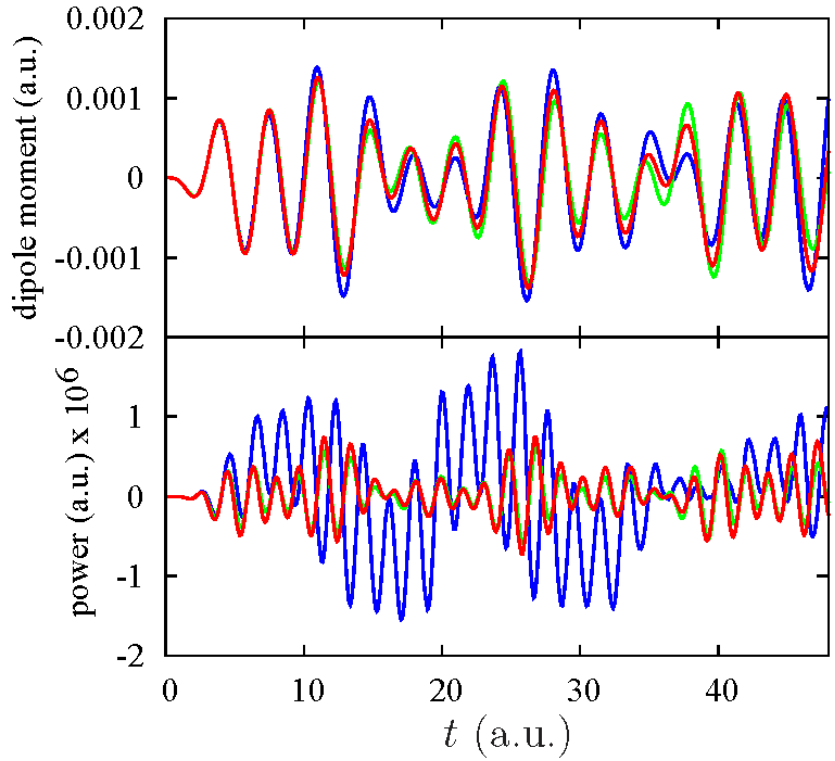
Driven oscillations

ω=11 meV



close to ω_{12} resonance

ω=20 meV

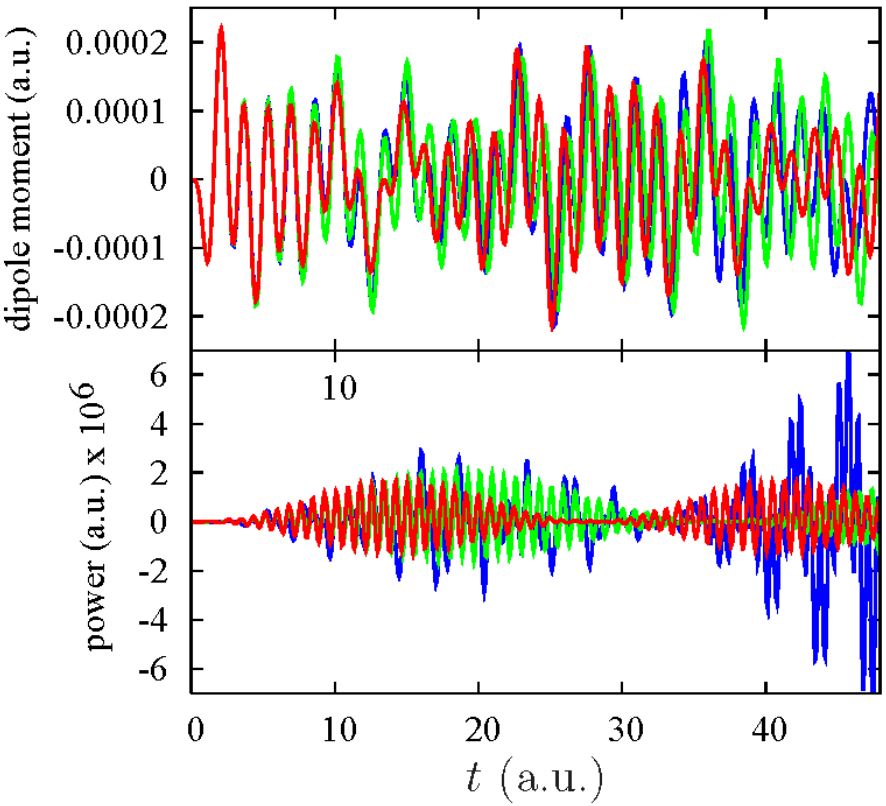


close to ω_{23} resonance

XC power: $$P(t) = \int dz\, j(z,t) \nabla_z \left[V_x(z,t) - V_x^0(z) \right]$$

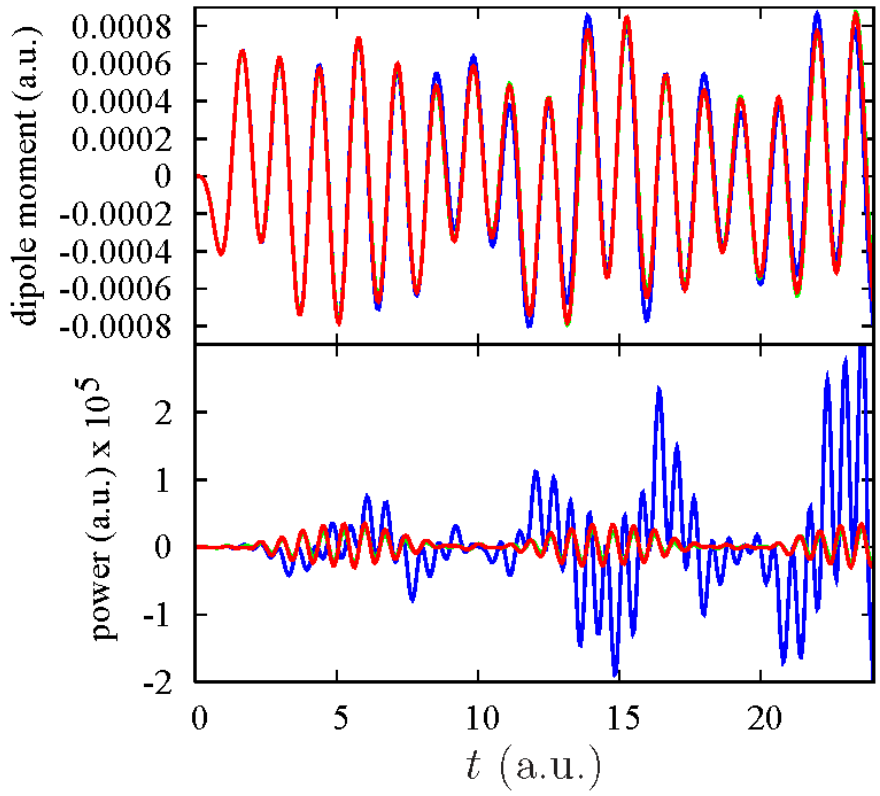
Driven oscillations

ω=40 meV



close to ω_{14} resonance

ω=50 meV



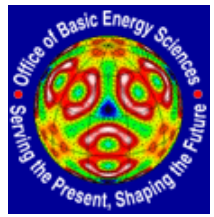
between ω_{14} and ω_{25}
(away from resonances)

Summary third part

- Stable algorithm for full TDOEP in quantum wells
- AOEP is very similar to TDKLI
- No problems with zero-force theorem in TDKLI
- Memory effects in TDOEP become significant for high frequencies and close to resonances
- Intrinsically nonadiabatic phenomena (multiple excitations, dissipation): need to go beyond exact-exchange

H.O. Wijewardane and C.A. Ullrich, PRL **100**, 056404 (2008)

... and finally...



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- Dr. Volodymyr Turkowski (now at UCF)
- Yonghui Li (grad student at MU)

Postdoc opening (TDDFT for excitonic effects in materials)