

Lecture 3

TDCDFT: Nonlinear regime

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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

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

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

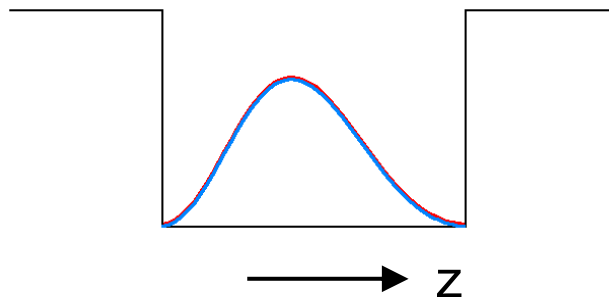
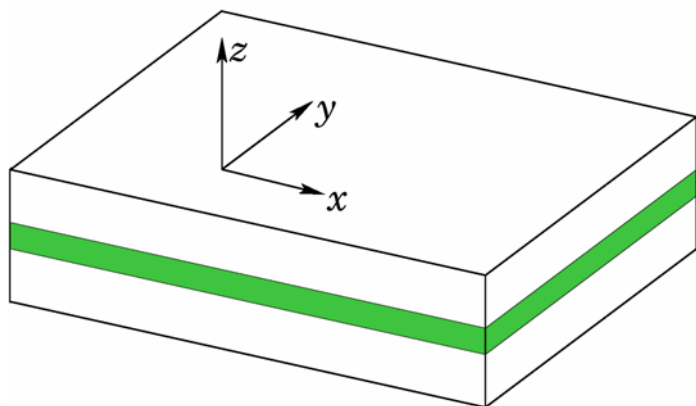
$$\begin{aligned} \sigma_{xc,ij}(\mathbf{r}, t) = & \int_{-\infty}^t dt' \eta_{xc}(\mathbf{r}, t, t') \left[\nabla_i v_j(\mathbf{r}, t') + \nabla_j v_i(\mathbf{r}, t') - \frac{2}{3} \nabla \cdot \mathbf{v}(\mathbf{r}, t') \delta_{ij} \right] \\ & + \int_{-\infty}^t dt' \zeta_{xc}(\mathbf{r}, t, t') \nabla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

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:

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

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

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

where the memory kernel is given by

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

Using the definition of the viscosity coefficients, one finds explicitly

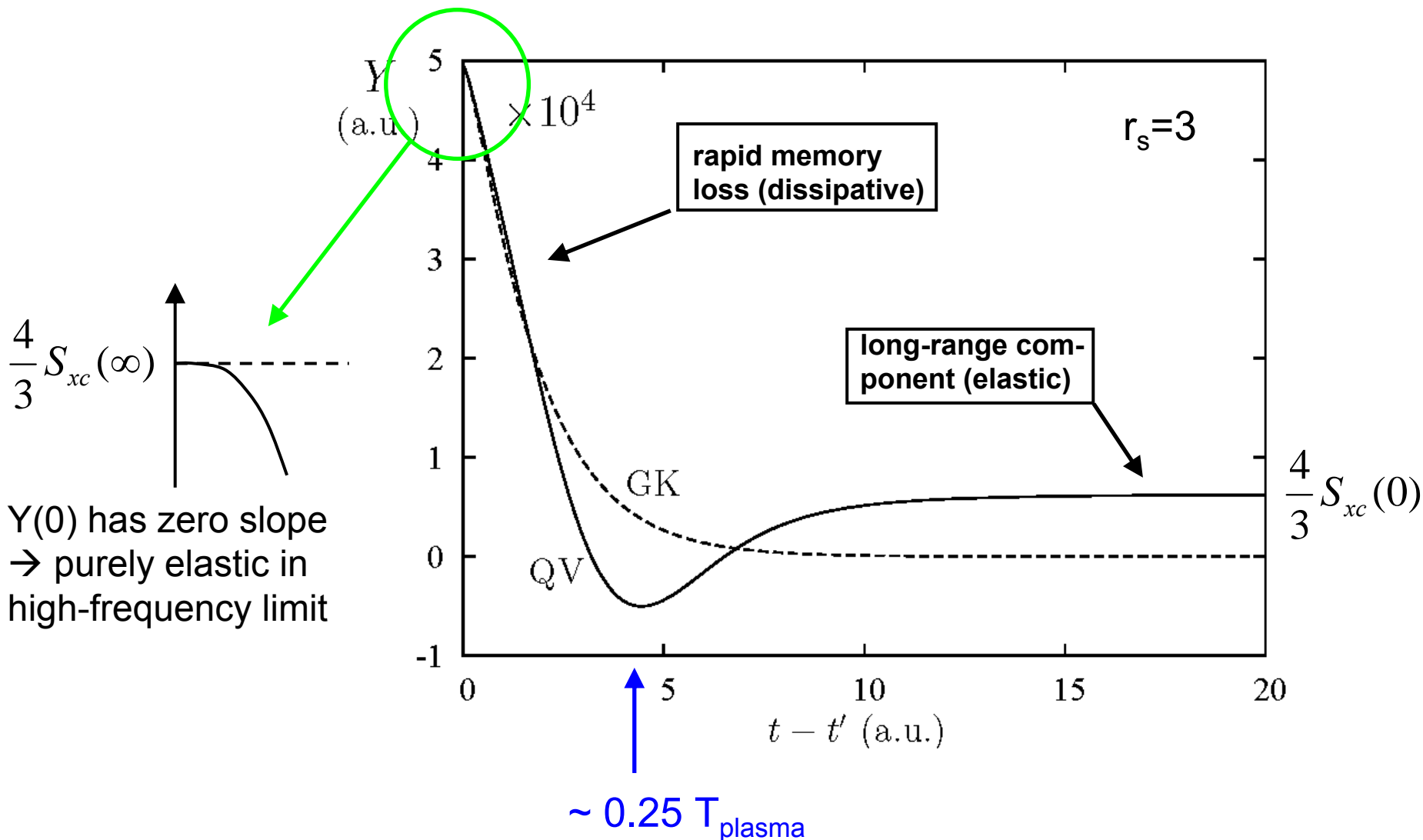
$$Y(n, t - t') = \frac{4}{3} S_{xc}(0) - \frac{n^2}{\pi} \int \frac{d\omega}{\omega} \text{Im} f_{xc}^L(\omega) \cos[\omega(t - t')]$$

static xc shear modulus



The xc memory kernel





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

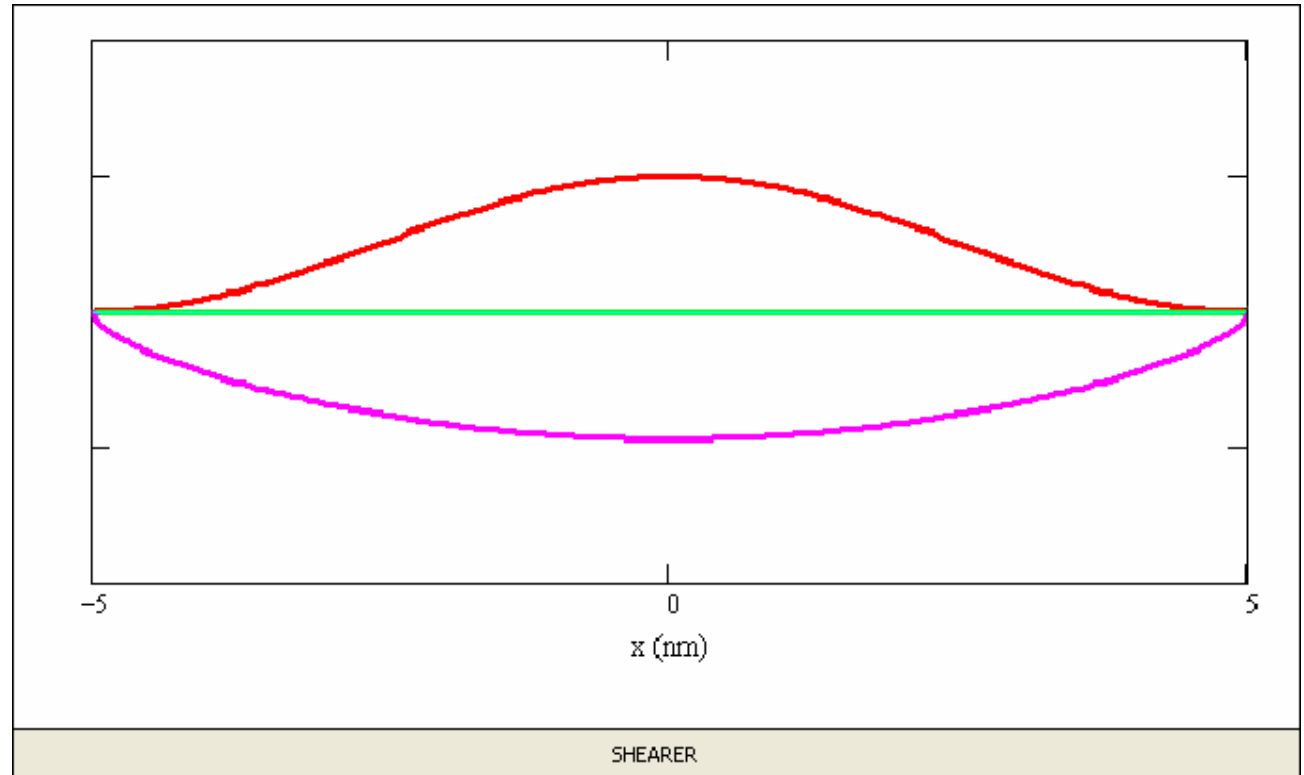




xc potential with memory: simple model

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

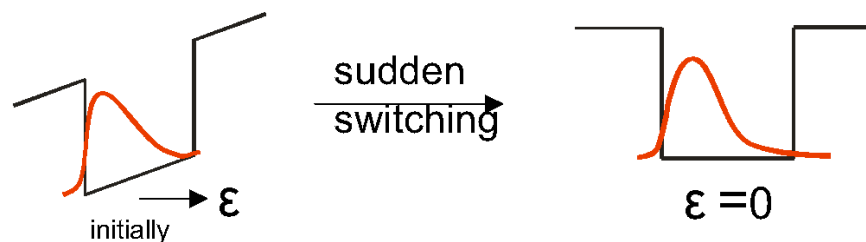
-  $n(z,t)$
-  $V_{xc}^{M,GK}(z,t)$
-  $V_{xc}^{M,QV}(z,t)$
-  $V_{xc}^{ALDA}(z,t)$



XC Memory \Rightarrow Phase Lag \Rightarrow Retardation Force

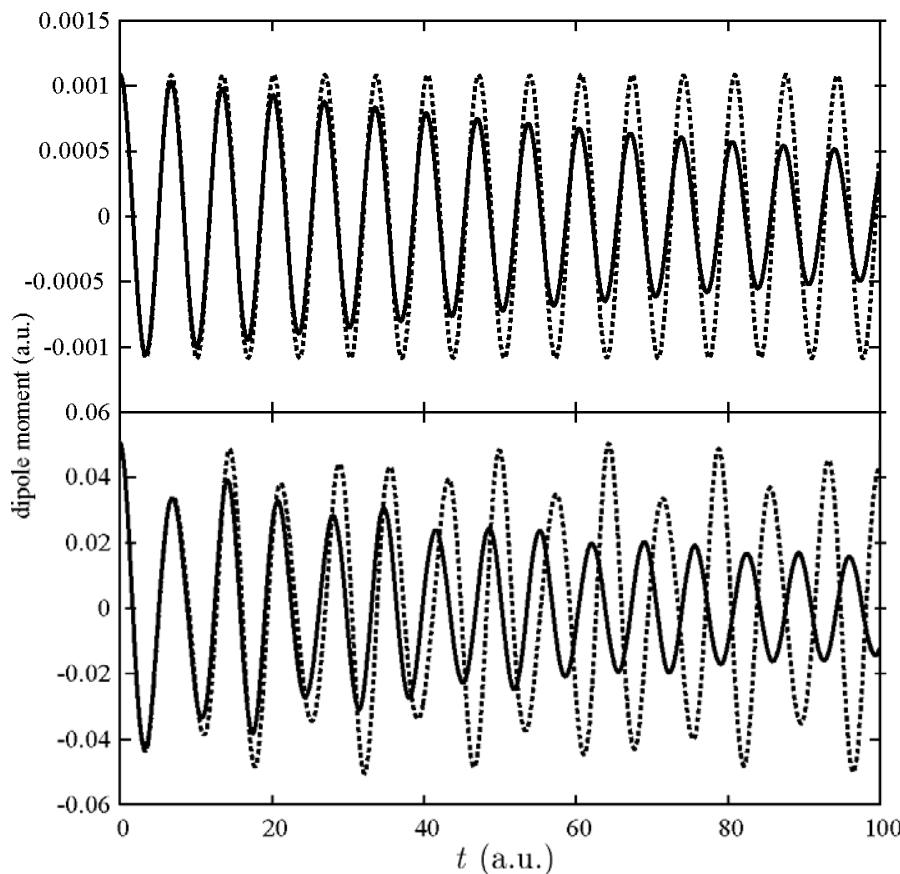


xc potential with memory: full TDKS calculation



40 nm
GaAs/AlGaAs

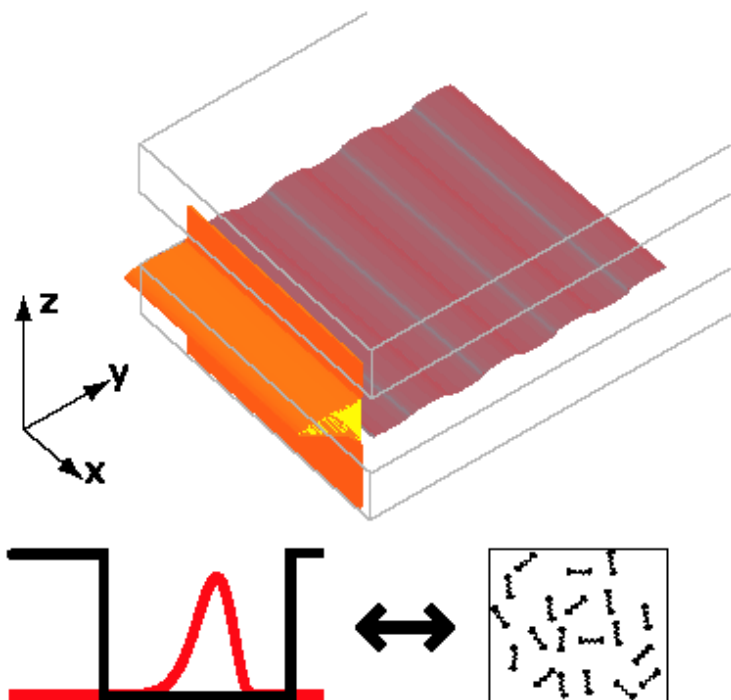
Weak excitation
(initial field 0.01)



Strong excitation
(initial field 0.5)

...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.



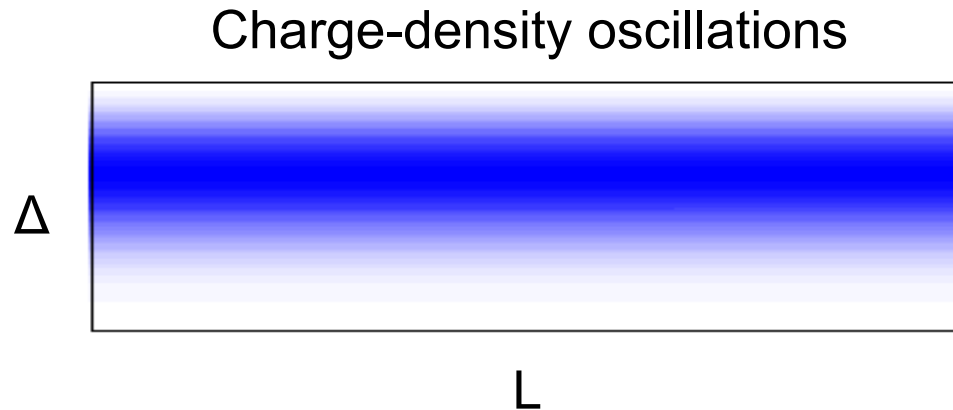
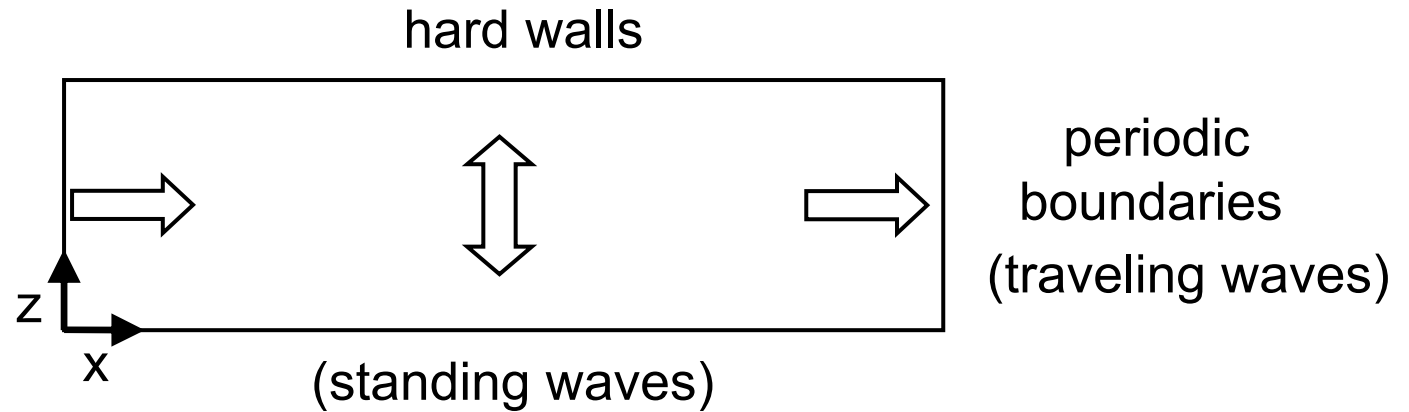
R. D'Agosta and G. Vignale,
PRL **96**, 016405 (2006)

- 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?

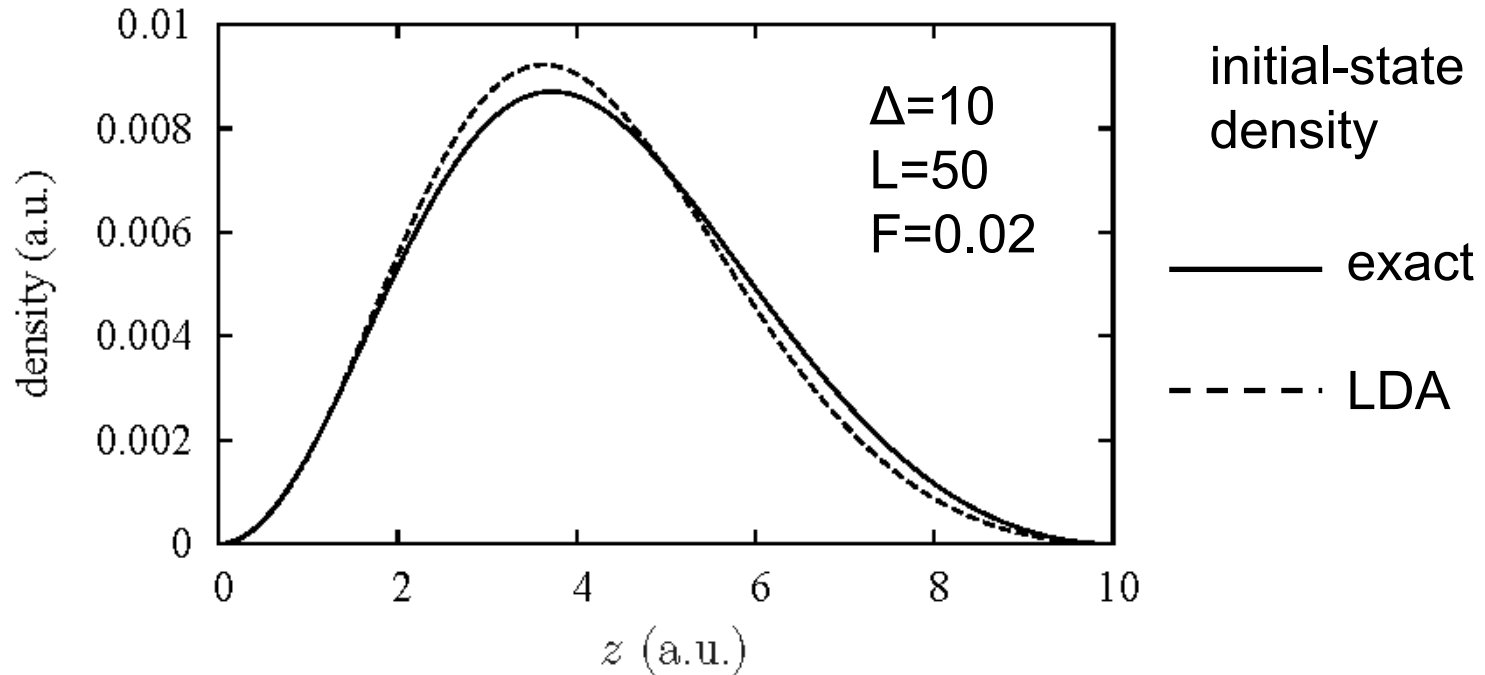


Example: two electrons on a 2D quantum strip





Example: two electrons on a 2D quantum strip

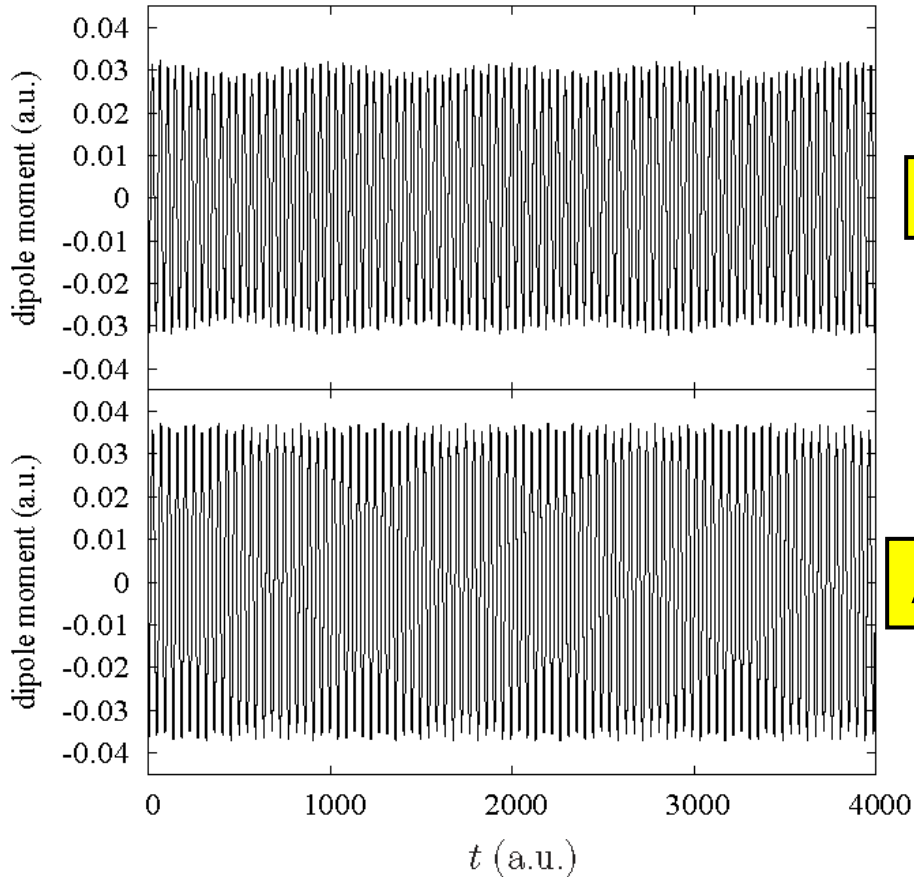


- Compare exact calculation (time-dependent CI) with TDKS
- Initial state: constant electric field, which is suddenly switched off
- After switch-off, free propagation of the charge-density oscillations

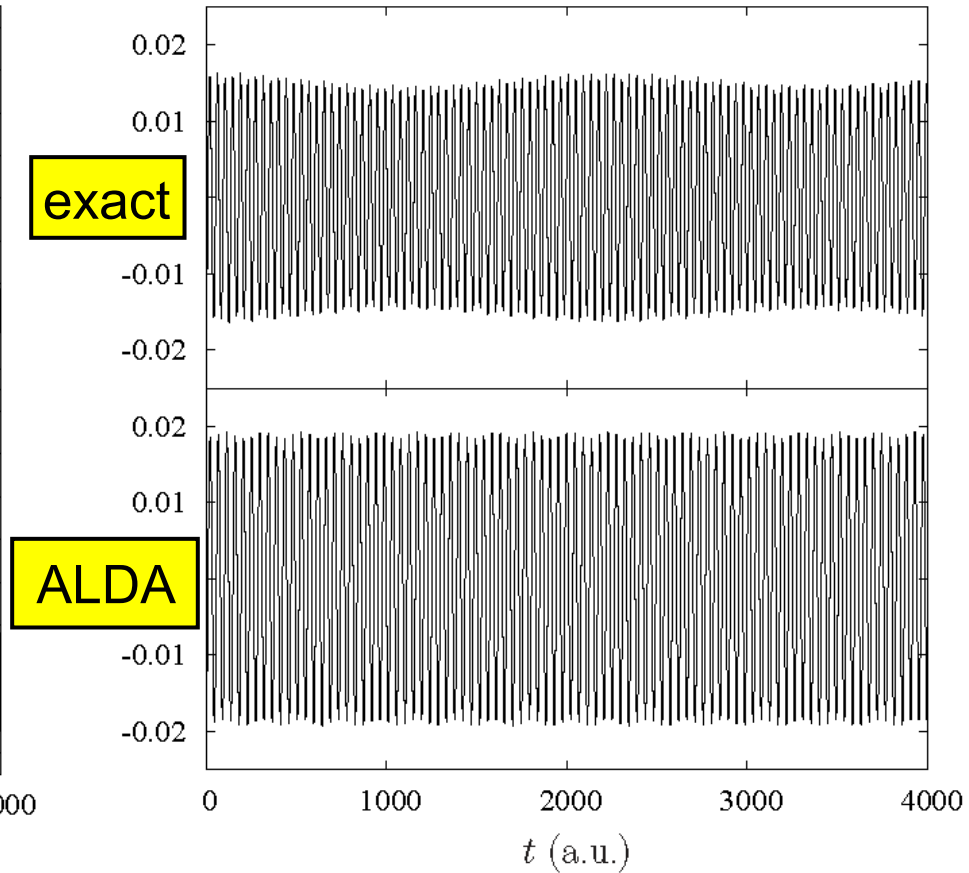


2D quantum strip: time-dependent dipole moment

$\Delta=10, L=50, F=0.02$



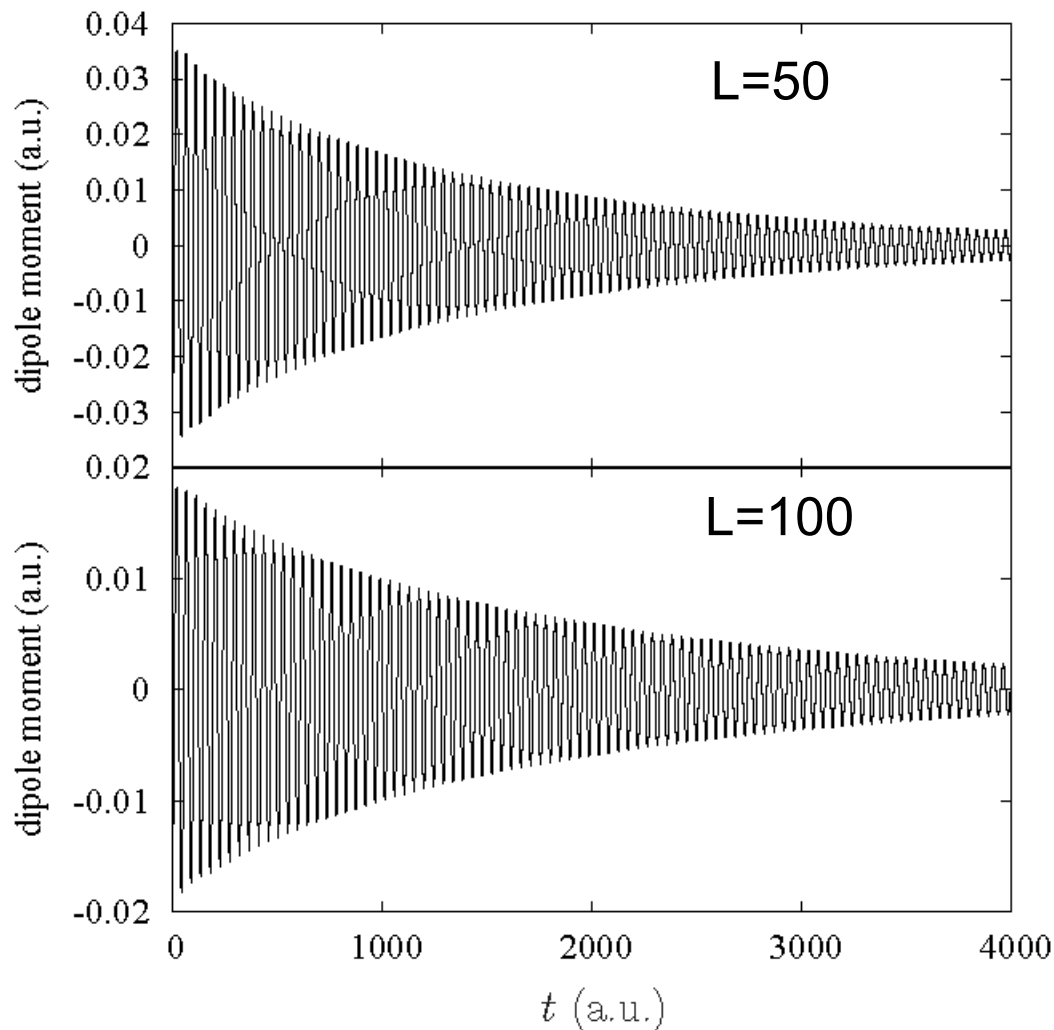
$\Delta=10, L=100, F=0.02$



- 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 thermodynamic limit of the system
- damping of $d(t)$ is due to decoherence, involving many excitations with a continuous spectrum



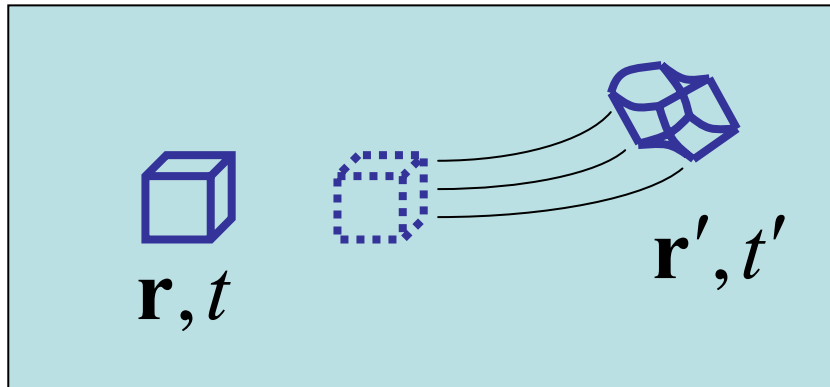
Summary first part

- 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 $\mathbf{r} = \mathbf{r}(\xi, t)$

$$\frac{\partial \mathbf{r}(\xi, t)}{\partial t} = \mathbf{v}(\mathbf{r}(\xi, t), t), \quad \mathbf{r}(\xi, 0) = \xi \quad \text{Lagrangian coordinate}$$

$$\bar{g}_{ij}(\mathbf{r}, t) = \frac{\partial \xi_k(\mathbf{r}, t)}{\partial r_i} \frac{\partial \xi_k(\mathbf{r}, t)}{\partial r_j} \quad \text{Cauchy's deformation tensor in the laboratory frame (a functional of the velocity)}$$

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



TDDFT in the Lagrangian frame: stress tensor

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

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

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

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

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.



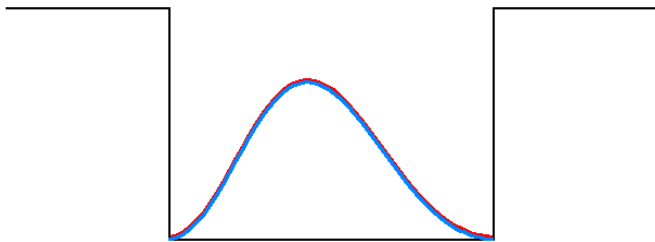
L-TDDFT versus VK-TDCDFT: simple “1D” models

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

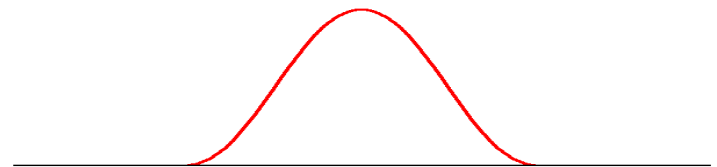
$$n(x,t) = \sqrt{\bar{g}(x,t)} n_0(\xi(x,t)) \quad \text{and} \quad \bar{g}(x,t) = \left(\frac{\partial \xi}{\partial t} \right)^2$$

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

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



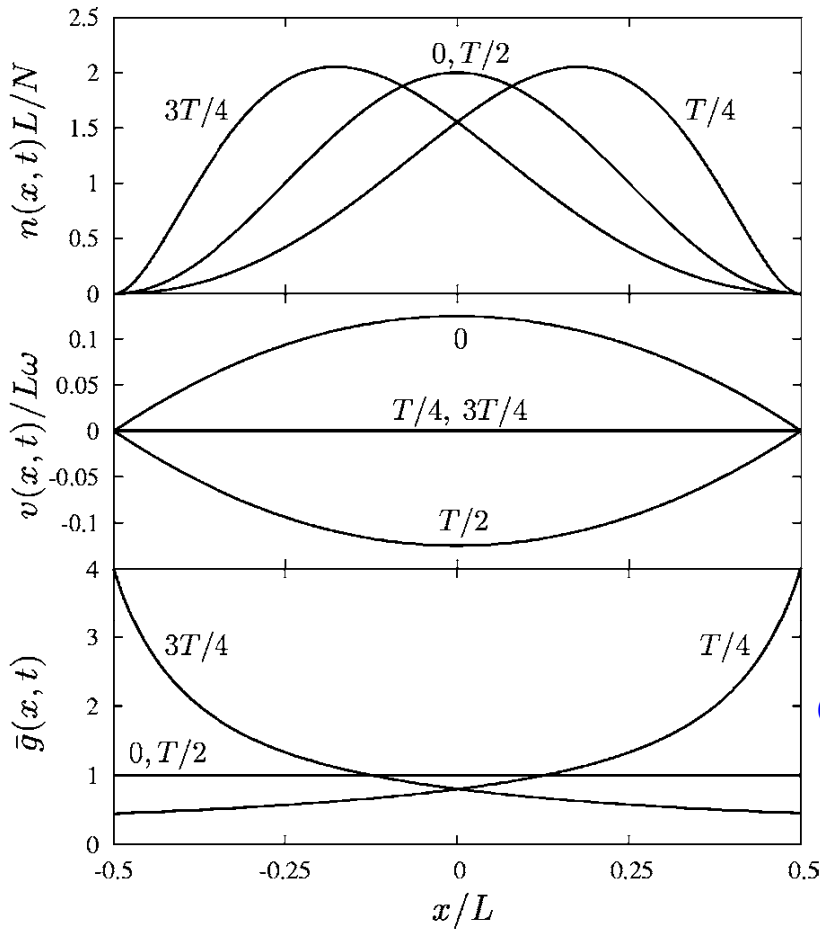
sloshing mode



breathing mode



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

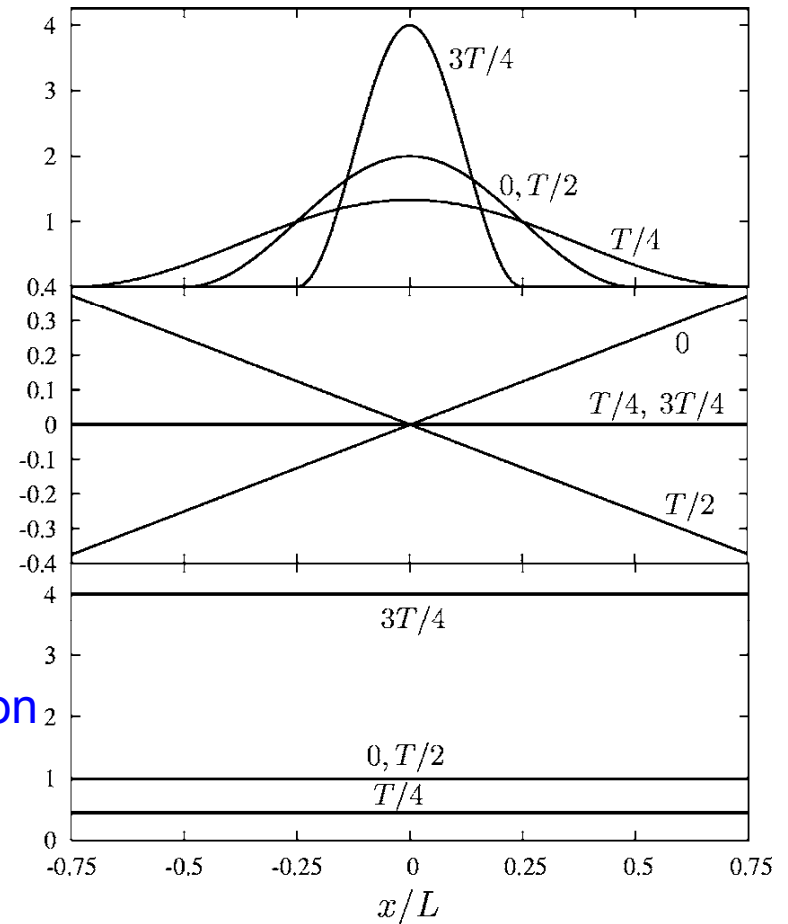


density

velocity

deformation

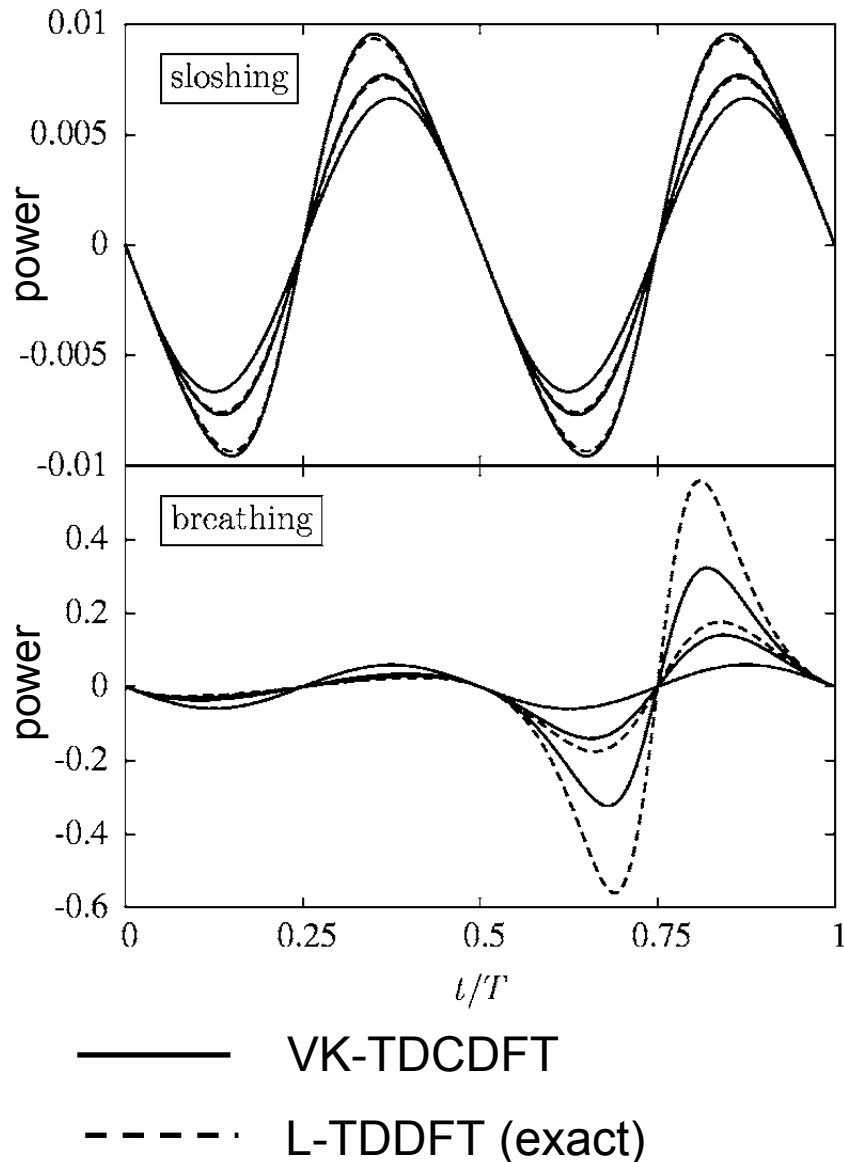
sloshing mode: not too strongly deformed (cousin of Kohn’s mode)



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!

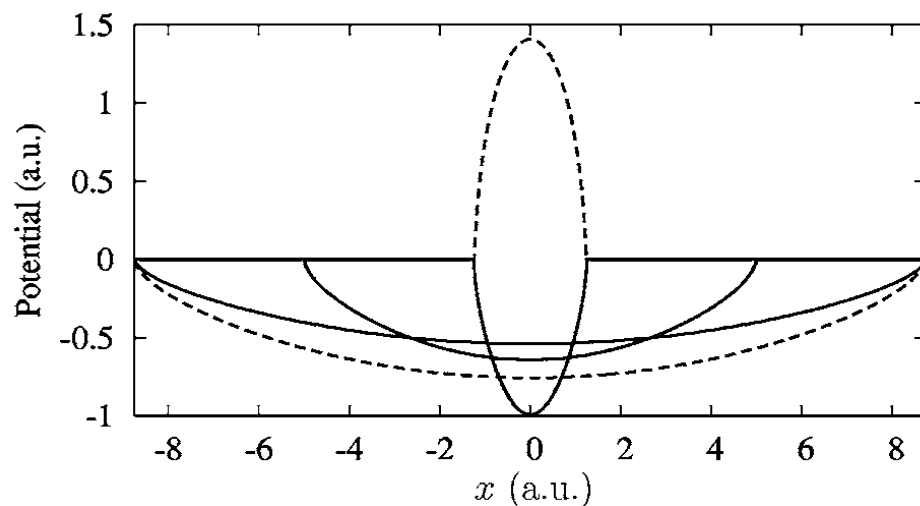
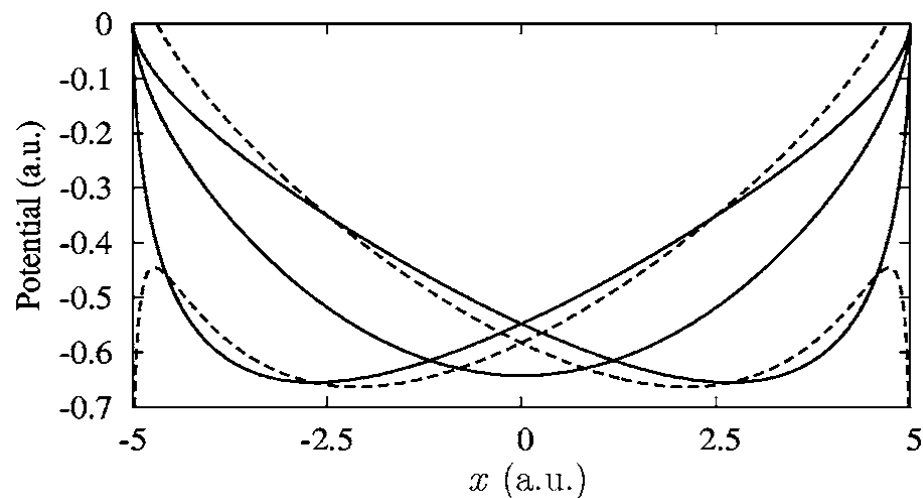


Breakdown of the ALDA

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

— 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)

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

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

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

Other derivations: R. van Leeuwen 1996, 1998 (Keldysh formalism, Sham-Schluter equation)
A. Görling 1997 (perturbation expansion)



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)

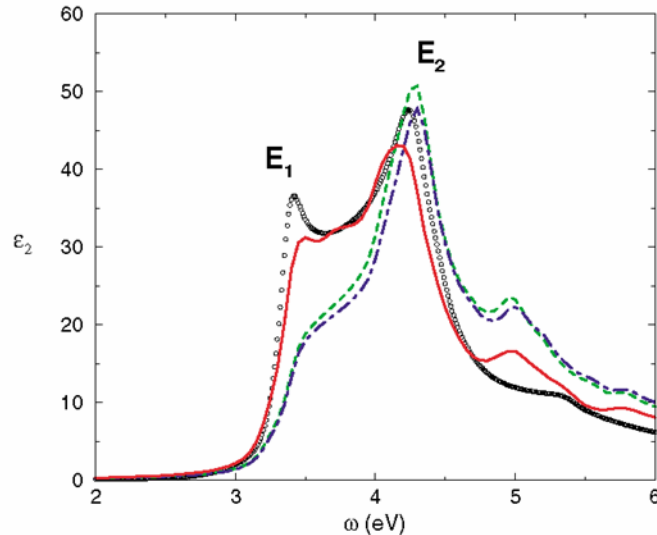
Shigeta, Hirao, Hirata, PRA **73**, 010502 (2006)

Hellgren and von Barth, JCP **131**, 044110 (2009)

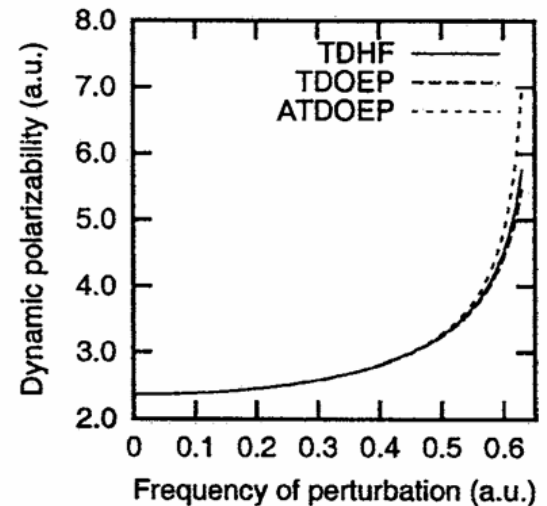
Hellgren and von Barth, PRB **78**, 115107 (2008)

} static ($\omega=0$)
kernel

} ω -dependent kernel



Kim and Goerling (Silicon)



Shigeta et al. (Neon)

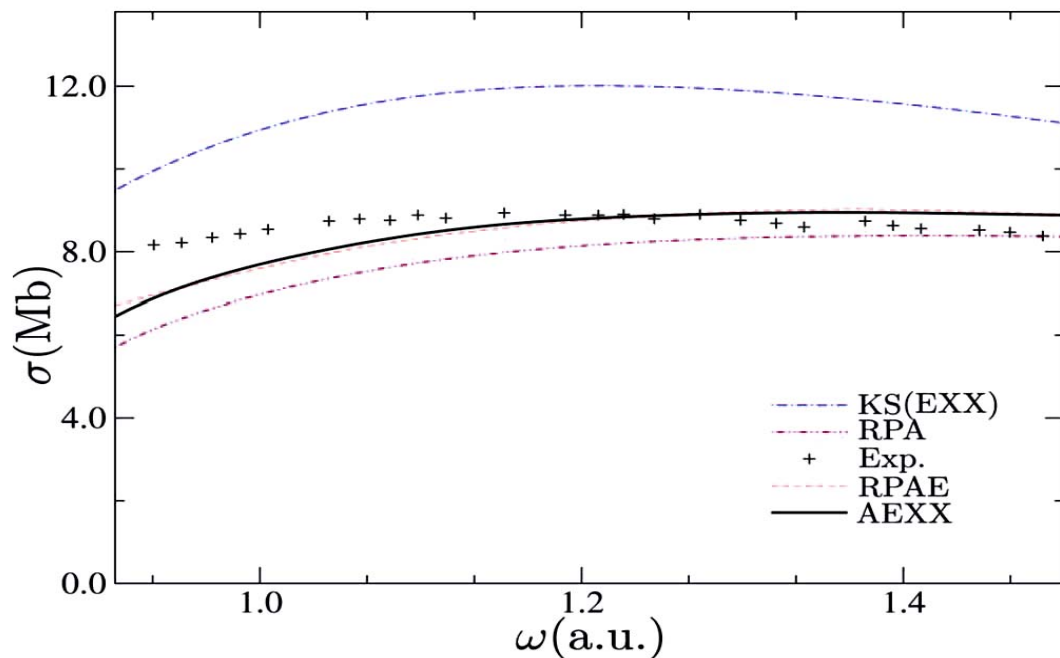


TDOEP – the frequency-dependent xc kernel

Hellgren and von Barth, PRB **78**, 115107 (2008) and JCP **131**, 044110 (2009)

Atom	KS	RPA	TDEXX	TDHF	Litt. ^c
He	1.487	1.199	1.322	1.322 ^a	1.38
Ne	2.838	2.234	2.372	2.377 ^a	2.67
Ar	16.965	9.883	10.737	10.758 ^a	11.08
Be	81.385	33.489	45.648	45.62 ^b	37.8
Mg	140.26	60.262	81.658	81.60 ^b	71.53

static polarizabilities:
TDOEP reproduces
TDHF



photoionization cross section
of neon:

- adiabatic TDOEP agrees well with experiment and with RPAE (=TDHF)
- frequency-dependent xc kernel has unphysical singularities (from inverse response function)

$$\begin{aligned}
 V_{xc\sigma}^{KLI}(\mathbf{r}, t) = & \sum_j \frac{n_{j\sigma}(\mathbf{r}, t)}{n_\sigma(\mathbf{r}, t)} u_{xcj\sigma}(\mathbf{r}, t) \quad \left. \vphantom{\sum_j} \right\} \text{Slater} \\
 & + \sum_j \frac{n_{j\sigma}(\mathbf{r}, t)}{n_\sigma(\mathbf{r}, t)} \int d^3 r' n_{j\sigma}(\mathbf{r}', t) \left\{ V_{xc\sigma}^{KLI}(\mathbf{r}', t) - u_{xcj\sigma}(\mathbf{r}', t) \right\} \quad \text{potential}
 \end{aligned}$$

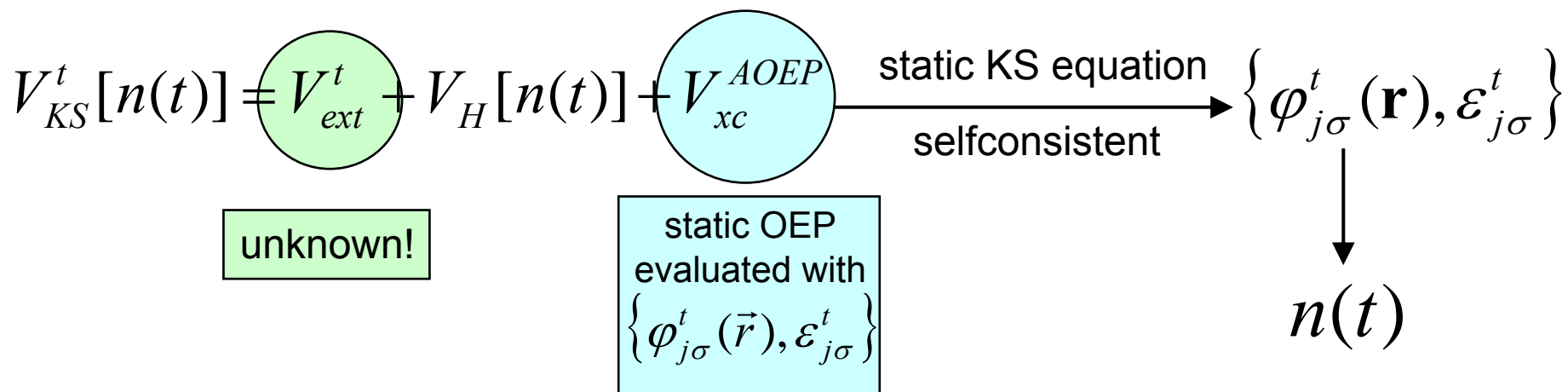
Applications of TDKLI in the nonlinear regime:

- 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: $n(t) \longrightarrow V_{KS}^t, \{\varphi_{j\sigma}^t(\mathbf{r}), \varepsilon_{j\sigma}^t\}$

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



Numerical solution of TDOEP: step-by-step?

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

- ▶ 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** $\varphi_j(T)$

$t=0$ → $t=T$ t

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

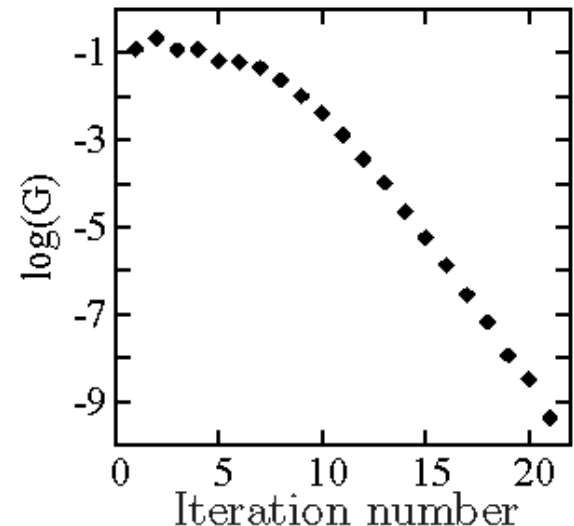
$\left\{ \varphi_j^{(n)}(t) \right\} \xrightarrow{\text{TDOEP}} V^{(n)}(t), \quad t = [0, T]$

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

⋮

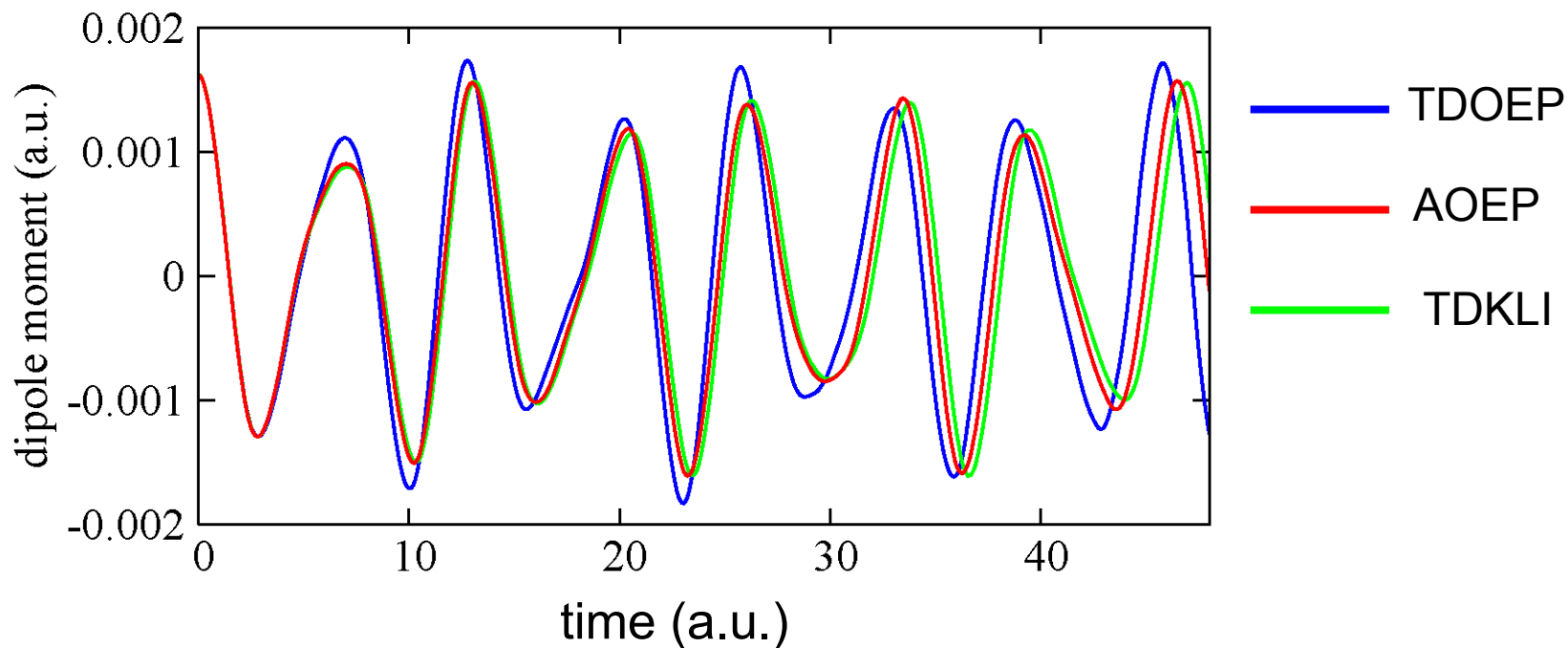
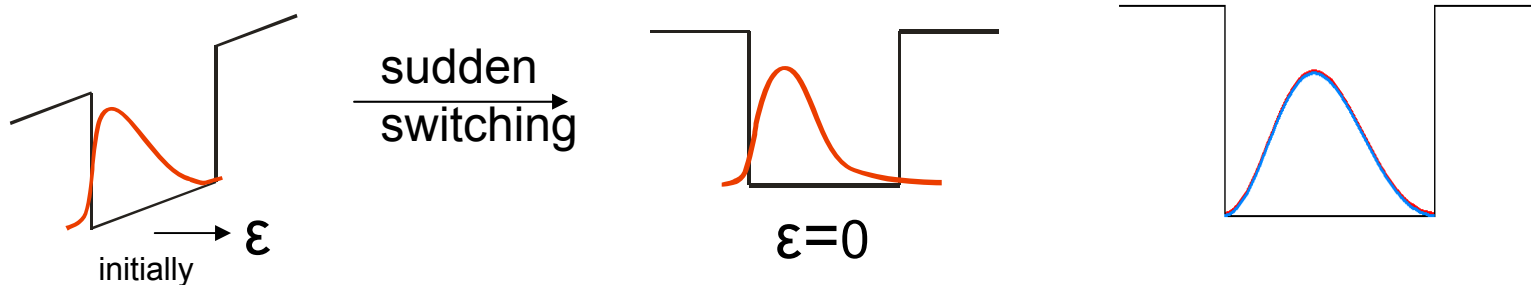
Convergence
index:

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





Free charge-density oscillations

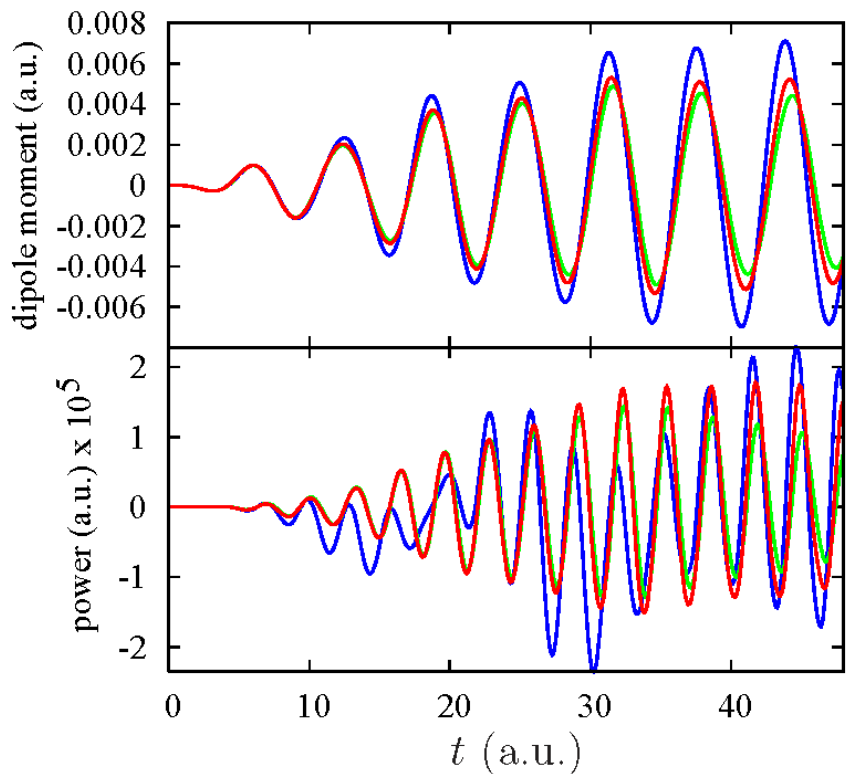


► TDOEP slightly blueshifted: memory gives rise to elastic contribution (x-only)



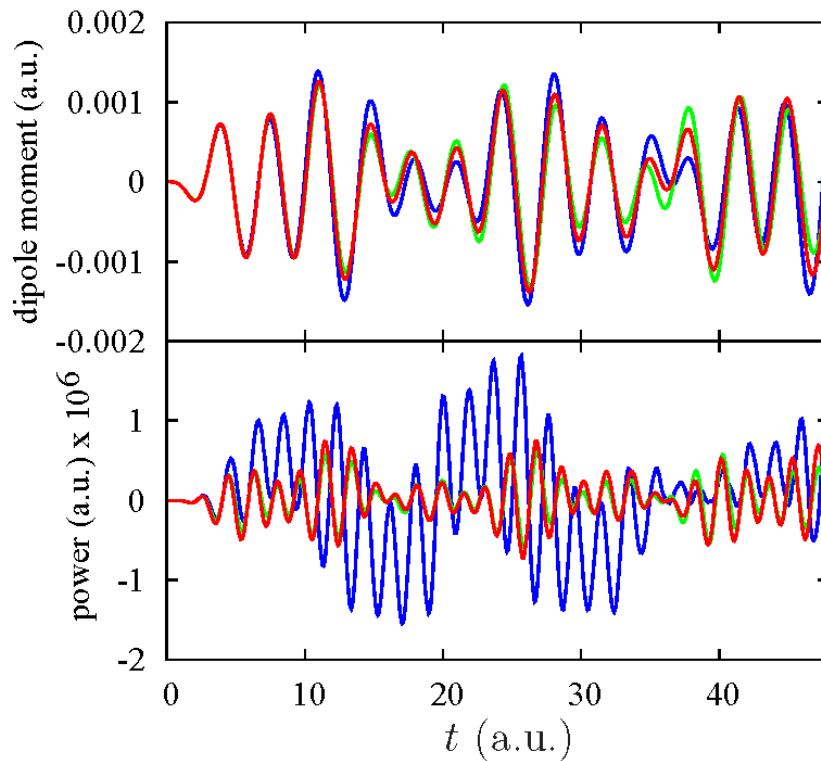
Driven oscillations

$\omega=11$ meV



close to ω_{12} resonance

$\omega=20$ meV



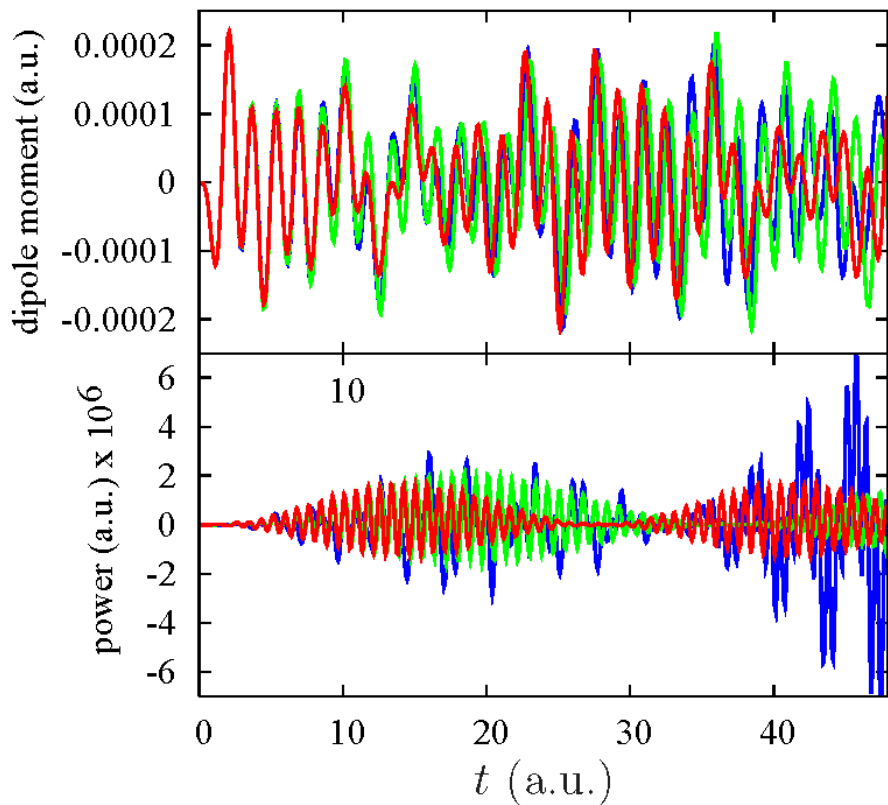
close to ω_{23} resonance

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



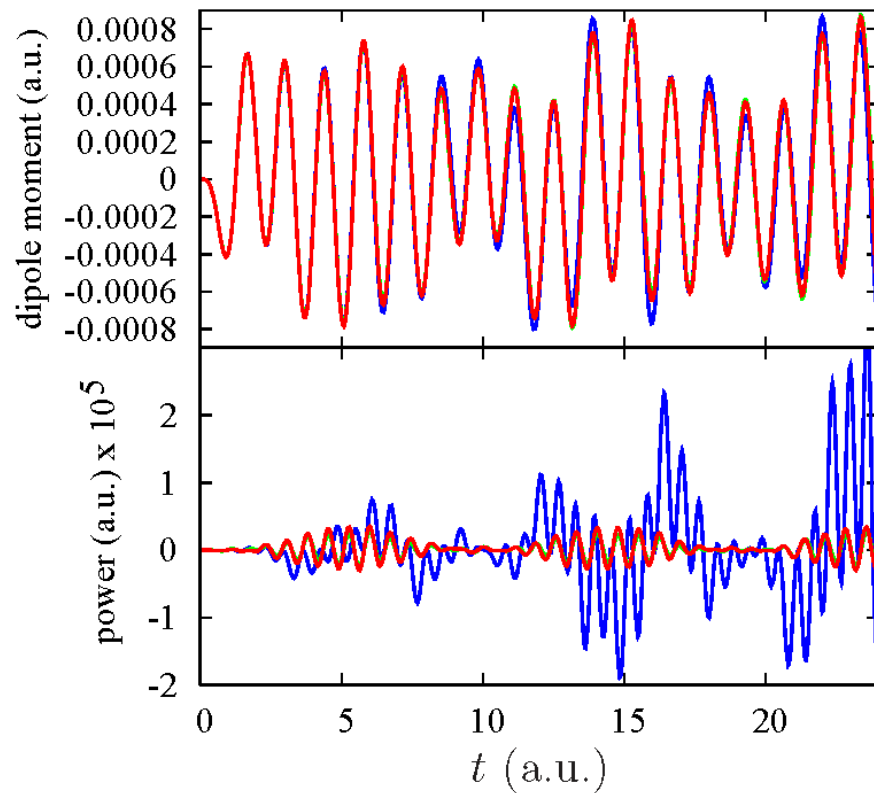
Driven oscillations

$\omega=40$ meV



close to ω_{14} resonance

$\omega=50$ 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
- Caution: the problems in linear response (Hellgren & v. Barth) will also show up in the real-time domain.
- 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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