

# **TDCDFT: Linear-response regime**

#### Carsten A. Ullrich University of Missouri



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## **Lecture I: Basic formalism of TDCDFT**

## **Lecture II: Applications of TDCDFT in linear response**

- ► The VK functional
- ► Polarizabilities in polymers
- ► Nanoscale transport, stopping power of metals
- Linewidths of collective excitations
- Excitations in atoms and molecules
- Optical properties of bulk metals and insulators

## Lecture III: TDCDFT in the nonlinear regime



#### TDCDFT overcomes several formal limitations of TDDFT:

- allows treatment of electromagnetic waves, vector potentials, uniform applied electric fields.
- works for all extended systems. One does not need the condition that the current density vanishes at infinity.
- But TDCDFT is also practically useful in situations that could, in principle, be fully described with TDDFT:
  - Upgrading to the current density can be a more "natural" way to describe dynamical systems.
  - Helps to deal with the **ultranonlocality** problem of TDDFT
  - Provides ways to construct **nonadiabatic** approximations

## **TDCDFT** beyond the ALDA: the VK functional

$$\mathbf{A}_{xc,1}^{VK}(\mathbf{r},\omega) = \mathbf{A}_{xc,1}^{ALDA}(\mathbf{r},\omega) - \frac{1}{i\omega n_0(\mathbf{r})} \nabla \cdot \vec{\sigma}_{xc}(\mathbf{r},\omega)$$
  
xc viscoelastic stress tensor:  

$$\sigma_{xc,\mu\nu}(\omega) = \eta_{xc} \left( \nabla_{\nu} u_{1,\mu} + \nabla_{\mu} u_{1,\nu} - \frac{2}{3} \nabla \cdot \mathbf{u}_1 \delta_{\mu\nu} \right) + \zeta_{xc} \nabla \cdot \mathbf{u}_1 \delta_{\mu\nu}$$
  

$$\mathbf{u}(\mathbf{r},\omega) = \mathbf{j}(\mathbf{r},\omega) / n_0(\mathbf{r}) \quad \text{velocity field}$$

automatically satisfies zero-force theorem/Newton's 3<sup>rd</sup> law
automatically satisfies the Harmonic Potential theorem
is local in the current, but nonlocal in the density
introduces dissipation/retardation effects

...but how on earth did they come up with this expression??



Derivation by "brute force" [G. Vignale and W. Kohn, PRL 77, 2037 (1996)]

Consider weakly inhomogeneous electron liquid, modulated by a charge-density wave of small amplitude and wavevector.

$$2\gamma \ddagger \frac{2\pi/k}{n_0(\mathbf{r}) = \overline{n}[1 + \gamma \cos(\mathbf{k} \cdot \mathbf{r})]}$$

► Calculate xc kernel  $f_{xc}(k+q,k,\omega)$  where  $k,q << k_F, \omega/v_F$ ► It turned out later that the resulting expression can be cast

into hydrodynamic form

Physical insight [G. Vignale, C.A.U., and S. Conti, PRL **79**, 4878 (1997), C.A.U. and G. Vignale, PRB **65**, 245102 (2002)]

- Classical theories of the dynamics of continuous media (elasticity and hydrodynamics) express many-body forces as divergences of stress tensors
- want local functionals of the displacement or velocity field
- use general symmetries and sum rules



#### xc viscosity coefficients

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

The xc viscosities have both real and imaginary parts, describing **dissipative** and **elastic** behavior.

Subtle (but important) point: the xc kernels of the homogeneous electron liquid are nonanalytic functions of q and  $\omega$ !

$$\lim_{q\to 0} f_{xc}^{L,T}(q,0) \neq \lim_{\omega\to 0} f_{xc}^{L,T}(0,\omega)$$



#### static limits of the xc kernels

$$\lim_{q \to 0} f_{xc}^{L}(q,0) = \frac{d^{2} e_{xc}^{unif}(n)}{dn^{2}}$$
$$\lim_{q \to 0} f_{xc}^{T}(q,0) = 0$$

$$\lim_{\omega \to 0} f_{xc}^{L}(0,\omega) = \frac{d^{2}e_{xc}^{unif}(n)}{dn^{2}} + \frac{4}{3}\frac{\mu_{xc}(0)}{n^{2}}$$
$$\lim_{\omega \to 0} f_{xc}^{T}(0,\omega) = \frac{\mu_{xc}(0)}{n^{2}}$$

 $\mu_{xc}(0)$ : Static xc shear modulus





The shear modulus of the electron liquid does **not** disappear for  $\omega \rightarrow 0$ . (as long as the limit  $q \rightarrow 0$  is taken first, which is what one should do for a Local approximation). Physical reason:

- Even very small frequencies  $<< E_F$  are large compared to relaxation rates  $\tau^{-1}$  from electron-electron collisions.
- The zero-frequency limit is taken such that local equilibrium is not reached.
- The Fermi surface remains stiff against deformations since we're above the electron-hole continuum.



#### 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)



## (A) In the (quasi)-static $\omega \rightarrow 0$ limit:

- Polarizabilities of π-conjugated polymers
- Nanoscale transport
- Stopping power of slow ions in metals

These applications profit from the fact that VK does not reduce to the ALDA in the static limit.

## **(B)** To describe excitations at finite frequencies:

- atomic and molecular excitation energies
- plasmon excitations in doped semiconductor structures
- optical properties of bulk metals and insulators

Here the picture is less clear. Some situations are well described, others fail. We'll try to analyze when and why.



## Long-chain molecule in a static field



Field-free ground state



Polarized state predicted by (semi)local functionals: Overestimation of the polarizability



### TDCDFT for $\pi$ -conjugated polymers



M. van Faassen et al., PRL 88, 186401 (2002) and JCP 118, 1044 (2003)



VK works extremely well for  $\pi$ -conjugated polymers, but not so well for other types of long-chain molecules.



H-chain: localized  $\sigma$ -bonds dominate, and we probe density regions with  $r_s < 1$  $\rightarrow$  XC viscosities not well known in these regions!

M. van Faassen et al., PRL 88, 186401 (2002) and JCP 118, 1044 (2003)



## **Stopping power of electron liquids**

#### Nazarov, Pitarke, Takada, Vignale, and Chang, PRB 76, 205103 (2007)



- Stopping power measures friction experienced by a slow ion moving in a metal due to interaction with conduction electrons
- ALDA underestimates friction (only single-particle excitations)
- TDCDFT gives better agreement with experiment: additional contribution due to viscosity





Total dissipated power in the junction:

$$RI^{2} = \int d^{3}r \int d^{3}r' \mathbf{j}(\mathbf{r}) \vec{\rho}(\mathbf{r},\mathbf{r}') \mathbf{j}(\mathbf{r}')$$

Total dissipated power in Landauer theory:

$$R_{s}I^{2} = \int d^{3}r \int d^{3}r' \mathbf{j}_{s}(\mathbf{r}) \vec{\rho}_{s}(\mathbf{r},\mathbf{r}') \mathbf{j}_{s}(\mathbf{r}')$$

Missing xc piece of the resistance:  $R = R_s + R_{xc}^{dyn}$ 



#### Nanoscale transport



For narrow junctions (small transmission coefficient), the xc piece of the resistance becomes as important as the Kohn-Sham resistance.

### Metallic systems vs. insulators



Excitation spectrum of simple metals:

- single particle-hole continuum (incoherent)
- collective plasmon mode
- RPA/ALDA misses plasmon damping (multiple e-h excitations)



## Electronic transitions in doped quantum wells



# ×

#### **Quantum well subbands**



Electrons in a quantum well:

- ► quantized in z-direction (discrete subbands)
- ► free in the x-y plane (each subband is parabolic)





Since this is a "1D" system, we can integrate the continuity equation:

$$\frac{\partial j_1}{\partial z} = i\omega n_1 \implies j_1(z,\omega) = i\omega \int_{-\infty}^{z} n_1(z',\omega) dz'$$

and we can construct the xc scalar potential from the xc vector potential:

$$\frac{\partial V_{xc,1}}{\partial z} = i\omega A_{xc,1} \implies V_{xc,1}(z,\omega) = i\omega \int_{-\infty}^{z} A_{xc,1}(z',\omega) dz'$$

We only need the zz component of the xc stress tensor:

$$\sigma_{xc,zz}(z,\omega) = \left(\zeta_{xc} + \frac{4}{3}\eta_{xc}\right) \frac{\partial v(z,\omega)}{\partial z}$$
where  $\zeta_{xc} + \frac{4}{3}\eta_{xc} = -\frac{n_0^2(z)}{i\omega} \left(f_{xc}^L(n,\omega) - \frac{d^2 e_{xc}^{unif}}{dn^2}\right)_{n=n_0(z)}$ 

## Explicit expression for the scalar xc kernel in 1D

$$f_{xc}^{VK}(z, z', \omega) = f_{xc}^{L}(z, \omega)\delta(z - z') - f_{xc}^{dyn}(z, \omega)\frac{n'_{0}(z)}{n_{0}(z)}\theta(z - z') - f_{xc}^{dyn}(z', \omega)\frac{n'_{0}(z')}{n_{0}(z')}\theta(z' - z) + \int dz''\theta(z'' - z)\theta(z'' - z')f_{xc}^{dyn}(z'', \omega)\left(\frac{n'_{0}(z'')}{n_{0}(z)}\right)^{2}$$

- long-range nature of the xc kernel explicitly visible
- satisfies Harmonic Potential Theorem and other symmetries

G. Vignale and W. Kohn, in "Electronic DFT" (Plenum, 1998)

## ISB plasmon frequency $\Omega$ and linewidth $\Gamma$

	Experiment	ALDA	$\mathrm{GK}_{\mathrm{GK}}$	$\mathrm{GK}_{\mathrm{NCT}}$	$\rm VK_{GK}$	$\rm VK_{\rm NCT}$
$\Omega$ (single) $\Gamma$ (single)	$10.7 \\ 0.53$	10.25	10.63 0.683	$10.23 \\ 0.655$	$10.31 \\ 0.128$	$\begin{array}{c} 10.24 \\ 0.104 \end{array}$
$\Omega$ (double) $\Gamma$ (double)	14.6 $1.17$	13.85	$14.24 \\ 1.00$	$13.88 \\ 0.403$	$20.64 \\ 8.55$	$\begin{array}{c} 12.55\\ 4.15\end{array}$

Single well: VK gives good results for electronic linewidth Double well: VK overestimates linewidth. The tunneling barrier makes the electronic flow very "non-hydrodynamic".

C.A. Ullrich and G. Vignale, Phys. Rev. B 58, 15756 (1998)

C.A.Ullrich and K. Burke, JCP **121**, 28 (2004)

Velocity field of 1→2 excitation:  $\mathbf{u}^{12} = \frac{\varphi_1(r)\nabla\varphi_2(r) - \varphi_2(r)\nabla\varphi_1(r)}{n_0(\mathbf{r})}$ 

Small-matrix approximation of TDCDFT with VK functional:

$$\Omega^{2} = \Omega_{ALDA}^{2} - \frac{i\Omega}{\omega_{12}} \sum_{jk} \int d^{3}r \,\sigma_{xc,jk}^{12}(\mathbf{r},\Omega) \nabla_{k} u_{j}^{12}(\mathbf{r})$$

compare with average rate of energy dissipation in a classic viscous fluid:

$$\dot{E}_{diss} = -\sum_{jk} \int d^3 r \, \sigma_{jk} \nabla_k \mathbf{u}_j$$

More general formalism for molecules: M. van Faassen, Int. J. Mod. Phys. B **20**, 3419 (2006)



## **Atomic excitation energies**

	Experiment	ALDA	$\rm VK_{\rm NCT}$	$\mathrm{VK}_\mathrm{QV}$
Be $2s \rightarrow 2p$	5.28	4.83	6.03	6.14
Be $2s \rightarrow 3s$	6.78	6.53	6.55	6.58
Mg $3s \rightarrow 3p$	4.35	4.50	7.17	7.08
${ m Mg}\; 3s  ightarrow 4s$	5.39	7.23	7.23	7.25



conditions for validity of the VK functional:

$$\left|\frac{\nabla n_0}{n_0}\right|, \left|\frac{\nabla j_v}{j_v}\right|, \left|\frac{\nabla u_v}{u_v}\right| << k_F, \frac{\omega}{v_F}$$

OK for  $s \rightarrow s$ , but badly violated for  $s \rightarrow p$ !



#### Frequency shifts:

- Generally in the right direction; but only small for s→s, and tend to overshoot for s→p excitations
- need more accurate  $f_{xc}^{L,T}(\omega)$ , especially around nucleus (r<sub>s</sub><<1)
- excitations with large  $\nabla j$  are problematic. Need higher gradients. [partial cure: Tao and Vignale, PRL 97, 036403 (2006)]

#### Imaginary parts:

- small but finite, often of the same order as frequency shifts.
- unphysical: a finite system ought to have zero linewidth. Difficult to achieve for a functional with the homogeneous electron gas as reference system!



## **TDCDFT** for bulk semiconductors

Berger, de Boeij, and van Leeuwen, PRB 75, 035116 (2007)



CNT: Conti, Nifosi, Tosi QV: Qian, Vignale

Experiment: Lautenschlager, Garriga, Vina and Cardona, PRB **36**, 4821 (1987)

- if shear modulus is ignored (CNT,QVA), marginal improvement over ALDA.
- including transverse shear modulus (QV), spectrum collapses.
- like in atoms, the inhomogeneity is too large; VK conditions violated
- usage of VK for insulators questionable, but can perhaps be improved

## **Macroscopic dielectric function of metals**

Berger, Romaniello, van Leeuwen, and de Boeij, PRB 74, 245117 (2006)



- cures deficiencies of ALDA (low-frequency Drude-like tail of spectrum)
- again, the transverse shear modulus causes trouble. Results are better if it is neglected. However, this might be fixed if we had better expressions for the shear modulus.

## The VK functional: summary and words of caution

- Relies on a "double-LDA": both the ground-state density and external perturbation are assumed to be slowly varying. In practice, these conditions are often violated, which can be a source of serious problems!
- ► Depends crucially on order of limits: q→0 first, then ω→0. Does therefore not reduce to ALDA in the ω→0 limit, due to xc shear modulus of electron liquid which stays finite.

The discontinuity in  $f_{xc}$  is a very subtle point, and sometimes seems to lead to unphysical results, depending on the system. How to take the static limits properly is still subject of research.

VK is based on the electron gas, which is an infinite reference system. Therefore, excitation energies have an imaginary part. For finite systems, this is unphysical, but for extended systems, this is the correct physics. VK is therefore ideal for plasmons.

► Required input for VK functional is only approximately known. Need more accurate expressions for  $f_{xc}^{L}(n,\omega)$ ,  $f_{xc}^{T}(n,\omega)$  especially at high densities.



#### **Today's summary:**

The VK functional in TDCDFT works great for polarizabilities of polymers and linewidths of collective plasmon excitations

The situation is less clear for excitations in atoms and molecules and optical spectra of metals and insulators. These seem hard to capture with electron-gas based functionals.

 $\blacktriangleright$  VK is promising, but needs improvements (e.g. local  $\rightarrow$  semilocal)

#### Thursday:

- Dynamics in the time domain: memory and dissipation in TDKS
- A rigorous extension of the LDA: TDDefFT versus TDCDFT
- Time-dependent optimized effective potential