

# Conserving approximations in time-dependent density-functional theory : Connections to many-body perturbation theory

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# Overview

## Time-dependent density functional theory

- Current status and need for improvements
- Nonlocality in space and time.

## Many-body approach to TDDFT

- Conserving memory functionals: how to make them?
- Functionals derived from the Luttinger-Ward action

## Conclusions and outlook

# Time-dependent Kohn-Sham equations

input known external potential

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right)\phi_i(\mathbf{r}) = i\partial_t\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{\infty} f_i |\phi_i(\mathbf{r})|^2$$

output density  $n[\mathbf{v}]$

All the memory and initial state dependence is contained in the xc-potential

# The xc-kernel

Many TDDFT calculations are carried out in the linear response regime.

$$v_{xc}(1) = v_s(1) - v(1) - v_H(1)$$

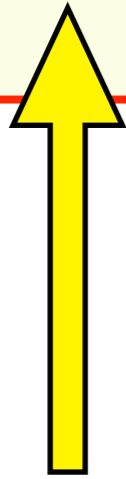
$$f_{xc}(1, 2) = \frac{\delta v_s(1)}{\delta n(2)} - \frac{\delta v(1)}{\delta n(2)} - \frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

We can then define the response functions

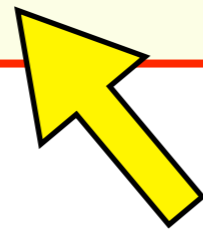
$$\chi(1, 2) = \frac{\delta n(1)}{\delta v(2)} \quad \chi_s(1, 2) = \frac{\delta n(1)}{\delta v_s(2)}$$

We obtain the well-known linear response equation

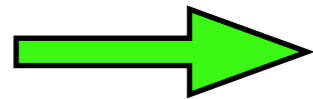
$$\chi(1, 2) = \chi_s(1, 2) + \int d3d4 \chi_s(1, 3)[w(3, 4) + f_{xc}(3, 4)]\chi(4, 2)$$



Poles at the true excitation energies



Poles at Kohn-Sham eigenvalue differences  
(singly excited determinants)



The xc-kernel must have frequency dependence to generate extra poles:

The memory in the xc-potential contains the physics of double and higher excitations, excitons....

In the adiabatic local density approximation (ALDA) we have

$$v_{xc}^{ALDA}(\mathbf{r}t) = \frac{d\epsilon_{xc}}{dn}(n(\mathbf{r}t))$$

$$f_{xc}^{ALDA}(\mathbf{r}t, \mathbf{r}'t') = \frac{d^2\epsilon_{xc}}{dn^2}(n_0(\mathbf{r}))\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

The adiabatic local density approximation is both local in space and in time.

One of the first functionals that went beyond the ALDA was the so-called Gross-Kohn kernel which was local in space and nonlocal in time.

However, this functional violated basic conservation laws.

Why is that?

# Spatial vs. temporal nonlocality

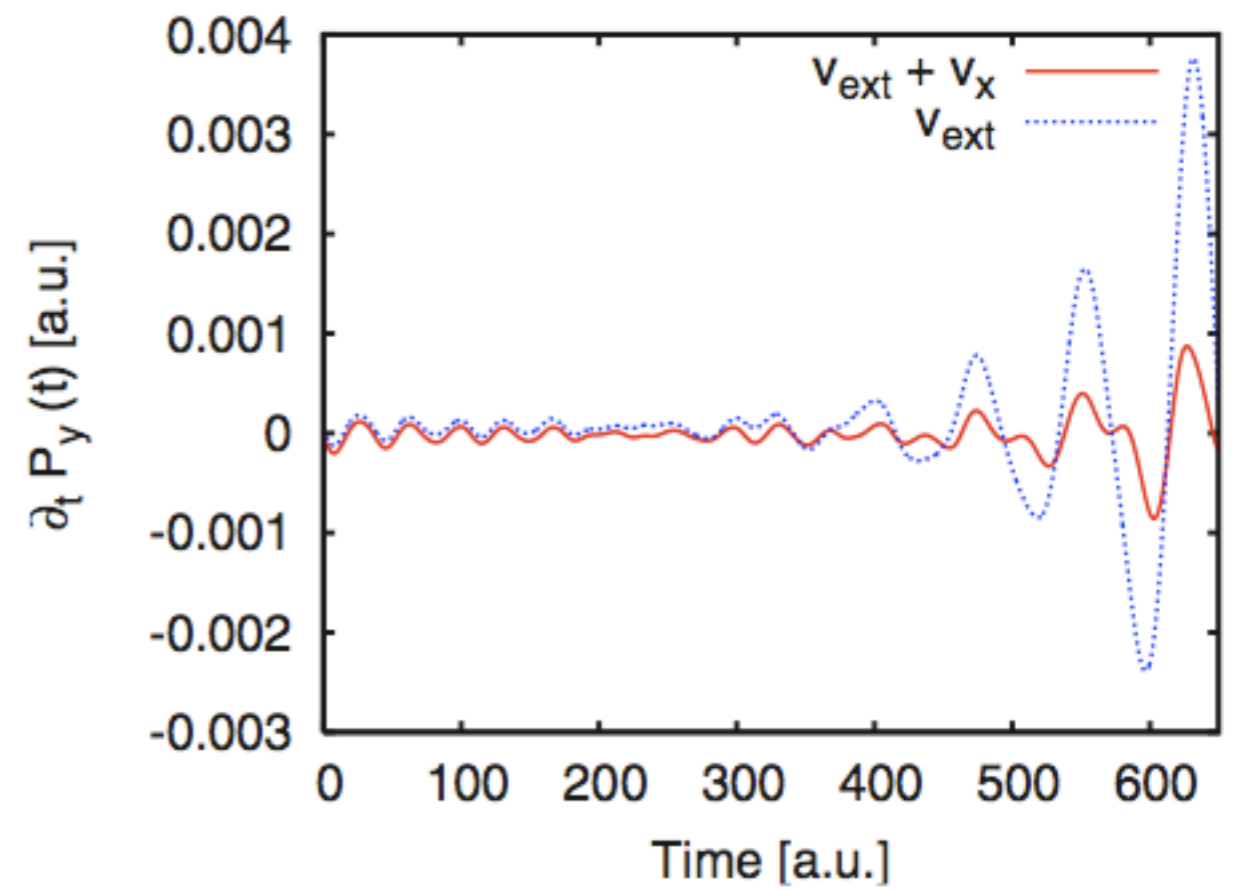
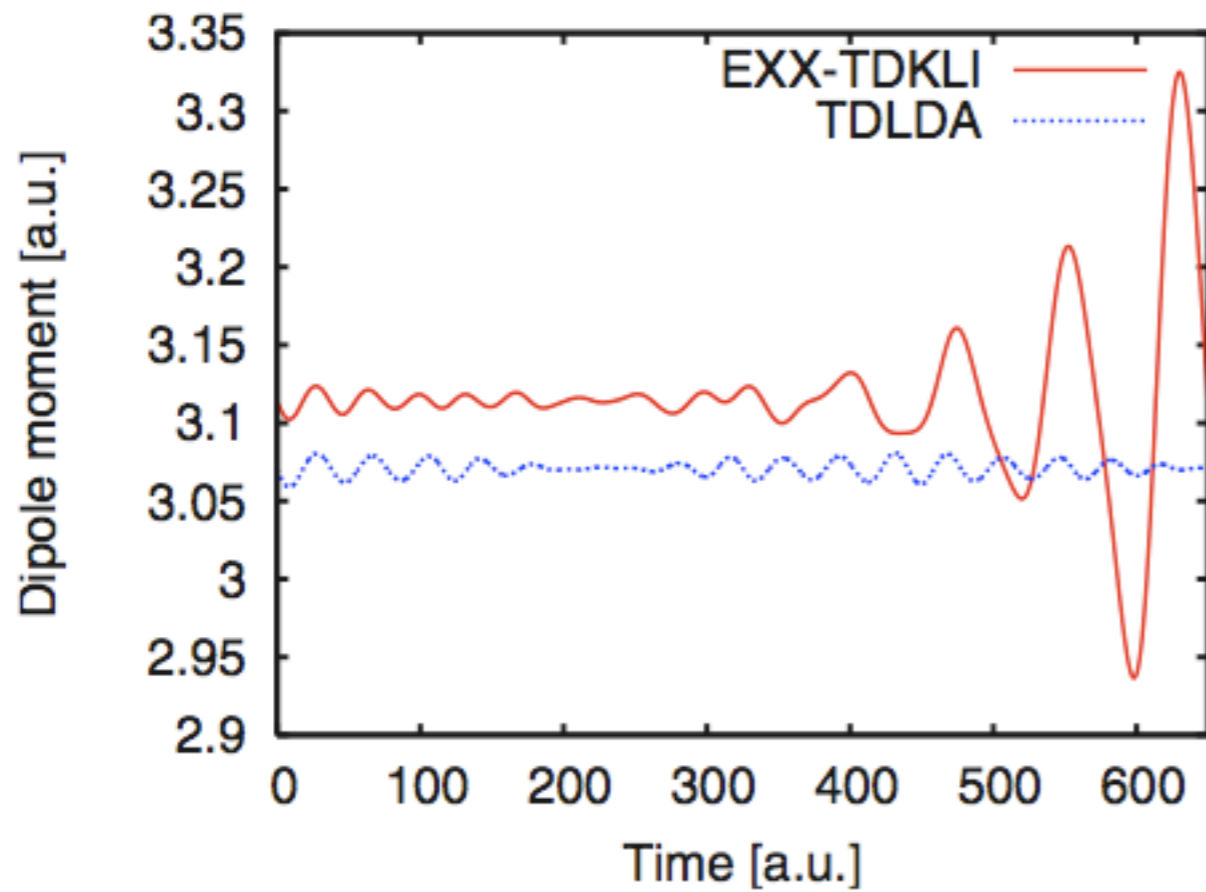
The zero-force theorem of TDDFT tells that

$$0 = \int d\mathbf{r} n(\mathbf{r}t) \nabla v_{xc}[n](\mathbf{r}t)$$

i.e. the xc-potential (being ‘internal’) does not exert a force on the system.

This relation is satisfied for the ALDA but will not in general be satisfied for approximate potentials:

For instance, the so-called KLI approximation for the exchange potential violates it, as does the Gross-Kohn approximation.



Example, TDKLI for a sodium cluster (  $\text{Na}_5$  )

M.Mundt, S.Kümmel, RvL, P-G.Reinhard, Phys.Rev.A75, 050501 (R) (2007)



Differentiation of the zero-force constraint with respect to the density leads to

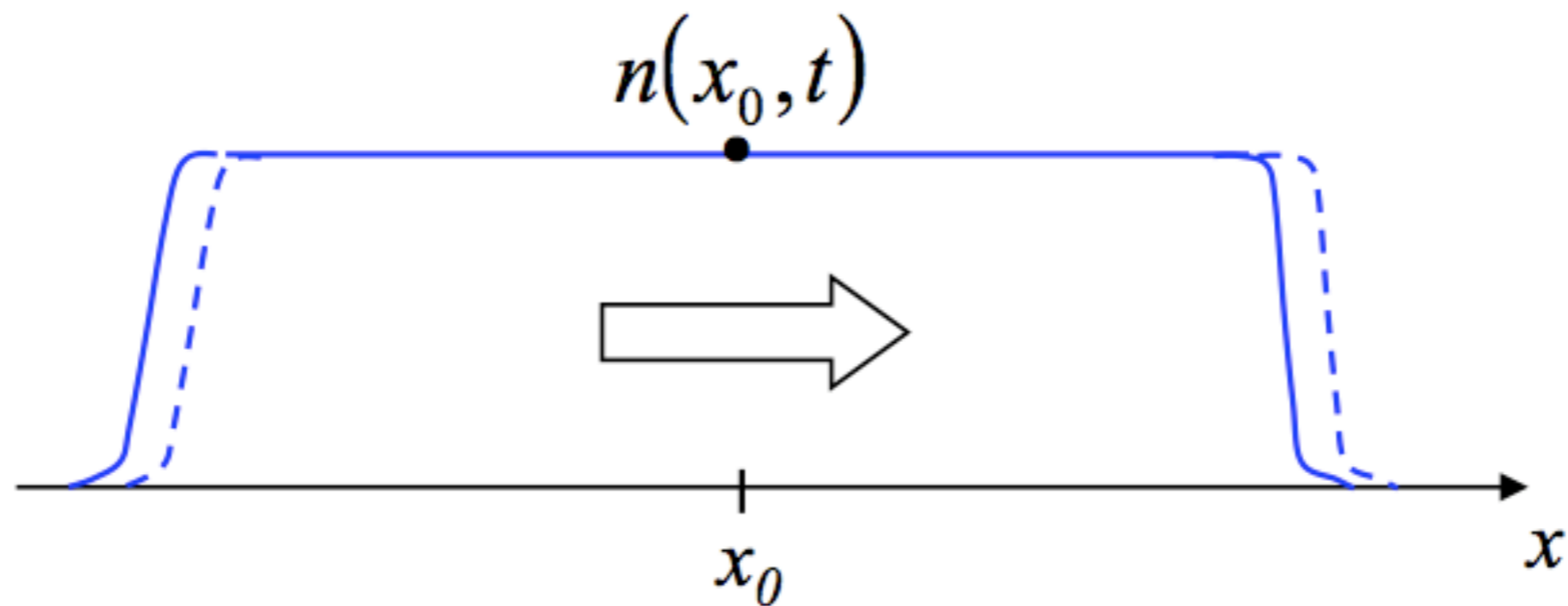
$$\int d\mathbf{r}' f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \nabla' n(\mathbf{r}') = \nabla v_{xc}(\mathbf{r})$$

Suppose in a weakly inhomogeneous system the xc-kernel has a finite range, then (Giovanni Vignale)

$$\nabla n(\mathbf{r}) \int d\mathbf{r}' f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = \nabla v_{xc}(\mathbf{r})$$

$$\int d\mathbf{r}' f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}(\mathbf{k} = 0, \omega)$$

Contradiction: Nonlocality in time incompatible with locality in space. Memory functionals are nonlocal in space and time



A density functional that only depends on the density or its gradients can not see the motion of the entire slab

The density functional needs to have a long range to see the density change at the edges

(picture from Carsten Ullrich)

# New functionals beyond ALDA: the many-body approach

It must be possible to derive the xc-potential from many-body methods

Why is this interesting or useful for TDDFT ?

1) Gives insight in how e-e interactions affect the properties of time-dependent xc-functionals (nonlocality, memory...)

“MBPT is easy while TDDFT is simple” (M.Gatti)

2) Leads to explicit constructions of functionals (with nice properties as e.g. conserving approximations)

We need a many-body approach for time-dependent systems

# Keldysh theory in 2 slides

## The time-dependent Hamiltonian

$$\hat{H}(t) = \hat{h}(t) + \hat{W} \quad \leftarrow \text{two-body interactions}$$

$$\hat{h}(t) = \sum_i^N h(\mathbf{r}_i t)$$

$$h(\mathbf{r}, t) = -\frac{1}{2} \nabla^2 + v(\mathbf{r}, t) - \mu$$

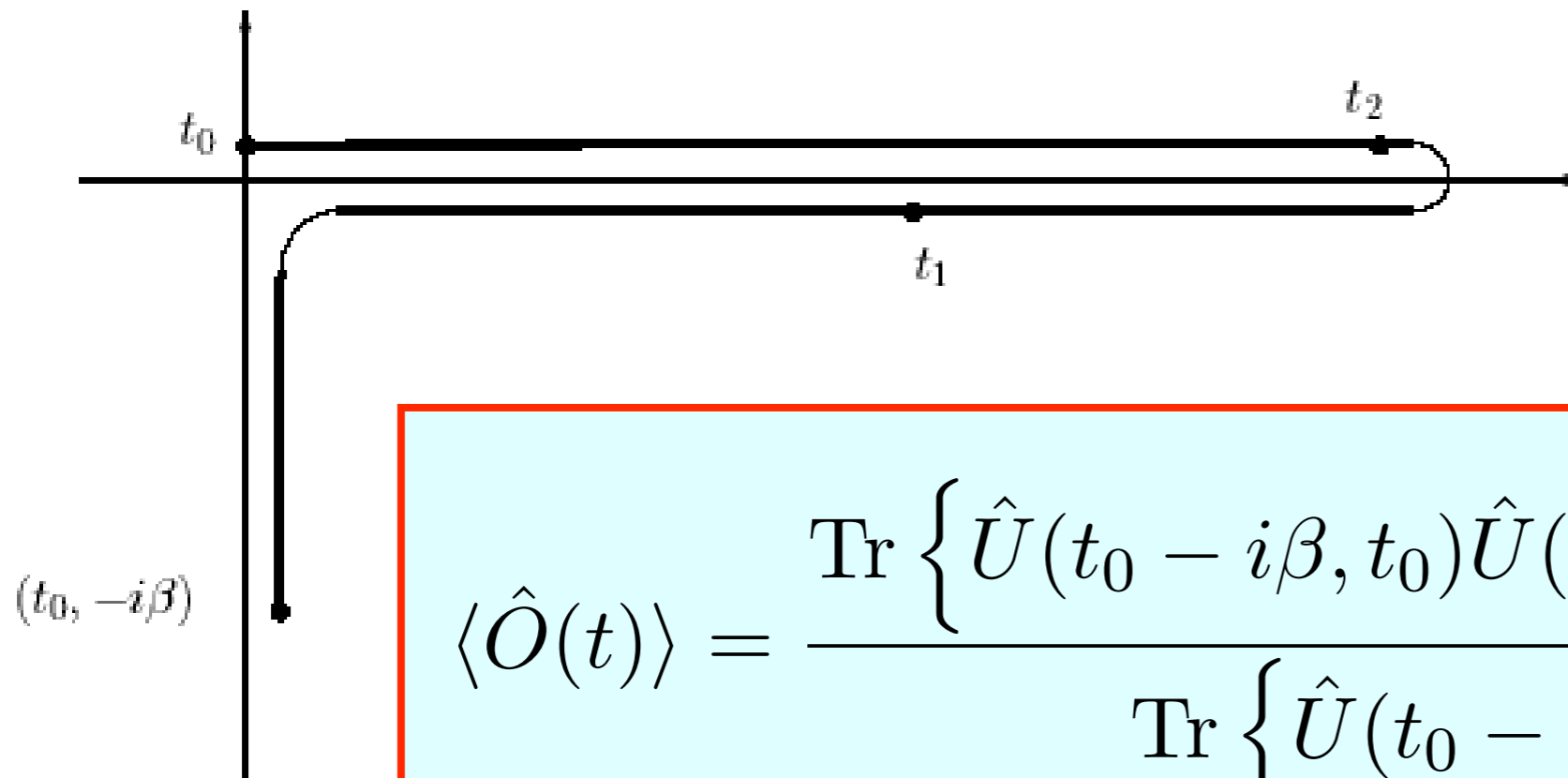
time-dependent  
external potential

Expectation values : Before switch-on of the field

$$\langle \hat{O} \rangle = \text{Tr} \left\{ \hat{\rho} \hat{O} \right\} \quad \hat{\rho} = \frac{e^{-\beta \hat{H}_0}}{\text{Tr} e^{-\beta \hat{H}_0}}$$

# The time contour

L.V.Keldysh, Sov.Phys.JETP20, 1018 (1965)



$$\langle \hat{O}(t) \rangle = \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

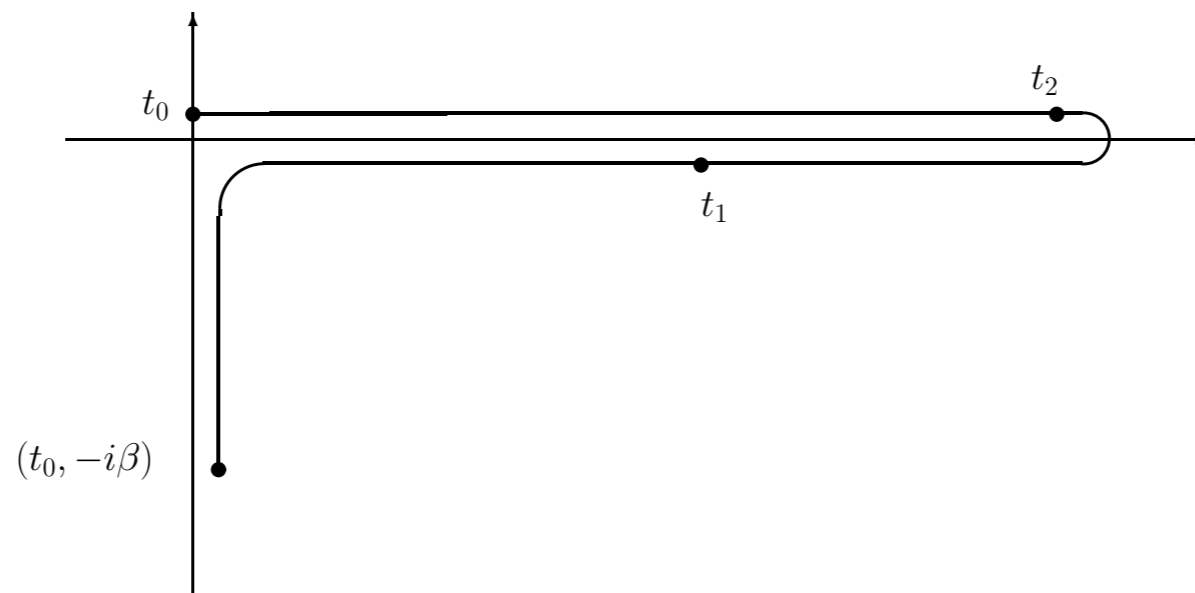
$$\langle \hat{O}(t) \rangle = \frac{\text{Tr} \left\{ T_C [\exp(-i \int_C d\bar{t} \hat{H}(\bar{t}) \hat{O}(t))] \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

# The time contour action functional

We define the following action functional :

$$\tilde{A}[v] = i \ln \text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}$$

Where we used the same time contour ordered evolution operator



## Why is the action defined like this ?

If we evaluate the action for a **static** potential then we find

partition  
function of  
statistical  
mechanics

$$i\tilde{A}[v] = -\ln \text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\} = -\ln Z = \beta \Omega$$

$$\lim_{T \rightarrow 0} \frac{i\tilde{A}}{\beta} = \lim_{T \rightarrow 0} \Omega = E - \mu N$$

The action functional is therefore a time-dependent generalization of the familiar energy functional

If one takes the derivative of the action respect to the potential one finds:

$$\frac{\delta \tilde{A}[v]}{\delta v(\mathbf{r}, t)} \Big|_{v_+ = v_-} = n(\mathbf{r}, t)$$

The action is therefore a generating function for the density if one makes changes in the potential.

(Just as the grand potential is in statistical mechanics)



## The action as a density functional

We then define the density functional :

$$A[n] = -\tilde{A}[v] + \int_C d1 n(1)v(1)$$

We regard  $v[n]$  as a functional of  $n$  (Runge-Gross theorem).

This functional has the property :

$$\frac{\delta A[n]}{\delta n(2)} = - \int_C d1 \frac{\delta \tilde{A}}{\delta v(1)} \frac{\delta v(1)}{\delta n(2)} + v(2) + \int_C d1 n(1) \frac{\delta v(1)}{\delta n(2)} = v(2)$$

$$\frac{\delta A[n]}{\delta n(\mathbf{r}, t)} = v(\mathbf{r}, t)$$

So this is our variational principle:

$$\frac{\delta A[n]}{\delta n(\mathbf{r}, t)} = v(\mathbf{r}, t)$$

output  
density  $n[v](rt)$

input  $v(rt)$   
known external potential  
of the system of interest

This requires in practice an approximation for the functional  $A[n]$ .

We are going to use the Kohn-Sham method to make the finding of such approximations easier

## Kohn-Sham equations

We define similar functionals for a noninteracting system:

$$\hat{H}_s(t) = \hat{T} + \hat{V}_s(t) \qquad \hat{V}_s(t) = \int d\mathbf{r} \hat{n}(\mathbf{r}) v_s(\mathbf{r}, t)$$

$$\tilde{A}_s[v_s] = i \ln \text{Tr} \left\{ \hat{U}_s(t_0 - i\beta, t_0) \right\}$$

There is nothing new to derive. We already know that

$$\left. \frac{\delta \tilde{A}_s[v_s]}{\delta v_s(\mathbf{r}, t)} \right|_{v_+ = v_-} = n(\mathbf{r}, t)$$

Similar to the interacting system we define


$$A_s[n] = -\tilde{A}_s[v_s] + \int_C d1 n(1) v_s(1) \qquad \frac{\delta A_s[n]}{\delta n(\mathbf{r}, t)} = v_s(\mathbf{r}, t)$$

The xc action functional is then defined as

$$A_{xc}[n] = A_s[n] - A[n] - \frac{1}{2} \int_C d1 \int_C d2 \delta(t_1, t_2) \frac{n(1)n(2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Differentiation gives :

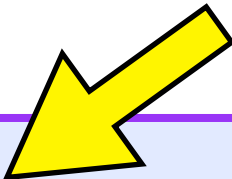
$$v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)} = \frac{\delta A_s}{\delta n(1)} - \frac{\delta A}{\delta n(1)} - v_H(1)$$


$$v_{xc}(1) = v_s(1) - v(1) - v_H(1)$$

$$v_s(1) = v(1) + v_H(1) + v_{xc}(1)$$

Since this is the potential for a noninteracting system with density  $n(\mathbf{r},t)$  we obtain the Kohn-Sham equations :

**input known external potential**


$$\left(-\frac{1}{2}\nabla^2 + v(1) + v_H(1) + v_{xc}(1)\right)\phi_i(1) = i\partial_t\phi_i(1)$$

$$n(1) = \sum_{i=1}^{\infty} f_i |\phi_i(1)|^2$$

$$v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)}$$



**output density  $n[v]$**



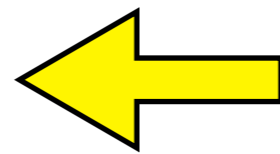
How to find an approximation for this ?

# Connection to the time-dependent pair-correlation function

We connect the true system to the Kohn-Sham system by means of a coupling constant integration (standard trick of ground state DFT):

$$\tilde{A}^\lambda[v_\lambda] = i \ln \text{Tr} \left\{ T_C \exp \left( -i \int_C dt (\hat{T} + \hat{V}_\lambda(t) + \lambda \hat{W}) \right) \right\}$$

$$\hat{V}_\lambda = \int d\mathbf{r} \hat{n}(\mathbf{r}) v_\lambda(\mathbf{r}t)$$



$\lambda$  dependence of the potential is such that density is  $\lambda$  independent

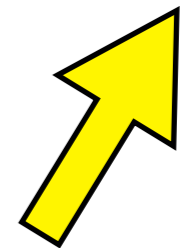
We then use

$$\tilde{A}^1[v_1] = \tilde{A}^0[v_0] + \int_0^1 d\lambda \frac{dA^\lambda[v_\lambda]}{d\lambda}$$

The differentiation with respect to the coupling constant then gives

$$\tilde{A}[v] = \tilde{A}_s[v_s] + \int_0^1 d\lambda \int_C d1 n(1) \frac{dv_\lambda(1)}{d\lambda} + \int_0^1 d\lambda \int_C d1 d2 w(1, 2) \Gamma^\lambda(1, 2)$$

$$w(1, 2) = \frac{\delta(t_1, t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$



Diagonal two-particle density matrix

from which we then directly obtain

$$A_{xc}[n] = \frac{1}{2} \int_C d1 d2 w(1, 2) \left( \int_0^1 d\lambda \Gamma^\lambda(1, 2) - n(1)n(2) \right)$$

We thus obtain the time-dependent generalization of the coupling constant integration formula of ground state DFT

$$A_{xc}[n] = \frac{1}{2} \int_C d1d2 \frac{\delta(t_1, t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} n(1)n(2)(\bar{g}(1, 2) - 1)$$

$$\bar{g}(1, 2) = \int_0^1 d\lambda g_\lambda(1, 2)$$

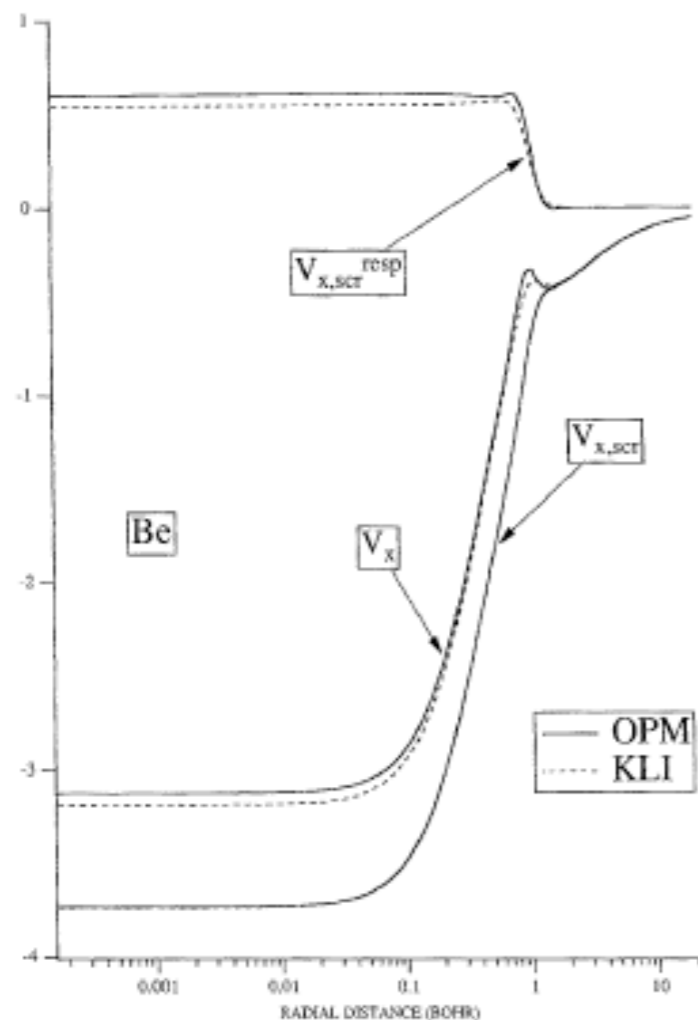
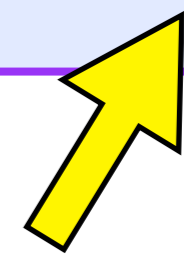
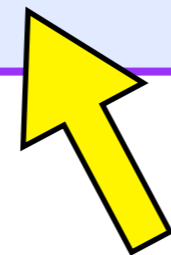
Coupling constant averaged pair correlation function

$$g(1, 2) = \frac{\Gamma(1, 2)}{n(1)n(2)}$$



# Time-dependent xc-potential

$$v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)} = \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2 t_1)(\bar{g}(\mathbf{r}_1, \mathbf{r}_2; t_1) - 1)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2} \int_C d^2d^3 \delta(t_2, t_3) \frac{n(2)n(3)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\delta \bar{g}(2, 3)}{\delta n(1)}$$



Long range  $-1/r$  behavior outside finite system

Short range with step structure

See for ground state DFT e.g. RvL, Oleg Gritsenko, Evert Jan Baerends, Zeitschrift für Physik D33, 229 (1995)

## The xc-kernel

Time-local part of the xc-kernel is proportional to the pair-correlation function

$$f_{xc}(1, 2) = \frac{\delta^2 A_{xc}}{\delta n(1)\delta n(2)} = \frac{\delta(t_1, t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\bar{g}(1, 2) - 1)$$

$$+ \int_C d^3 n(3) \frac{\delta(t_1, t_3)}{|\mathbf{r}_1 - \mathbf{r}_3|} \left[ \frac{\delta \bar{g}(1, 3)}{\delta n(2)} + \frac{\delta \bar{g}(1, 2)}{\delta n(3)} \right]$$

$$+ \frac{1}{2} \int_C d^3 d4 \frac{\delta(t_3, t_4)}{|\mathbf{r}_3 - \mathbf{r}_4|} n(3)n(4) \frac{\delta^2 \bar{g}(3, 4)}{\delta n(3)\delta n(4)}$$

Time  
nonlocal part  
of the  
xc-kernel

Responsible for frequency dependence : memory

# Many-body perturbation theory

We define the contour-ordered Green function as :

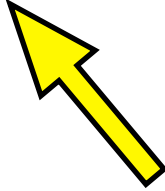
$$G(1, 2) = -i \langle T_C [\hat{\psi}_H(1) \hat{\psi}_H^\dagger(2)] \rangle = \theta(t_1, t_2) G^>(1, 2) + \theta(t_2, t_1) G^<(1, 2)$$

$$G^>(1, 2) = -i \langle \hat{\psi}_H(1) \hat{\psi}_H^\dagger(2) \rangle \quad \text{Propagation of a "particle" (added electron)}$$

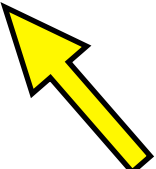
$$G^<(1, 2) = i \langle \hat{\psi}_H^\dagger(2) \hat{\psi}_H(1) \rangle \quad \text{Propagation of a "hole" (removed electron)}$$

# The equation of motion

$$(i\partial_{t_1} - h(1))G(1, 2) = \delta(1, 2) + \int d^3 \Sigma[G](1, 3)G(3, 2)$$



Time-dependent  
external fields  
are treated exactly  
nonperturbatively



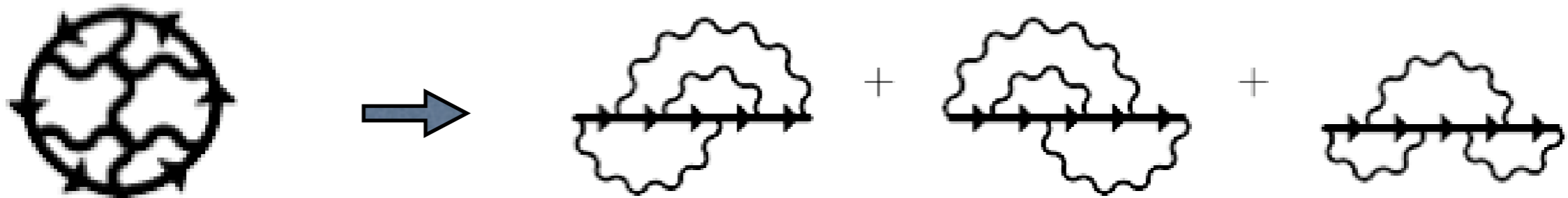
The self-energy operator  $\Sigma [G]$  is  
nonhermitian and nonlocal  
in space and time.  
All the physics of electron correlations  
is contained in  $\Sigma [G]$ !

# The conservation laws

( G.Baym, Phys.Rev. 127, 1391 (1962))

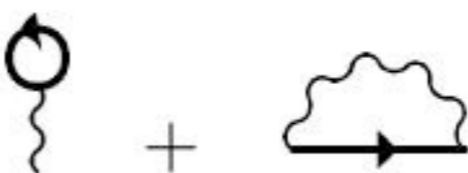
Conservation laws, such as those of energy, momentum, angular momentum and particle number, are automatically obeyed when we use so-called Phi-derivable approximations for the self-energy.


$$\Sigma(1, 2) = \frac{\delta\Phi}{\delta G(2, 1)}$$

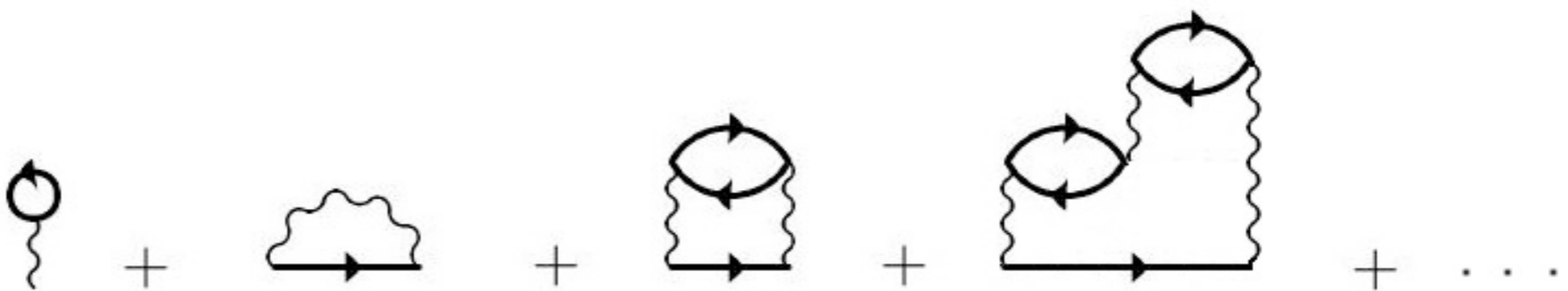


For Phi-derivable approximations the expectation values are independent from the way they are calculated

# Conserving many-body approximations

**Hartree-Fock**  $\Sigma =$  

**2<sup>nd</sup> Born**  $\Sigma =$  

**GW**  $\Sigma =$  

# Action functionals

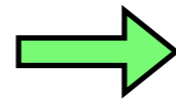
The equation of motion of the Green function can be derived from an action principle with action:

$$iA[G] = \Phi[G] - \text{tr} \left\{ \ln(-G^{-1}) + (G_0^{-1}G - 1) \right\}$$

where



Baym's Phi-functional



$$\frac{\delta\Phi}{\delta G} = \Sigma$$

and

$$G_0^{-1}(1, 2) = (i\partial_{t_1} - h(1))\delta(1, 2)$$

(Ulf von Barth, Nils Erik Dahlen, RvL, Gianluca Stefanucci, Phys.Rev.B72, 235109 (2005) )

Proof:

$$iA[G] = \Phi[G] - \text{tr} \left\{ \ln(-G^{-1}) + (G_0^{-1}G - 1) \right\}$$

$$\rightarrow 0 = i \frac{\delta A}{\delta G} = \frac{\delta \Phi}{\delta G} + G^{-1} - G_0^{-1} \quad \times G$$

$$\rightarrow G_0^{-1}G = 1 + \Sigma G$$

$$(i\partial_{t_1} - h(1))G(1, 2) = \delta(1, 2) + \int d^3 \Sigma(1, 3)G(3, 2)$$

$$\frac{\delta \Phi}{\delta G} = \Sigma$$



# Constructing new conserving xc-functionals with memory

Let us now restrict the domain of Green functions to those of noninteracting systems with external potential  $v_s$

$$A[v_s] = A[G_s[v_s]]$$

where  $(i\partial_{t_1} - h_s(1))G_s(1, 2) = \delta(1, 2)$

We can now look for the stationary point in the restricted domain:

$$\frac{\delta A}{\delta v_s} = 0$$

Because of the density-potential relation this is a density functional theory!!

Let us see what we get :

$$iA[v_s] = \Phi[G_s] - \text{tr} \left\{ \ln(-G_s^{-1}) + (G_0^{-1}G_s - 1) \right\}$$

$$\longrightarrow 0 = i\delta A = \text{tr} \left\{ (\Sigma[G_s] - G_s^{-1} + G^{-1}) \frac{\delta G_s}{\delta v_s} \delta v_s \right\}$$

We obtain the following equation for the xc-potential :

$$\int_C d2 \chi_s(1, 2) v_{xc}(2) = -i \int_C d2 d3 G_s(1, 2) (\Sigma[G_s](2, 3) - \delta(2, 3) v_H(3)) G_s(3, 1)$$

Kohn-Sham density  
reponse function

These are the TDOEP equations

We can take another functional derivative and obtain equations for the xc-kernel of TDDFT.

We obtain, for instance, within the x-only approximation:

$$\begin{array}{c}
 \text{Bubble} \text{---} \text{Diamond } f_x \text{---} \text{Bubble} = \text{Bubble} \text{---} \text{Vertex } iV_x \text{---} \text{Bubble} + \text{Bubble} \text{---} \text{Wavy} \text{---} \text{Bubble} \\
 + \text{Bubble} \text{---} \text{Vertex } iV_x \text{---} \text{Bubble} + \text{Bubble} \text{---} \text{Wavy} \text{---} \text{Bubble} \\
 + \text{Bubble} \text{---} \text{Wavy} \text{---} \text{Bubble}
 \end{array}$$

$$\text{Wavy} = -iv (1,2)$$

This equation has recently been solved for atomic systems (M.Hellgren,U.von Barth, Phys.Rev.B78, 115107 (2008), J.Chem.Phys. 131, 044110 (2009))

# Example II: GW within TDDFT (Klein functional)

$$\Phi_{\text{GW}} = -\frac{1}{2} \text{[Diagram 1]} - \frac{1}{4} \text{[Diagram 2]} - \frac{1}{6} \text{[Diagram 3]} + \dots$$

$$\Sigma_{\text{GW}} = \text{[Diagram 4]} + \text{[Diagram 5]} + \text{[Diagram 6]} + \dots$$

The expression for the xc-kernel becomes :

$$\begin{aligned}
 & \text{[Diagram 7]} = \text{[Diagram 8]} + \text{[Diagram 9]} + \text{[Diagram 10]} + \text{[Diagram 11]} + \text{[Diagram 12]} + \text{[Diagram 13]} + \text{[Diagram 14]} \\
 & \text{[Diagram 15]} = -i W
 \end{aligned}$$

## Important properties of the variationally derived functionals

- The zero-force, zero-torque theorems of TDDFT are obeyed

$$0 = \int d\mathbf{r} n(\mathbf{r}t) \nabla v_{xc}[n](\mathbf{r}t)$$

- The density response functions derived from the xc-kernels satisfy important sumrules.
- Correlation induced memory naturally included

(Ulf von Barth, Nils Erik Dahlen, RvL, Gianluca Stefanucci, Phys.Rev.B72, 235109 (2005) )

## Luttinger Ward form of the functional

By using the Dyson equation we can transform the functional to a different form:

$$i\tilde{A}_0[G] = \Phi[G] - \text{tr} \left\{ \ln(-G^{-1}) + (G_0^{-1}G - 1) \right\}$$

Klein functional (Phys.Rev.121,950, (1961))

$$i\tilde{A}_0[G] = \Phi[G] - \text{tr} \left\{ \Sigma G + \ln(\Sigma - G_0^{-1}) \right\}$$

Luttinger-Ward functional (Phys.Rev.118,1417 (1960))

Nils Erik Dahlen, RvL, Ulf von Barth, Phys.Rev.A73, 012511 (2006)

If we differentiate the LW functional at fixed external potential we find that

$$i\delta\tilde{A} = \text{tr} \left\{ \left( \frac{\delta\Phi}{\delta G} - \Sigma \right) \delta G \right\} - \text{tr} \left\{ \left( G - (\Sigma - G_0^{-1})^{-1} \right) \delta \Sigma \right\} = 0$$

The Luttinger-Ward functional is stationary when the Dyson equation is obeyed and when the self-energy is Phi-derivable :

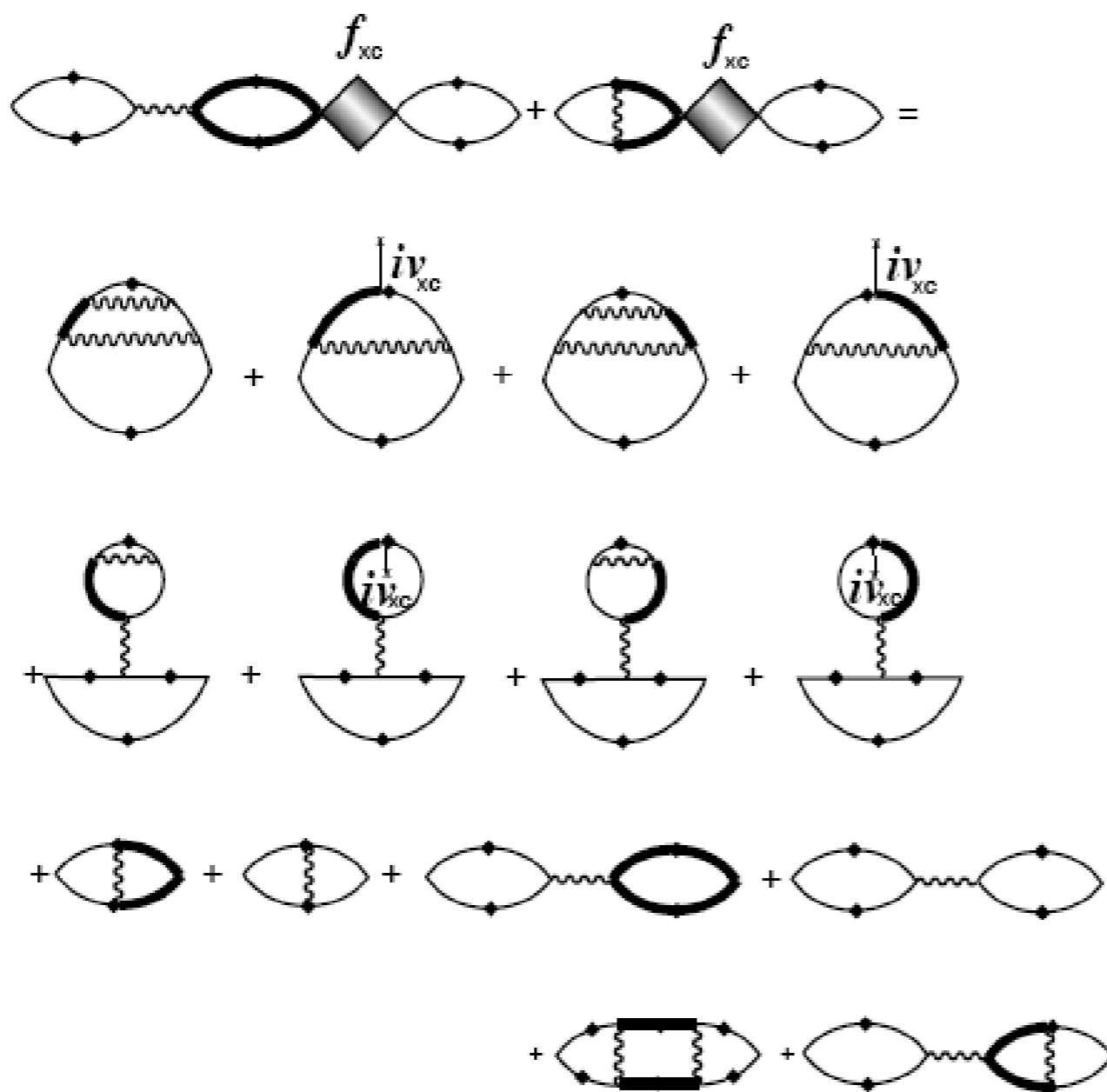
$$G = G_0 + G_0 \Sigma G \qquad \frac{\delta\Phi}{\delta G} = \Sigma$$

The Klein and LW functional are equivalent when evaluated for interacting Green functions but different when evaluated on a smaller domain.

# Variational TDDFT : The Luttinger-Ward functional

$$i\tilde{A}_{LW}[v_s] = \Phi[G_s] - \text{tr} \left\{ \Sigma[G_s]G_s + \ln(\Sigma[G_s] - G_0^{-1}) \right\}$$

The expression for the xc-kernel from an x-only Phi functional :



$$\Phi = -\frac{1}{2} \text{ (diagram of a loop with a wavy line) }$$

$$\Sigma = \text{ (diagram of a loop with a wavy line) }$$

$$\tilde{G} = G_0 + G_0 \Sigma[G_s] \tilde{G}$$



# Luttinger-Ward functional applied to atoms and molecules

$$\Phi_{\text{MP2}} = -\frac{1}{2} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)}$$

$$\Sigma_{\text{MP2}} = \text{ (diagram)} + \text{ (diagram)} + \text{ (diagram)}$$

TABLE I: Total energies calculated from the self-consistent Green function and from the Luttinger-Ward functional evaluated at the HF and LDA Green functions. All energies are in Hartrees.

	$E_{\text{LW}}^{(2)}[G_{\text{LDA}}]$	$E_{\text{LW}}^{(2)}[G_{\text{HF}}]$	SC
He	-2.8937	-2.8969	-2.8969
Be	-14.5953	-14.6405	-14.6409
Ne	-128.8068	-128.8332	-128.8339
Mg	-199.8933	-199.9093	-199.9097
Mg <sup>2+</sup>	-199.0918	-199.1025	-199.1020
H <sub>2</sub>	-1.1595	-1.1658	-1.1659
LiH	-8.0394	-8.0526	-8.0528

(Nils Erik Dahlen, RvL, J.Chem.Phys. 122, 164102 (2005),  
Nils Erik Dahlen, RvL, Ulf von Barth, Phys.Rev.A73, 012511 (2006) )

# Luttinger-Ward (GW)

## Total energies

	SC-GW	LW[ $G_{\text{HF}}$ ]
He	-2.9278	-2.9277
Be	-14.7024	-14.7017
Ne	-129.0499	-129.0492
Mg	-200.1762	-200.1752
H <sub>2</sub>	-1.1887	-1.1888
LiH	-8.0995	-8.0997

## 2-electron removal energies

	SC-GW	HF	LW[ $G_{\text{HF}}$ ]	Exp
Mg-Mg <sup>2+</sup>	22.59 eV	21.33 eV	22.58 eV	22.68 eV
Be-Be <sup>2+</sup>	27.59 eV	26.17 eV	27.57 eV	27.53 eV

# Conclusions

- There is clear need to go beyond the adiabatic approximation to describe various physical phenomena (double excitations, quantum transport,..)
- Temporal nonlocality implies spatial nonlocality, in order to comply with basic conservation laws
- The nonequilibrium many-body theory can be used to derive new TDDFT functionals with nice properties
  - Conserving
  - Memory
  - Derivative discontinuities

This is a very nice feature of the variational schemes based on the Luttinger-Ward functional

# Outlook

- We aim to test variationally derived functionals for quantum transport phenomena as a first test case (work in progress in Jyväskylä)  
Collaboration with Gianluca Stefanucci (Rome)
- Maria Hellgren and Ulf von Barth have been exploring in detail the xc-kernels that can be derived from the action formalism.  
The Klein functionals leads to problems for spectral properties:  
there is a need to explore the Luttinger-Ward functionals.
- However:  
Correlation energies and potentials, van der Waals coefficients and polarizabilities have turned out to be of excellent quality  
(the Peuckert iteration scheme)

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