Part II

Density functionals from many-body theory

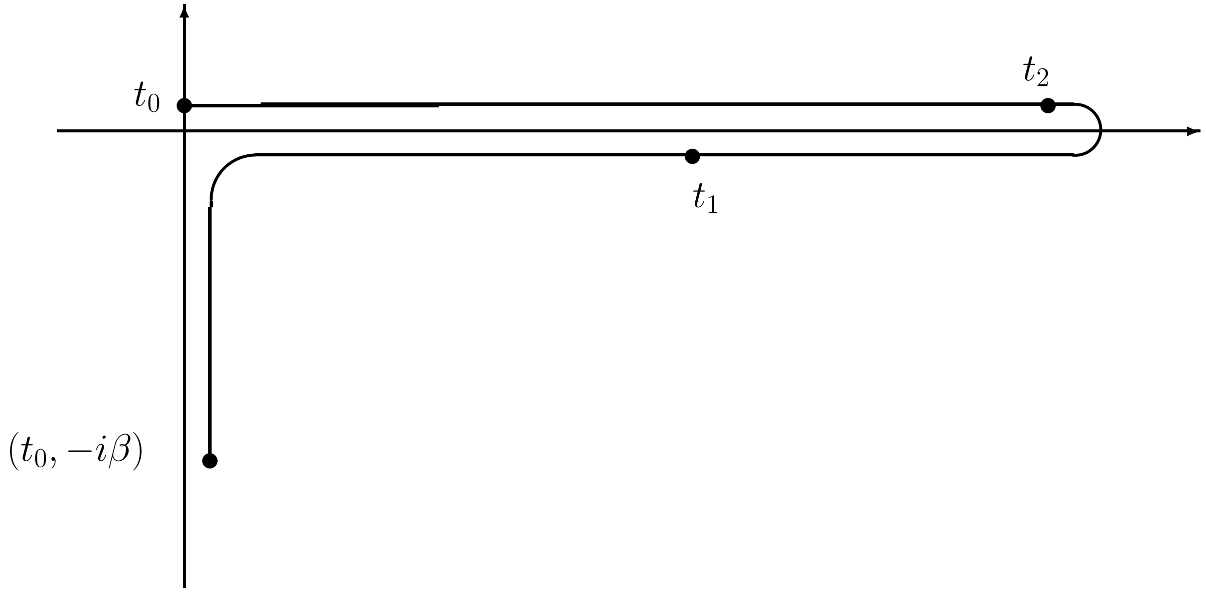
- Kohn-Sham equations and the action functional
- Adiabatic connection in TDDFT
- Conserving density functionals and the xc-kernel

The time contour action functional

We define the following action functional :

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

Where we used the time contour ordered evolution operator of nonequilibrium Green function theory



Why is the action defined like this ?

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

partition function of statistical mechanics

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

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

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

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

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

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The action as a density functional

We then define the density functional :

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

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

This functional has the property :

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

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

So this is our variational principle:

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

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:

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

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

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

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

Differentiation gives :

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

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

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

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

input known external potential

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

$$n(1) = \sum_{i=1}^{\infty} f_i\,|\phi_i(1)|^2 \qquad v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)}$$

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):

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

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

λ dependence of the potential is such that density is λ 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

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

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

Coupling constant averaged pair correlation function

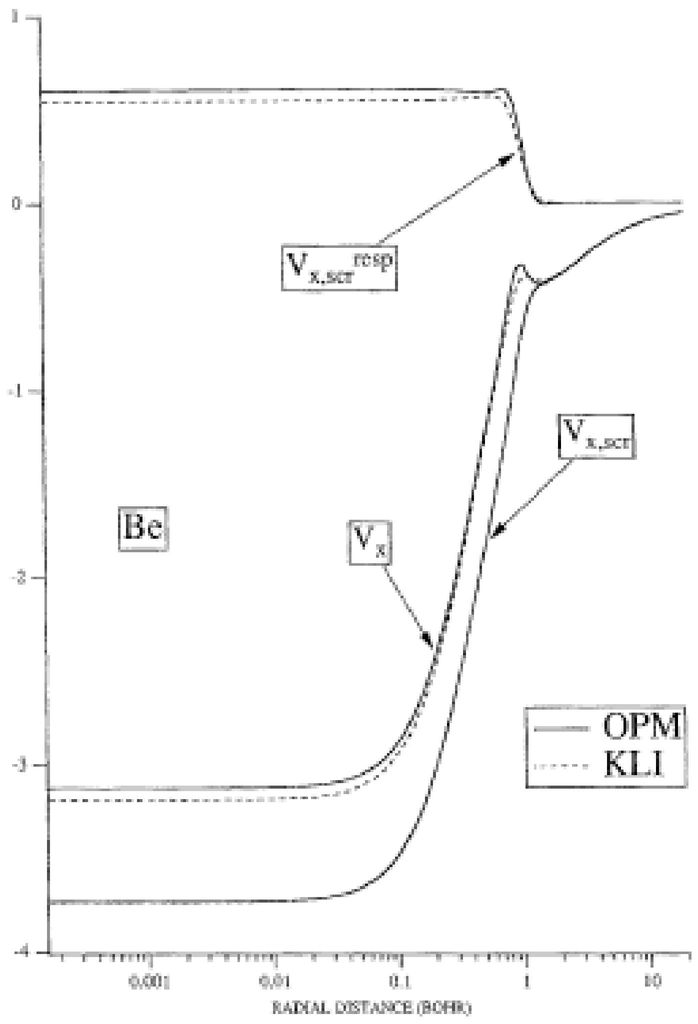
$$g(1,2) = \frac{\Gamma(1,2)}{n(1)n(2)}$$

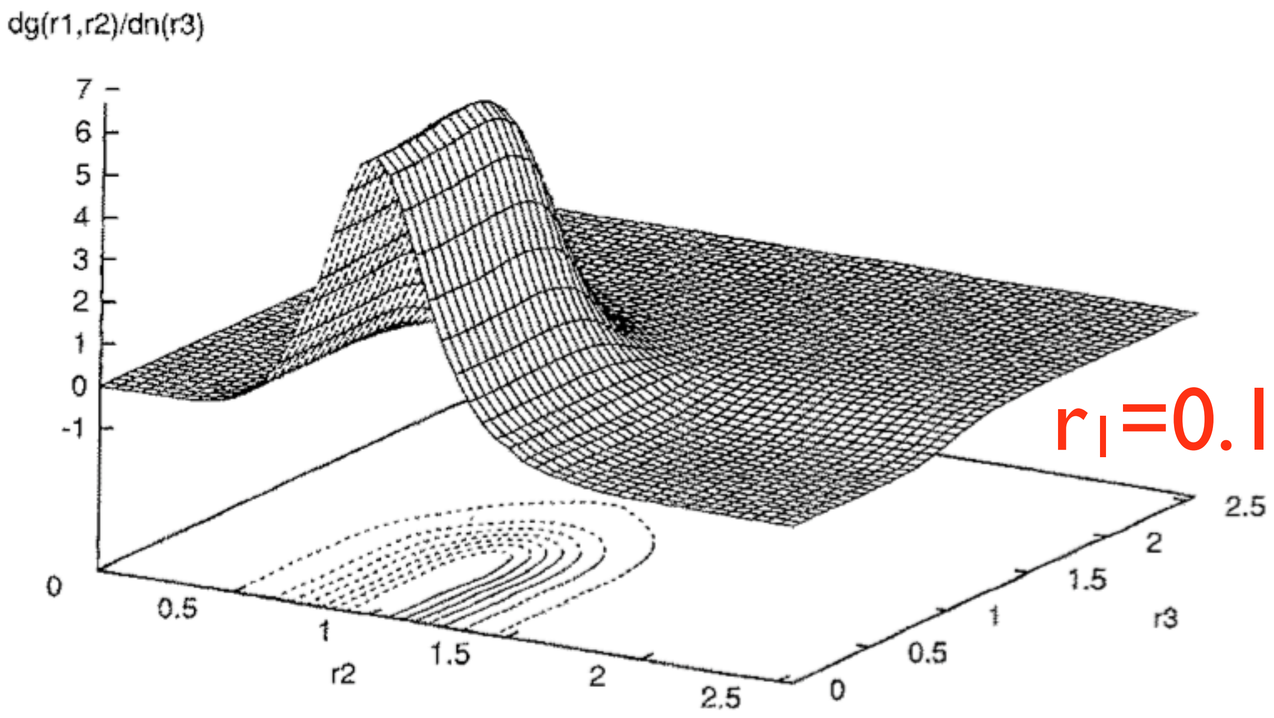
Time-dependent xc-potential

$$v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)} = \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2 t_1)(\bar{g}(\mathbf{r}_1, \mathbf{r}_2; t_1) - 1)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{2} \int_C d2d3\, \delta(t_2, t_3) \frac{n(2)n(3)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\delta \bar{g}(2,3)}{\delta n(1)}$$

Long range -1/r behavior outside finite system

Short range with step structure





r_1=0.1

See RvL, O.Gritsenko, E.J.Baerends, Zeitschrift für Physik D33, 22(1995)

The xc-kernel

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

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

$$+ \int_C d3\, n(3) \frac{\delta(t_1,t_3)}{|\mathbf{r}_1 - \mathbf{r}_3|} \left[\frac{\delta \bar{g}(1,3)}{\delta n(2)} + \frac{\delta \bar{g}(1,2)}{\delta n(3)} \right]$$

$$+ \frac{1}{2} \int_C d3d4\, \frac{\delta(t_3,t_4)}{|\mathbf{r}_3 - \mathbf{r}_4|}\, n(3)n(4)\, \frac{\delta^2 \bar{g}(3,4)}{\delta n(3)\delta n(4)}$$

Time nonlocal part of the xc-kernel

Responsible for frequency dependence : memory

Action functionals

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

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

where

Baym's Phi-functional ⇨ $\dfrac{\delta\Phi}{\delta G} = \Sigma$

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:

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

➡ $$0 = i\frac{\delta A}{\delta G} = \frac{\delta \Phi}{\delta G} + G^{-1} - G_0^{-1}$$ **x G**

➡ $$G_0^{-1}G = 1 + \Sigma G$$

$$(i\partial_{t_1} - h(1))G(1,2) = \delta(1,2) + \int d3\, \Sigma(1,3)G(3,2)$$

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

Constructing new conserving xc-functionals with memory

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

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

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:

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

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

Let us see what we get :

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

$$\Longrightarrow \quad 0 = i\delta A = \mathrm{tr}\;\left\{(\Sigma[G_s] - G_s^{-1} + G^{-1})\frac{\delta G_s}{\delta v_s}\,\delta v_s\right\}$$

We obtain the following equation for the xc-potential :

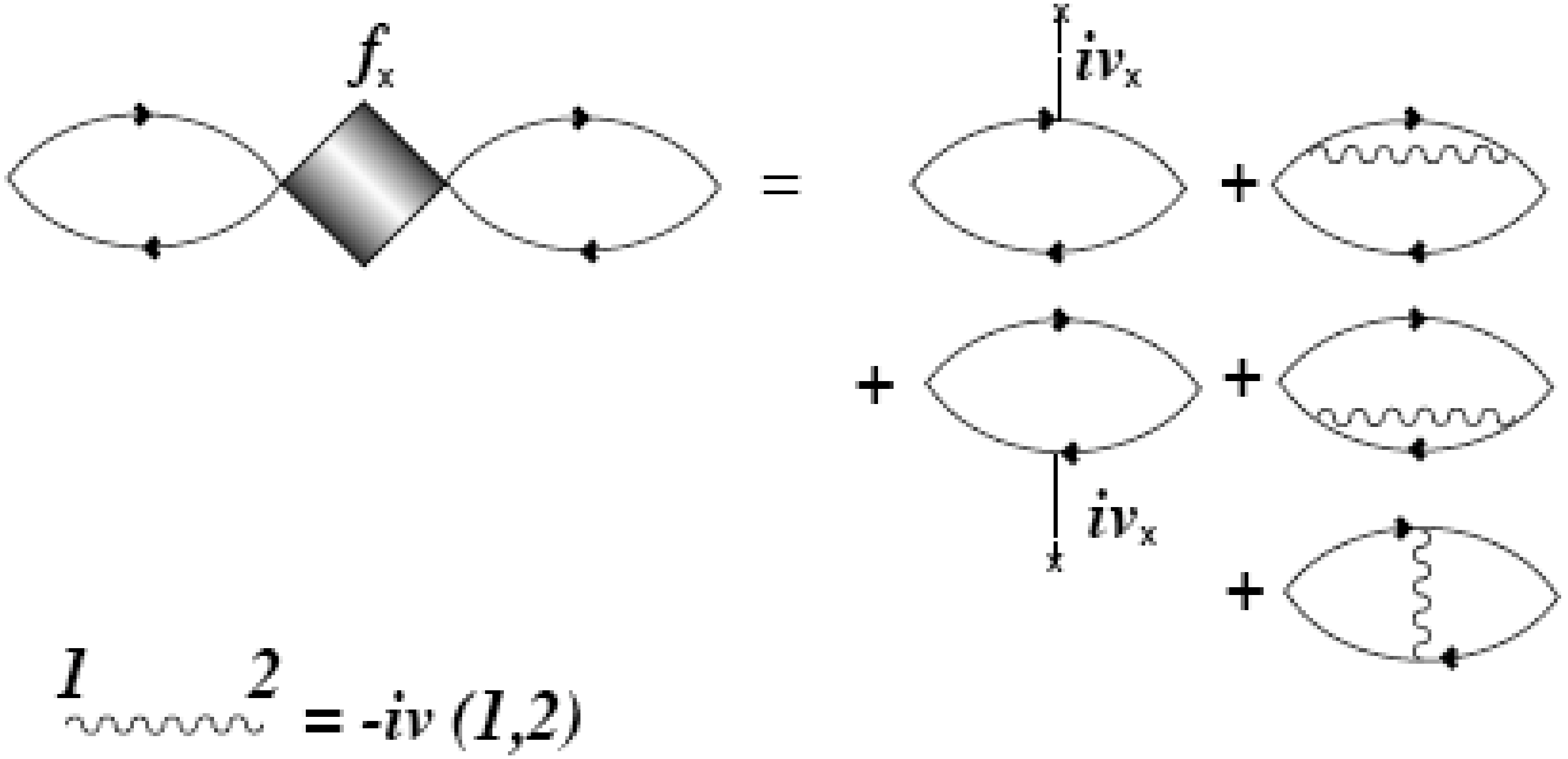
$$\boxed{\int_C d2\underset{\Uparrow}{\chi_s}(1,2)v_{xc}(2) = -i\int_C d2d3G_s(1,2)(\Sigma[G_s](2,3) - \delta(2,3)v_H(3))G_s(3,1)}$$

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:



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

The corresponding fx-kernel has unphysical double pole structure that make inner shell excitations disappear from the atomic spectra

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:

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

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

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

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

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

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

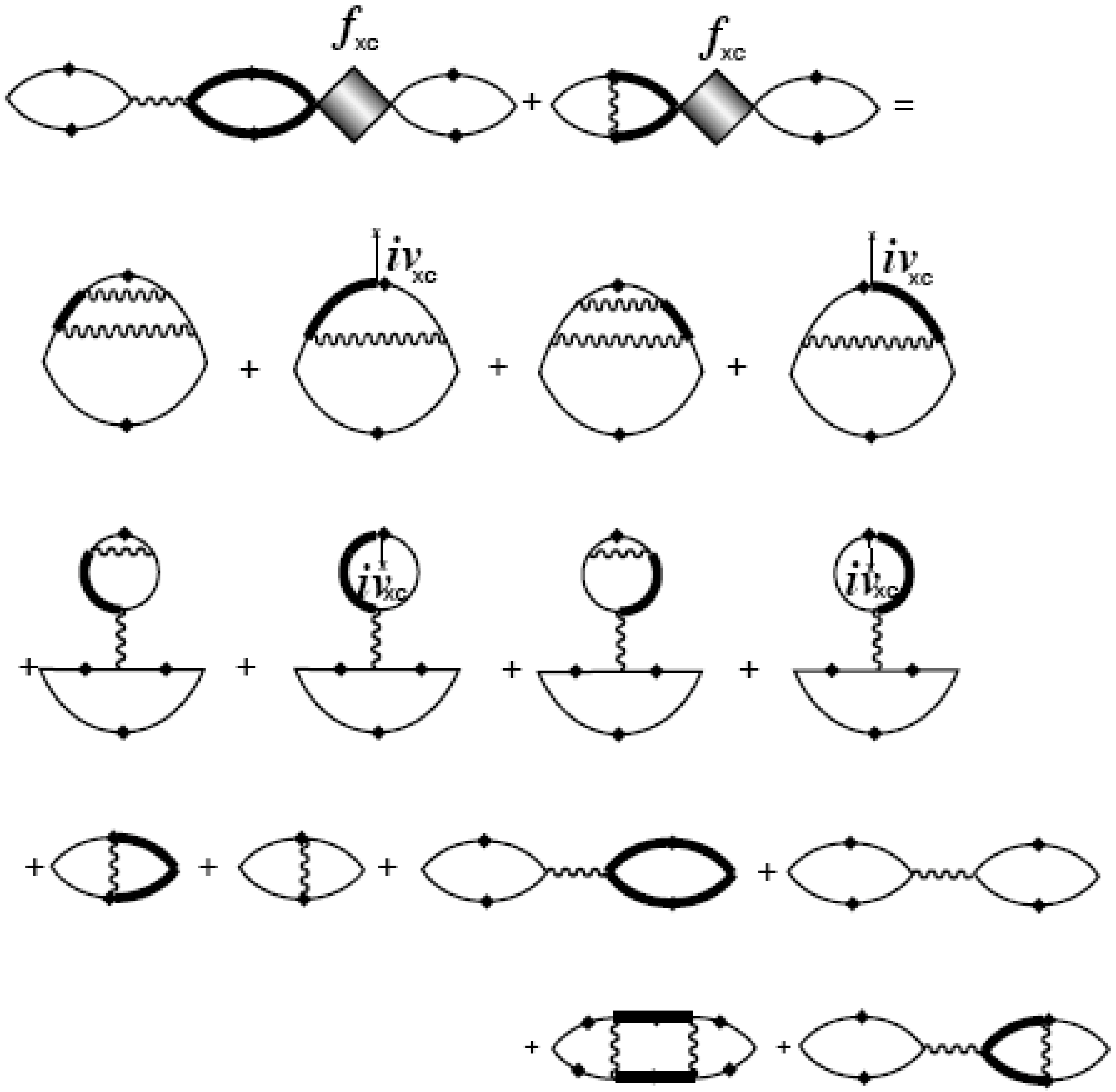
$$G = G_0 + G_0\Sigma G \qquad \frac{\delta\Phi}{\delta G} = \Sigma$$

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

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

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



$$\Phi = -\frac{1}{2}$$

$$\Sigma =$$

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

The corresponding fxc-kernel has now a proper single-pole structure

Conclusions

- There is clear need to go beyond the adiabatic approximation to describe various physical phenomena (double excitations, quantum transport,..)

- The nonequilibrium many-body theory can be used to derive new TDDFT functionals with nice properties
  - Conserving
  - Memory
  - Derivative discontinuities