Lecture 2

- Memory and causality in TDDFT
- The time contour action principle
- The Vignale action principle
The Runge-Gross theorem

\[
\begin{align*}
(i \partial_t - (\hat{T} + \hat{V}_1(t) + \hat{W}))\Psi_1(t) &= 0 \\
(i \partial_t - (\hat{T} + \hat{V}_2(t) + \hat{W}))\Psi_2(t) &= 0 \\
\Psi_1(t_0) &= \Psi_2(t_0) = \Psi_0
\end{align*}
\]

\[\hat{V}_1(t) \neq \hat{V}_2(t) + C(t) \implies n_1(t) \neq n_2(t)\]

Any observable is a functional of the density and the initial state

\[O[n, \Psi_0](t) = \langle \Psi[n](t) | \hat{O} | \Psi[n](t) \rangle\]
causality and memory (I)

Direct consequence of the RG theorem:

If \( v_1 = v_1 \) for \( t < T \) but different for later times then

\[ n[v_1](t) \]

\[ n[v_2](t) \]

\( v[n] \) in the interval \([0,T] \) can only be determined by the density in the interval \([0,T] \) and cannot depend on the density at later times \((\text{causality})\)
causality and memory (2)

\[ n[v_1](t) \]

\[ n[v_2](t) \]

same density at t=T,
different potentials

\[ v[n](T) \] not determined by \( n(T) \) alone
\[ v[n] \] must have memory of the density at earlier times
General remarks on the action principle in TDDFT

- The time-dependent Kohn-Sham equations can be derived without recourse to an action principle (see lectures Hardy Gross)

- There is no unique action principle

- The value of the time-dependent action is in general not interesting

The main practical use of the action principle in TDDFT is to derive equations for xc-functionals that have nice properties automatically build in (conservation laws, symmetries) (see Lecture 1)
The time contour action functional

We define the following action functional:

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

Where we used the same time contour evolution operator of Lecture 1 where we discussed many-body perturbation theory.
Why is the action defined like this?

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

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

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

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:

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

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:

\[ A[n] = -\tilde{A}[v] + \int_C d1n(1)v(1) \]

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

This functional has the property:

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

\[
\frac{\delta A[n]}{\delta n(r, t)} = v(r, t)
\]
So this is our variational principle:

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

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:

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

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

There is nothing new to derive. We already know that

\[
\frac{\delta \tilde{A}_s[v_s]}{\delta v_s(\mathbf{r}, t)} \bigg|_{v_+ = v_-} = n(\mathbf{r}, t)
\]
As for the interacting system we define

\[ A_s[n] = -\tilde{A}_s[v_s] + \int_C d1n(1)v_s(1) \]

\[ \frac{\delta A_s[n]}{\delta n(r, t)} = v_s(r, t) \]

The xc action functional is then defined as

\[ A_{xc}[n] = A_s[n] - A[n] - \frac{1}{2} \int_C d1 \int_C d2 \delta(t_1, t_2) \frac{n(1)n(2)}{|r_1 - r_2|} \]

Differentiation gives:

\[ v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)} = \frac{\delta A_s}{\delta n(1)} - \frac{\delta A}{\delta n(1)} - v_H(1) \]
Since this is the potential for a noninteracting system with density $n(r,t)$ we obtain the Kohn-Sham equations:

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

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

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

**input known external potential**

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

**How to find an approximation for this?**
Finding explicit expressions for $A_{xc}$

This has all been rather abstract, but we managed to find some useful equations.

Let us try to calculate an explicit expression for the exchange-correlation part of the action using perturbation theory.

$$A_{xc}[n] = A_s[n] - A[n] - \frac{1}{2} \int_C d1 \int_C d2 \delta(t_1, t_2) \frac{n(1)n(2)}{|r_1 - r_2|}$$

$$= i \ln \text{Tr} \left\{ T_C \exp \left( -i \int_C dt \, \hat{H}(t) \right) \right\} - \int_C dr dt n(rt)v(rt)$$

$$- i \ln \text{Tr} \left\{ T_C \exp \left( -i \int_C dt \, \hat{H}_s(t) \right) \right\} + \int_C dr dt n(rt)v_s(rt)$$

$$- \frac{1}{2} \int_C dr_1 dt_1 \int_C dr_2 dt_2 \delta(t_1, t_2) \frac{n(r_1t_1)n(r_2t_2)}{|r_1 - r_2|}$$
Let’s expand the true Hamiltonian around the Kohn-Sham one

\[ \hat{H}_\lambda(t) = \hat{H}_s(t) + \lambda(\hat{H}(t) - \hat{H}_s(t)) \]

To first order in \( \lambda \) we find:

\[
\tilde{A}_\lambda[v] = i \ln \text{Tr} \left\{ T_C \exp \left( -i \int_C dt \hat{H}_s(t) + \lambda(\hat{H}(t) - \hat{H}_s(t)) \right) \right\}
\]

\[
= \tilde{A}_s[v_s] + \lambda \int_C \frac{\text{Tr} \left\{ \hat{U}_s(t_0 - i\beta, t)(\hat{H}(t) - \hat{H}_s(t))\hat{U}_s(t, t_0) \right\}}{\text{Tr} \left\{ \hat{U}_s(t_0 - i\beta, t_0) \right\}} + O(\lambda^2)
\]

\[
= \tilde{A}_s[v_s] + \lambda \int_C dt \langle \hat{W} + \hat{V}(t) - \hat{V}_s(t) \rangle_s + O(\lambda^2)
\]

\[
= \tilde{A}_s[v_s] + \lambda \int_C dt \langle \hat{W} \rangle_s + \lambda \int_C dtdr n(rt)(v(rt) - v_s(rt)) + O(\lambda^2)
\]
After some algebra we find to first order

\[ A_x[n] = \frac{1}{2} \int_C d1d2 \delta(t_1, t_2) \frac{|\gamma(1, 2)|^2}{|r_1 - r_2|} \]

\[ \gamma(1, 2) = \sum_i f_i \phi_i(r_1 t_1) \phi^*_i(r_2 t_1) \]

For stationary systems at zero temperature this yields the exchange energy functional known from stationary DFT:

\[ E_x[n] = \lim_{T \to 0} \frac{iA_x[n]}{\beta} = \sum_{i,j} \int dr_1 dr_2 \frac{\phi_i(r_1) \phi^*_i(r_2) \phi_j(r_2) \phi^*_j(r_1)}{|r_1 - r_2|} \]
The optimized effective potential (TDOEP)

How to obtain the xc-potential from an orbital functional? One can use the chain rule to obtain:

\[
v_{xc}(1) = \frac{\delta A_{xc}}{\delta n(1)} = \int_{C'} d^2 \frac{\delta A_{xc}}{\delta v_s(2)} \frac{\delta v_s(2)}{\delta n(1)}
\]

\[
\int_{C'} d^2 \chi_s(1, 2) v_{xc}(2) = \frac{\delta A_{xc}}{\delta v_s(1)} = Q_{xc}(1)
\]

In real time one has:

\[
\int_{t_0}^{t_1} d^2 (\chi_s^> (1, 2) - \chi_s^< (1, 2)) v_{xc}(2) + \int_0^{-i\beta} d^2 \chi_s^\dagger (1, 2) v_{xc}(2) = Q_{xc}(1)
\]

Retarded density response function
Some intermediate conclusions

- There is a well-defined action principle that yield can be used to derive the time-dependent Kohn-Sham equations

- The action reduces to the usual energy functional in the stationary case

- The action can be used to derive expressions for the xc potential using perturbation expansions

(in fact, there is a diagrammatic expansion in terms of nonequilibrium Green functions, not discussed here)

What about the action defined in the Runge-Gross paper?
The Vignale Action Principle


We consider the action functional

\[ A_v[n] = \int_{0}^{T} dt \langle \Psi[n](t) | i \partial_t - \hat{H}_v(t) | \Psi[n](t) \rangle \]

The density does not determine the phase of the wave function uniquely (see lectures Hardy Gross)

We choose the phase in \( \Psi[n](t) \) by requiring that it is generated by a Hamiltonian in which the external potential vanishes at infinity (this is a gauge choice)
Let's look at a variation of the action

\[ \delta A_v = \int_0^T dt \langle \delta \Psi[n](t) | i \partial_t - \hat{H}_v(t) | \Psi[n](t) \rangle \]

\[ \quad + \int_0^T dt \langle \Psi[n](t) | i \partial_t - \hat{H}_v(t) | \delta \Psi[n](t) \rangle \]

Which after a partial integration yields

\[ \delta A_v = \int_0^T dt \langle \delta \Psi[n](t) | i \partial_t - \hat{H}_v(t) | \Psi[n](t) \rangle + c.c. \]

\[ \quad + i \langle \Psi(T) | \delta \Psi(T) \rangle - i \langle \Psi(0) | \delta \Psi(0) \rangle \]

In TDDFT the variations must be \( \nu \)-representable!
In the Runge-Gross theorem we consider systems starting from a common initial state. We can therefore require that

$$\delta \Psi(0) = 0$$

However, for v-representable variations $\delta \Psi(T) \neq 0$

Our variational equation therefore becomes

$$\delta A_v - i \langle \Psi(T) | \delta \Psi(T) \rangle$$

$$= \int_0^T dt \langle \delta \Psi[n](t) | i \partial_t - \hat{H}_v(t) | \Psi[n](t) \rangle + c.c.$$
We have therefore established the following variational principle

\[
\delta A_v - i\langle \Psi(T) | \delta \Psi(T) \rangle = 0
\]

\[
\text{---} \quad \quad (i\partial_t - \hat{H}(t))|\Psi(t)\rangle = 0 \quad \text{---}
\]

The determining principle for the density is therefore

\[
\frac{\delta A_v}{\delta n(\mathbf{r}t)} - i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = 0
\]

Vignale variational principle
Let us work out this in more detail. We can write (copying the RG paper)

\[ A_v[n] = \int_0^T dt \langle \Psi[n](t) | i\partial_t - \hat{T} - \hat{V}(t) - \hat{W} | \Psi[n](t) \rangle \]

\[ = A_0[n] - \int_0^T dt d\mathbf{r} \ n(\mathbf{r}t) v(\mathbf{r}t) \]

where we defined

\[ A_0[n] = \int_0^T dt \langle \Psi[n](t) | i\partial_t - \hat{T} - \hat{W} | \Psi[n](t) \rangle \]

The Vignale variational principle then tells us that

\[ i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = \frac{\delta A_v}{\delta n(\mathbf{r}t)} = \frac{\delta A_0}{\delta n(\mathbf{r}t)} - v(\mathbf{r}t) \]
The external potential is thus determined by the functional derivative of an action plus a boundary term

\[ v(\mathbf{r}t) = \frac{\delta A_0}{\delta n(\mathbf{r}t)} - i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle \]

The boundary term is real, as can derived from the wave function normalization

\[ 0 = \frac{\delta}{\delta n} \langle \Psi | \Psi \rangle = \langle \frac{\delta \Psi}{\delta n} | \Psi \rangle + \langle \Psi | \frac{\delta \Psi}{\delta n} \rangle \]
The Kohn-Sham equations

The whole procedure can be repeated for a noninteracting system with Hamiltonian

$$\hat{H}_s(t) = \hat{T} + \hat{V}_s(t)$$

and action

$$A_s[n] = A_{0,s}[n] - \int_0^T dt dr \ n(rt) v_s(rt)$$

$$A_{s,0}[n] = \int_0^T dt \langle \Phi[n](t)| i\partial_t - \hat{T} |\Phi[n](t)\rangle$$

From the Vignale action principle we have

$$v_s(rt) = \frac{\delta A_{0,s}}{\delta n(rt)} - i \langle \Phi(T)| \frac{\delta \Phi(T)}{\delta n(rt)} \rangle$$
We now define the Hartree and xc-action by

\[ A_{xc}[n] = A_{s,0}[n] - A_0[n] - A_H[n] \]

\[ A_H[n] = \frac{1}{2} \int_0^T dt \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1 t)n(\mathbf{r}_2 t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \]

The action of the interacting system can therefore be written as

\[ A_v[n] = A_{s,0}[n] - \int d\mathbf{r} n(1)v(1) - A_H[n] - A_{xc}[n] \]

Let us now apply the Vignale action principle

\[ \frac{\delta A_v}{\delta n(\mathbf{r} t)} - i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r} t)} \rangle = 0 \]
This yields the variational equation

\[ 0 = \frac{\delta A_v}{\delta n} - i \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n} \rangle = v_s + i \langle \Phi(T) | \frac{\delta \Phi(T)}{\delta n} \rangle - v - v_H - \frac{\delta A_{xc}}{\delta n} - i \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n} \rangle \]

We thus obtain the expressions:

\[ v_s = v + v_H + v_{xc} \]

\[ v_{xc} = \frac{\delta A_{xc}}{\delta n} + i \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n} \rangle - i \langle \Phi(T) | \frac{\delta \Phi(T)}{\delta n} \rangle \]
Since this is the potential for a noninteracting system with density $n(r,t)$ we obtain the Kohn-Sham equations:

\[
\begin{align*}
\left( -\frac{1}{2}\nabla^2 + v(1) + v_H(1) + v_{xc}(1) \right) \phi_i(1) &= i\partial_t \phi_i(1) \\
n(1) &= \sum_{i=1}^{\infty} f_i |\phi_i(1)|^2 \\
v_{xc} &= \frac{\delta A_{xc}}{\delta n} + i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n} \rangle - i\langle \Phi(T) | \frac{\delta \Phi(T)}{\delta n} \rangle
\end{align*}
\]

This should be a causal functional. What about the dependence on $T$?
What about the T-dependence?

For the potential

\[ v(\mathbf{r}t) = \frac{\delta A_0}{\delta n(\mathbf{r}t)} - i\langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle \]

it can be shown that (...see extra slides skipped here..)

\[ \frac{dv(\mathbf{r}t)}{dT} = \frac{d}{dT} \left( \frac{\delta A_0}{\delta n(\mathbf{r}t)} \right) - i \frac{d}{dT} \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = 0 \quad (T > t) \]

The dependence on T is therefore only appearance, in practice we can take T=t⁺
The xc-kernel

What can the Vignale action tell us about the xc-kernel?

In the lectures of Hardy Gross you have seen that

\[ v_{xc}(1) = v_s(1) - v(1) - v_H(1) \]

\[ f_{xc}(1, 2) = \frac{\delta v_s(1)}{\delta n(2)} - \frac{\delta v(1)}{\delta n(2)} - \frac{\delta(t_1 - t_2)}{|r_1 - r_2|} \]

Let us therefore look at the density derivative of the potential

\[ \frac{\delta v(rt)}{\delta n(r't')} = \frac{\delta}{\delta n(r't')} \left( \frac{\delta A_0}{\delta n(rt)} - i \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(rt)} \rangle \right) \]
No causality-symmetry paradox

\[
\frac{\delta v(rt)}{\delta n(r't')} = \frac{\delta^2 A_0}{\delta n(r't') \delta n(rt)} - i\langle \Psi(T) \mid \frac{\delta^2 \Psi(T)}{\delta n(r't') \delta n(rt)} \rangle
\]

Due to the causality of \(v[n]\) we have for \(t > t'\)

\[
\frac{\delta v(rt)}{\delta n(r't')} = \frac{\delta v(rt)}{\delta n(r't')} - \frac{\delta v(r't')}{\delta n(rt)}
\]

vanishes
For \( t > t' \) we then find

\[
\frac{\delta v(r t)}{\delta n(r' t')} = -i \left[ \langle \frac{\delta \Psi(T)}{\delta n(r' t')} | \frac{\delta \Psi(T)}{\delta n(r t)} \rangle - \langle \frac{\delta \Psi(T)}{\delta n(r t)} | \frac{\delta \Psi(T)}{\delta n(r' t')} \rangle \right]
\]

\[
= 2 \text{Im} \langle \frac{\delta \Psi(T)}{\delta n(r' t')} | \frac{\delta \Psi(T)}{\delta n(r t)} \rangle
\]

At equal times there is a dependence of the form

\[
C_0(r, r')\delta(t - t') + C_1(r, r')\partial_t \delta(t - t') + C_2(r, r')\partial_t^2 \delta(t - t')
\]
This leads to the following expression for the xc-kernel

\[ f_{xc}(\mathbf{r}t, \mathbf{r}'t') = 2 \text{Im} \left( \left< \frac{\delta \Phi(T)}{\delta n(\mathbf{r}'t')} \right| \frac{\delta \Phi(T)}{\delta n(\mathbf{r}t)} \right> - \left< \frac{\delta \Psi(T)}{\delta n(\mathbf{r}'t')} \right| \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \right> \\
+ \Delta C_0(\mathbf{r}, \mathbf{r}') \delta(t - t') \]
Conclusions

- Memory and causality in the xc-potential is an immediate consequence of the Runge-Gross theorem

- Both the time contour and the Vignale action principle are well-defined action principles in TDDFT and can be used to derive the time-dependent Kohn-Sham equations

- When making variations it is important to stay in the domain of v-representable densities, otherwise paradoxes may arise.

- The Vignale action principle has lead to a new expression for the xc-kernel
  ......useful for derivation of new xc-kernels ?...
Since
\[
(i\partial_t - \hat{T} - \hat{V}[n](t) - \hat{W})|\Psi[n](t)\rangle = 0
\]

the action
\[
A_0[n] = \int_0^T dt \langle \Psi[n](t) | i\partial_t - \hat{T} - \hat{W} | \Psi[n](t) \rangle
\]
can also be written as
\[
A_0[n] = \int_0^T dt \langle \Psi[n](t) | \hat{V}(t) | \Psi[n] \rangle = \int_0^T dt \int dr \ n(rt)v[n](rt)
\]

We then have
\[
\frac{dA_0}{dT}[n] = \int dr \ n(rT)v[n](rT)
\]
and therefore for $t < T$

$$\frac{d}{dT} \left( \frac{\delta A_0}{\delta n(rt)} \right) = \int dr' n(r'T) \frac{\delta v[n](r'T)}{\delta n(rt)}$$

Let us now consider the $T$-derivative of the second term:

$$-i \frac{d}{dT} \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(rt)} \rangle =$$

$$-i \langle \frac{d \Psi(T)}{dT} | \frac{\delta \Psi(T)}{\delta n(rt)} \rangle - i \langle \Psi(T) | \frac{\delta}{\delta n(rt)} \left( \frac{d \Psi(T)}{dT} \right) \rangle$$

We now use

$$\partial_T \Psi(T) = -i \hat{H}(T) \Psi(T)$$
and we obtain

\[-i \frac{d}{dT} \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = \]

\[
\langle \hat{H}(T) \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle - \langle \Psi(T) | \frac{\delta}{\delta n(\mathbf{r}t)} \hat{H}(T) \Psi(T) \rangle
\]

\[
= -\langle \Psi(T) | \frac{\delta \hat{H}(T)}{\delta n(\mathbf{r}t)} | \Psi(T) \rangle = -\langle \Psi(T) | \frac{\delta \hat{V}[n](T)}{\delta n(\mathbf{r}t)} | \Psi(T) \rangle
\]

For the second term we then find

\[-i \frac{d}{dT} \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = - \int d\mathbf{r}' n(\mathbf{r}'T) \frac{\delta v[n](\mathbf{r}'T)}{\delta n(\mathbf{r}t)} \]

We thus find

\[
\frac{dv(\mathbf{r}t)}{dT} = \frac{d}{dT} \left( \frac{\delta A_0}{\delta n(\mathbf{r}t)} \right) - i \frac{d}{dT} \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle = 0 \quad (T > t)
\]

The dependence on T is therefore only appearance, in practice we can take T=t\(^+\).

Let us now look at the density derivative of the potential

\[
\frac{\delta v(\mathbf{r}t)}{\delta n(\mathbf{r}'t')} = \frac{\delta}{\delta n(\mathbf{r}'t')} \left( \frac{\delta A_0}{\delta n(\mathbf{r}t)} - i \langle \Psi(T) | \frac{\delta \Psi(T)}{\delta n(\mathbf{r}t)} \rangle \right)
\]