Time-dependent many-particle systems (Lecture 8)

We now consider many-particle systems in the presence of time-dependent external fields. So we have a time-dependent Hamiltonian:

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

Here $\hat{T}$ and $\hat{W}$ are the usual kinetic energy and two-particle interactions. However, the external potential is now time-dependent

$$\hat{V}(t) = \sum_{i=1}^{N} v(\vec{r}_i, t)$$

For instance, for a atom with charge Z in a time-dependent dipole field we have

$$v(\vec{r}t) = -\frac{Z}{|\vec{r}|} + \vec{r}\cdot\vec{E}(t)$$

where $\vec{E}(t)$ is a time-dependent electric field.

Instead of the stationary Schrödinger equation we now have to solve the time-dependent Schrödinger equation:

$$i\,\partial_t \Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}\sigma_N, t) = \hat{H}(t)\,\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N, t)$$

(: ∂_t is a convenient short notation for $\frac{\partial}{\partial t}$)

Instead of a boundary value problem we now have an initial value problem.

$$\Psi(\vec{r}\sigma_1, \ldots, \vec{r}_N\sigma_N, t=0) = \Psi_0(\vec{r}\sigma_1, \ldots, \vec{r}_N\sigma_N)$$

where $\Psi_0(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$ is an initial state.

All the reduced quantities, such as densities and pair-correlation functions have the same form in a time-dependent theory.

The density is given as

$$n(\vec{r}t) = N \sum_{\sigma_1 \ldots \sigma_N} \int d^3\vec{r}_2 \ldots d^3\vec{r}_N \; |\Psi(\vec{r}\sigma_1, \vec{r}_2\sigma_2, \ldots, \vec{r}_N\sigma_N)|^2$$

$$= \langle \Psi(t) | \hat{n}(\vec{r}) | \Psi(t) \rangle$$

The time-dependent diagonal density matrix is

$$\Gamma(\vec{r}_1, \vec{r}_2, t) = \langle \Psi(t) | \hat{\Gamma}(\vec{r}_1, \vec{r}_2) | \Psi(t) \rangle$$

The Ehrenfest theorem

For any operator $\hat{A}$ we can calculate its time-dependent expectation value $\langle A \rangle(t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle$. The time-derivative of the expectation value is then given as

$$\partial_t \langle A(t) \rangle = \partial_t \langle \Psi(t) | \hat{A} | \Psi(t) \rangle$$

$$= \langle \partial_t \Psi(t) | A | \Psi(t) \rangle + \langle \Psi(t) | \partial_t \hat{A} | \Psi(t) \rangle$$

$$+ \langle \Psi(t) | \hat{A} | \partial_t \Psi(t) \rangle$$

$$= i \langle \hat{H} \Psi(t) | \hat{A} | \Psi(t) \rangle - i \langle \Psi(t) | \hat{A} | \hat{H} \Psi(t) \rangle$$

$$+ \langle \Psi(t) | \partial_t \hat{A} | \Psi(t) \rangle$$

$$= i \langle \Psi(t) | \hat{H}\hat{A} - \hat{A}\hat{H} | \Psi(t) \rangle + \langle \Psi(t) | \partial_t \hat{A} | \Psi(t) \rangle$$

$$= -i \langle \Psi(t) | [\hat{A}, \hat{H}(t)] | \Psi(t) \rangle + \langle \Psi(t) | \partial_t \hat{A} | \Psi(t) \rangle$$

So we find the Ehrenfest theorem:

$$\partial_t \langle \hat{A} \rangle(t) = -i \langle [\hat{A}(t), \hat{H}(t)] \rangle + \langle \partial_t \hat{A}(t) \rangle$$

We can apply the Ehrenfest theorem to the density operator

$$\hat{A} = \hat{n}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)$$

Then $\partial_t n(\vec{r}t) = \partial_t \langle \hat{n}(\vec{r})\rangle(t) = -i\langle [\hat{n}(\vec{r}), \hat{H}(t)]\rangle$

So we have to evaluate the commutator

$$[n(\vec{r}), \hat{H}(t)] = [n(\vec{r}), \hat{T} + \hat{V}(t) + \hat{W}] = [n(\vec{r}), \hat{T}]$$

since $[n(\vec{r}), \hat{V}(t)] = [\hat{n}(\vec{r}), \hat{W}] = 0$ (check!).

$$[n(\vec{r}), \hat{T}] = n(\vec{r})\hat{T} - \hat{T}\hat{n}(\vec{r})$$

$$= \sum_{ij}^{N} -\delta(\vec{r}-\vec{r}_i)\frac{1}{2}\nabla_j^2 + \sum_{ij}^{N} \frac{1}{2}\nabla_j^2 \delta(\vec{r}-\vec{r}_i)$$

$$= \sum_{ij}^{N} -\delta(\vec{r}-\vec{r}_i)\frac{1}{2}\nabla_j^2 + \sum_{ij}^{N} \delta(r-r_i)\frac{1}{2}\nabla_j^2$$

$$+ \sum_{ij}^{N} \underbrace{\nabla_j \delta(r-\vec{r}_i)}_{\text{zero if } i\neq j}\cdot\nabla_j + \sum_{ij}^{N} \frac{1}{2}\Big(\underbrace{\nabla_j^2 \delta(r-r_i)}_{\text{zero if } i\neq j}\Big)$$

(Remember that we are acting on wavefunctions and therefore $\nabla^2(f\Psi) = 2\nabla f\cdot\nabla\Psi + f\nabla^2\Psi + (\nabla^2 f)\Psi$
i.e.

$$\nabla^2 f = 2\nabla f\cdot\nabla + (\nabla^2 f) + f\nabla^2$$)

So we have

$$[\hat{n}(\vec{r}), \hat{T}] = \sum_{j}^{N} \nabla_j \delta(\vec{r}-\vec{r}_j)\cdot\nabla_j + \frac{1}{2}\left(\nabla_j^2 \delta(\vec{r}-\vec{r}_j)\right)$$

Since $\nabla_{\vec{r}}\delta(\vec{r}-\vec{r}_j) = -\nabla_j \delta(r-\vec{r}_j)$
we can also write

$$[\hat{n}(\vec{r}), \hat{T}] = -\nabla_{\vec{r}}\Big\{\sum_{j} \delta(\vec{r}-\vec{r}_j)\nabla_j + \underbrace{\frac{1}{2}\left(\nabla_j \delta(\vec{r}-\vec{r}_j)\right)}_{= \nabla_j \delta(r-\vec{r}_j) - \delta(\vec{r}-\vec{r}_j)\nabla_j}\Big\}$$

$$= -\nabla_{\vec{r}}\frac{1}{2}\Big(\sum_{j}^{N} \delta(\vec{r}-\vec{r}_j)\nabla_j + \nabla_j \delta(r-\vec{r}_j)\Big)$$

We therefore obtain

$$-i\,[n(\vec{r}),\hat{T}] = -\nabla_{\vec{r}}\left\{\frac{1}{2i}\sum_j^N \nabla_j\delta(\vec{r}-\vec{r}_j)+\delta(r-\vec{r}_j)\nabla_j\right\}$$

$$= -\nabla_{\vec{r}}\,\hat{j}(\vec{r})$$

where we defined the current operator

$$\hat{j}(\vec{r}) = \frac{1}{2i}\sum_{j=1}^N\left(\nabla_j\delta(r-\vec{r}_j)+\delta(\vec{r}-\vec{r}_j)\nabla_j\right)$$

We therefore find the following equation for the density

$$\partial_t n(\vec{r}t) = \partial_t\langle\hat{n}(\vec{r})\rangle(t) = \langle -\nabla_{\vec{r}}\,j(\vec{r})\rangle$$

$$= -\nabla_{\vec{r}}\,\langle\Psi(t)|\hat{j}(\vec{r})|\Psi(t)\rangle = -\nabla_{\vec{r}}\,\vec{j}(\vec{r}t)$$

The equation

$$\partial_t n(\vec{r}t) + \nabla_{\vec{r}}\,j(\vec{r}t) = 0$$

is called the continuity equation.

The current has the more explicit form

$$\vec{j}(\vec{r}t) = \sum_{\sigma_1\ldots\sigma_N}\int d\vec{r}_1^3\ldots d\vec{r}_N^3\;\Psi^*(\vec{r}_1\sigma_1,\ldots,\vec{r}_N\sigma_N)\,\hat{j}(\vec{r})\,\Psi(\vec{r}_1\sigma_1,\ldots,\vec{r}_N\sigma_N)$$

$$= \sum_{\sigma_1\ldots\sigma_N}\sum_{j=1}^N\int d^3\vec{r}_1\ldots d^3\vec{r}_N\;\Psi^*\left\{\nabla_j\delta(\vec{r}-\vec{r}_j)+\delta(r-\vec{r}_j)\nabla_j\right\}\Psi$$

$$= \sum_{\sigma_1\ldots\sigma_N}\sum_{j=1}^N\int d^3\vec{r}_1\ldots d^3\vec{r}_N\;\delta(r-\vec{r}_j)\left\{\Psi^*\nabla_j\Psi-(\nabla_j\Psi^*)\Psi\right\}$$

(partial integration)

$$= \sum_{\sigma_1\ldots\sigma_N} N\int d^3\vec{r}_2\ldots d\vec{r}_N\left\{\Psi^*(\vec{r}\sigma_1,\ldots\vec{r}_N\sigma_N)\nabla_{\vec{r}}\Psi(\vec{r}\sigma_1,\vec{r}_2\sigma_2\ldots\vec{r}_N\sigma_N)\right.$$
$$\left.-\left(\nabla_{\vec{r}}\Psi^*(\vec{r}\sigma_1,\vec{r}_2\sigma_2\ldots\vec{r}_N\sigma_N)\right)\Psi(\vec{r}_1\sigma_1,\ldots\vec{r}_N\sigma_N)\right\}$$

Linear response theory

Consider a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

where $\hat{H}_0$ is a time-independent Hamiltonian and $\hat{V}(t)$ a time-dependent perturbation.

We take $V(t) = 0$ for $t < t_0$
and $\Psi(t=0)$ the ground state of $\hat{H}_0$, i.e. $\hat{H}_0 \Psi_0 = E_0 \Psi_0$

We want to solve the time-dependent Schrödinger equation

$$i\partial_t \Psi = \hat{H}(t)\Psi \qquad , \quad \Psi(t=0) = \Psi_0$$

One can derive a solution in powers of the perturbation $\hat{V}(t)$ as follows.

We first define a wavefunction Ψ_I in the so-called interaction picture

$$\Psi_I(t) = e^{i\hat{H}_0 t}\Psi$$

Then

$$\begin{aligned} i\partial_t \Psi_I(t) &= e^{i\hat{H}_0 t} i\partial_t \Psi - e^{i\hat{H}_0 t}\hat{H}_0 \Psi \\ &= e^{i\hat{H}_0 t}(\hat{H} - \hat{H}_0)\Psi \\ &= \underbrace{e^{i\hat{H}_0 t}\hat{V}(t)e^{-i\hat{H}_0 t}}_{V_I(t)} e^{i\hat{H}_0 t}\Psi = \hat{V}_I(t)\Psi_I(t) \end{aligned}$$

We therefore obtain

$$i\partial_t \Psi_I(t) = \hat{V}_I(t)\Psi_I(t) \quad , \qquad \Psi_I(t=0) = \Psi_0 \qquad (*)$$

$$V_I(t) = e^{i\hat{H}_0 t}\hat{V}(t)e^{-i\hat{H}_0 t}$$

If we integrate both sides of (*) from 0 to t we obtain

$$\Psi_I(t) = \Psi_0 - i \int_0^t dt' \; \hat{V}_I(t') \Psi_I(t')$$

$$= \Psi_0 - i \int_0^t dt' \; \hat{V}_I(t') \left\{ \Psi_0 - i \int_0^{t'} dt'' \; \hat{V}_I(t'') \Psi_I(t'') \right\}$$

$$= \Psi_0 - i \int_0^t dt' \; V_I(t') \Psi_0 + (-i)^2 \int_0^t dt' \int_0^{t''} dt'' \; V_I(t) V_I(t'') \Psi_I(t'')$$

For weak perturbations $\hat{V}(t)$ we can keep only the term linear in $\hat{V}(t)$

$$\Psi_I(t) = \Psi_0 - i \int_0^t dt' \; \hat{V}_I(t') \Psi_0 \qquad (**)$$

The first order change in an expectation value $\langle \hat{A} \rangle$ is then

$$\delta \langle \hat{A} \rangle (t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle - \langle \Psi_0 | \hat{A} | \Psi_0 \rangle$$

$$= \langle \Psi_I(t) | \underbrace{e^{i\hat{H}_0 t} A \, e^{-iH_0 t}}_{\hat{A}_I(t)} | \Psi_I(t) \rangle - \langle \Psi_0 | \hat{A} | \Psi_0 \rangle$$

If we then insert (**) we find to lowest order

$$\delta \langle A \rangle (t) = i \int_0^t dt' \; \langle \Psi_0 | \hat{V}_I(t') \hat{A}_I(t) | \Psi_0 \rangle$$

$$- i \int_0^t dt' \; \langle \Psi_0 | \hat{A}_I(t) \hat{V}_I(t') | \Psi_0 \rangle$$

$\Longrightarrow$

$$\delta \langle \hat{A} \rangle (t) = -i \int_0^t dt' \; \langle \Psi_0 | [\hat{A}_I(t), \hat{V}_I(t')] | \Psi_0 \rangle$$

Another way of phrasing our result is.

If we make at time-dependent perturbation $\hat{V}(t)$ to a time-independent Hamiltonian $\hat{H}$ then the first order change in an expectation value $\langle \hat{A} \rangle$ is given by

$$\delta \langle \hat{A} \rangle (t) = -i \int_0^t dt' \langle \Psi_0 | [\hat{A}_H(t), \hat{V}_H(t)] | \Psi_0 \rangle \qquad (***)$$

where $\hat{A}_H(t) = e^{i\hat{H}t} \hat{A} e^{-i\hat{H}t}$ and similarly for $\hat{V}$

Of particular interest for density functional theory is the density operator. $\langle \hat{n} \rangle$

The external perturbation is of the form

$$\hat{V}(t) = \int d^3\vec{r}\ \hat{n}(\vec{r}) \delta v(\vec{r}t)$$

We therefore obtain

$$\delta n(\vec{r}t) = -i \int_0^t dt' \int d\vec{r}' \langle \Psi_0 | [\hat{n}_H(\vec{r}t), \hat{n}_H(\vec{r}'t')] | \Psi_0 \rangle \delta v(\vec{r}'t')$$

$$= \int_{-\infty}^{+\infty} dt' \int d^3\vec{r}'\ \chi(\vec{r}t, \vec{r}'t') \delta v(\vec{r}'t') \qquad (****)$$

(since $\delta v = 0$ for $t < t_0$)

where we defined the density response function as

$$\chi(\vec{r}t, \vec{r}'t') = -i\,\theta(t-t') \langle \Psi_0 | [\hat{n}_H(\vec{r}t), \hat{n}_H(\vec{r}'t')] | \Psi_0 \rangle$$

Eq. (****) is equivalent to the result

$$\frac{\delta n(\vec{r}t)}{\delta v(\vec{r}'t')} = \chi(\vec{r}t, \vec{r}'t')$$

The Lehmann representation

The density response function contains a lot of information about the expectation spectrum of the system with Hamiltonian $\hat{H}$.

We have

$$\chi(\vec{r}t, \vec{r}'t') = -i\theta(t-t')\langle \Psi_0 | [\hat{n}_H(\vec{r}t), \hat{n}_H(\vec{r}'t')] | \Psi_0 \rangle$$

$$= -i\,\theta(t-t') \sum_s \Big\{ \langle \Psi_0 | \hat{n}_H(\vec{r}t) | N,s \rangle \langle N,s | \hat{n}_H(\vec{r}'t') | \Psi_0 \rangle$$

$$- \langle \Psi_0 | \hat{n}_H(\vec{r}'t') | N,s \rangle \langle N,s | \hat{n}_H(\vec{r}t) | \Psi_0 \rangle \Big\} \qquad (\Delta)$$

where we used that

$$1 = \sum_s |N,s\rangle\langle N,s|$$

where $|N,s\rangle$ is an N-particle excited state of Hamiltonian $\hat{H}$, i.e.

$$\hat{H}\,|N,s\rangle = E_{N,s}\,|N,s\rangle$$

We further have that

$$\langle \Psi_0 | \hat{n}_H(\vec{r}t) | N,s \rangle = \langle \Psi_0 | e^{i\hat{H}t}\, \hat{n}(\vec{r})\, e^{-i\hat{H}t} | N,s \rangle$$

$$= e^{i(E_0 - E_{N,s})t} \langle \Psi_0 | \hat{n}(\vec{r}) | N,s \rangle$$

If we define the excitation energy to be

$$\Omega_s = E_{N,s} - E_0$$

and $$f_s(\vec{r}) = \langle \Psi_0 | \hat{n}(\vec{r}) | N,s \rangle$$

then Eq. (Δ) becomes

$$\chi(\vec r t, \vec r' t') = -i\,\Theta(t-t') \sum_s e^{-i\Omega_s(t-t')} f_s(\vec r) f_s^*(\vec r') + i\,\Theta(t-t') \sum_s e^{i\Omega_s(t-t')} f_s^*(\vec r) f_s(\vec r')$$

we see that χ only depends on the time-combination $t-t'$.
We can therefore write

$$\chi(\vec r t, \vec r' t') = \chi(\vec r, \vec r'; t-t')$$

The equation for the density response is therefore of the convolution form.

$$\delta n(\vec r t) = \int d\vec r' \int_{-\infty}^{+\infty} dt' \, \chi(r, r'; t-t') \, \delta v(\vec r' t')$$

This equation can be deconvoluted using Fourier transforms. We have

$$\delta n(\vec r \omega) = \int d\vec r' \, \chi(\vec r, \vec r'; \omega) \, \delta v(\vec r' \omega)$$

Where
$$\chi(r, r'; \omega) = \int_{-\infty}^{+\infty} d\tau \, \chi(r, r'; \tau) \, e^{i\omega\tau}$$
$$\chi(r, r'; \tau) = \int \frac{d\omega}{2\pi} \, \chi(r, r'; \omega) \, e^{-i\omega\tau}$$

and similar Fourier transforms for $\delta n(r\omega)$ and $\delta v(r\omega)$

Let us look at these Fourier transforms in more detail.

It will be useful to use the following identity for the Heaviside function

$$\Theta(t) = \lim_{\eta \to 0^+} \frac{-1}{2\pi i} \int_{-\infty}^{+\infty} d\omega \, \frac{e^{-i\omega t}}{\omega + i\eta}$$

(You can check this for yourself using complex integrations)

Then

$$\chi(\vec r, \vec r\,'; t-t') = -i \sum_s \lim_{\eta\to 0^+} \frac{-1}{2\pi i} \int_{-\infty}^{+\infty} d\omega \left\{ \frac{e^{-i\omega(t-t')}}{\omega + i\eta} e^{-i\Omega_s(t-t')} f_s(\vec r) f_s^*(\vec r\,') \right.$$

$$\left. - \frac{e^{-i\omega(t-t')}}{\omega+i\eta} e^{i\Omega_s(t-t')} f_s^*(\vec r) f_s(\vec r\,') \right\}$$

$$= \sum_s \lim_{\eta\to 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \left\{ \frac{e^{-i(\omega+\Omega_s)(t-t')}}{\omega + i\eta} f_s(\vec r) f_s^*(\vec r\,') - \frac{e^{-i(\omega-\Omega_s)(t-t')}}{\omega+i\eta} f_s^*(\vec r) f_s(\vec r\,') \right\}$$

Subsitutions $\omega \to \omega + \Omega_s$ $\qquad$ $\omega \to \omega - \Omega_s$

$$= \sum_s \lim_{\eta\to 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \left\{ \frac{e^{-i\omega(t-t')}}{\omega - \Omega_s + i\eta} f_s(\vec r) f_s^*(\vec r\,') - \frac{e^{-i\omega(t-t')}}{\omega+\Omega_s+i\eta} f_s^*(\vec r) f_s(\vec r\,') \right\}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \, \chi(\vec r, \vec r\,'; \omega) \, e^{-i\omega(t-t')}$$

where

$$\chi(r, r'; \omega) = \lim_{\eta\to 0^+} \sum_s \left\{ \frac{f_s(\vec r) f_s^*(\vec r\,')}{\omega - \Omega_s + i\eta} - \frac{f_s^*(r) f_s(\vec r\,')}{\omega+\Omega_s+i\eta} \right\} \qquad (\mathrm{II})$$

This is the density response function in frequency space (Lehmann representation).

We see that the poles of this function are the excitation energies of the system.

Noninteracting particles

Let's consider the density response for a system of noninteracting particles.

Then we have to calculate

$$\Omega_s = E_s - E_0$$

$$f_s(\vec{r}) = \langle \Psi_0 | \hat{n}(\vec{r}) | N, s \rangle$$

for noninteracting particles.

The ground-state wave function is a Slater determinant

$$\Psi_0(\vec{r}_1\sigma_1, \dots \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1\sigma_1) & \cdots & \phi_1(\vec{r}_N\sigma_N) \\ \vdots & & \vdots \\ \phi_N(\vec{r}_1\sigma_1) & \cdots & \phi_N(\vec{r}_N\sigma_N) \end{vmatrix} = |1 \dots N\rangle$$

a general excited state $|N,s\rangle$ is of the form

$$|N,s\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(\vec{r}_1\sigma_1) & \cdots & \phi_{i_1}(\vec{r}_N\sigma_N) \\ \vdots & & \vdots \\ \phi_{i_N}(\vec{r}_1\sigma_1) & \cdots & \phi_{i_N}(\vec{r}_N\sigma_N) \end{vmatrix} = |i_1 \dots i_N\rangle$$

and

$$\Omega_s = E_s - E_0 = (\epsilon_{i_1} + \dots + \epsilon_{i_N}) - (\epsilon_1 + \dots + \epsilon_N)$$

We need to evaluate $f_s(\vec{r})$.

We first use the following statement:

The expectation value $\langle i_1 \dots i_N | \hat{O} | j_1 \dots j_N \rangle$, where

$$\hat{O} = \sum_{i=1}^{N} \hat{o}(\vec{x}_i)$$

is a one-body operator, is zero if $(i_1 \dots i_N)$ and $(j_1 \dots j_N)$ differ in more than one value

So for instance $\langle 12345 | \hat{O} | 12367 \rangle = 0$

2 indices different

(Prove this yourself!)

Since $\hat{n}(\vec{r})$ is a one-body operator the function $f_s(\vec{r})$ vanishes for all Slater determinants $|N,s\rangle$ that differ in more than one value from $|\Psi_0\rangle = |1 \ldots N\rangle$

We take $\Psi_0 = |1 \ldots N\rangle$ and $\Phi_{(kl)} = |1 \ldots k \ldots N\rangle$ where we replaced value l by k. (i.e. $k > N$, $l \leq N$)

Then for a one-body operator

$\hat{O} = \sum_{i=1}^{N} \hat{o}(\vec{x}_i)$ we have (prove yourself!)

$$\langle \Psi_0 | \hat{O} | \Phi_{(kl)} \rangle = \langle l | \hat{o} | k \rangle = \int d\vec{x}_1 \, \phi_l^*(\vec{x}_1) \hat{o}(\vec{x}_1) \phi_k(\vec{x}_1)$$

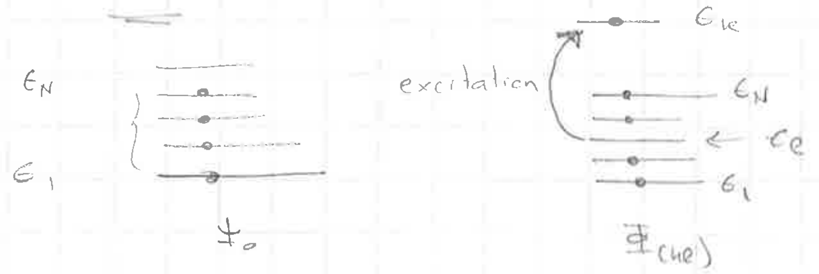
Since $\hat{n}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$ we have

$$f_{(kl)}(\vec{r}) = \langle \Psi_0 | \hat{n}(\vec{r}) | \Phi_{(kl)} \rangle = \int d\vec{x}_1 \, \phi_l^*(\vec{x}_1) \delta(\vec{r} - \vec{r}_1) \phi_k(\vec{x}_1)$$

$$= \sum_\sigma \phi_l^*(\vec{r}\sigma) \phi_k(\vec{r}\sigma) \, \mu_l (1 - \mu_k)$$

where we defined $\mu_l = 1$ $(l \leq N)$, $\mu_l = 0$ $(l > N)$

$$\Omega_{(kl)} = E_{(kl)} - E_0 = \epsilon_k - \epsilon_l$$



The density response function for noninteracting particles

$$\chi_0(\bar r \bar r'; \omega) = \lim_{\eta\to 0^+} \sum_{kl} \left\{ \frac{f_{(kl)}(\bar r) f^*_{(kl)}(\bar r')}{\omega - \Omega_{(kl)} + i\eta} - \frac{f^*_{(kl)}(\bar r) f_{(kl)}(\bar r')}{\omega + \Omega_{(kl)} + i\eta} \right\}$$

$$= \lim_{\eta\to 0^+} \sum_{kl}\sum_{\sigma\sigma'} \left\{ \mu_l(1-\mu_k) \frac{\phi^*_l(\bar r\sigma)\phi_k(\bar r\sigma)\phi_l(\bar r'\sigma')\phi^*_k(\bar r'\sigma')}{\omega - (\epsilon_k - \epsilon_l) + i\eta} \right.$$

$$\left. - \mu_l(1-\mu_k) \frac{\phi_l(\bar r\sigma)\phi^*_k(\bar r\sigma)\phi^*_l(\bar r'\sigma')\phi_l(\bar r'\sigma')}{\omega + (\epsilon_k - \epsilon_l) + i\eta} \right\}$$

Interchange $l \leftrightarrow k$ in the second term

$$= \lim_{\eta\to 0^+} \sum_{kl}\sum_{\sigma\sigma'} \left(\mu_l(1-\mu_k) - \mu_k(1-\mu_l)\right) \frac{\phi^*_l(\bar r\sigma)\phi_k(\bar r\sigma)\phi_l(\bar r'\sigma')\phi^*_k(\bar r'\sigma')}{\omega - (\epsilon_k - \epsilon_l) + i\eta}$$

$$= \lim_{\eta\to 0^+} \sum_{kl}\sum_{\sigma\sigma'} (\mu_l - \mu_k) \frac{\phi^*_l(\bar r\sigma)\phi_k(\bar r\sigma)\phi_l(\bar r'\sigma')\phi^*_k(\bar r'\sigma')}{\omega - (\epsilon_k - \epsilon_l) + i\eta}$$

For the case of a spin-compensated system

$$\{\phi_k(\bar r\sigma)\} = \phi_1(\bar r\sigma), \phi_2(\bar r\sigma), \phi_3(\bar r\sigma), \ldots$$
$$= \varphi_1(\bar r)\delta_{\sigma,\uparrow}, \varphi_1(\bar r)\delta_{\sigma,\downarrow}, \varphi_2(\bar r)\delta_{\sigma,\uparrow}, \ldots$$

We can write (check yourself!)

$$\chi_0(\bar r \bar r'; \omega) = 2 \lim_{\eta\to 0^+} \sum_{kl} (\mu_l - \mu_k) \frac{\varphi^*_l(\bar r)\varphi_k(\bar r)\varphi_l(\bar r')\varphi^*_k(\bar r')}{\omega - (\epsilon_k - \epsilon_l) + i\eta}$$

The noninteracting density response function has poles at the eigenvalue differences

It corresponds to excitations from the ground state to singly-excited Slater determinants $\Phi_{(kl)}$

Time-dependent density functional theory

We can wonder if in the time-dependent case there is an equivalent of the Hohenberg-Kohn theorem. This is indeed the case. However, since the time-dependent Schrödinger equation represents an initial state problem, there are a few changes.

We have (Runge-Gross theorem)

$$(\Psi_0, n(\vec{r}t)) \overset{1-1}{\longleftrightarrow} v(\vec{r}t) \quad \text{modulo} \quad C(t)$$

; i.e. a given time-dependent density $n(\vec{r}t)$ and an initial state $n(\vec{r}t)$ uniquely determines the time-dependent potential that produced it, upto a purely time-dependent function $C(t)$.

The function $C(t)$ is related to the phase of the wave function.

If, for instance, a single particle $\varphi(\vec{r}t)$ satisfies the equation

$$i\partial_t \varphi(\vec{r}t) = h(\vec{r}t)\varphi(\vec{r}t) \qquad , \quad \varphi(\vec{r}0) = \varphi_0$$

Then $\tilde{\varphi}(\vec{r}t) = e^{-i\alpha(t)}\varphi(\vec{r}t)$ satisfies

$$\begin{aligned} i\partial_t \tilde{\varphi}(\vec{r}t) &= \partial_t \alpha(t)\, e^{-i\alpha(t)}\varphi(\vec{r}t) + e^{-i\alpha(t)}\, i\partial_t \varphi(\vec{r}t) \\ &= \partial_t \alpha(t)\, \tilde{\varphi}(\vec{r}t) + e^{-i\alpha(t)}\, h(\vec{r}t)\varphi(\vec{r}t) \\ &= \left(h(\vec{r}t) + \partial_t \alpha(t)\right)\tilde{\varphi}(\vec{r}t) \qquad , \quad \partial_t \alpha = C(t) \end{aligned}$$

So if $\partial_t \varphi = h\varphi$ with $\varphi(\vec{r}0) = \varphi_0$ then the solution of $\partial_t \tilde{\varphi} = (h + C(t))\tilde{\varphi}$ with $\tilde{\varphi}(\vec{r}0) = \varphi_0$ is given by

$$\tilde{\varphi}(\vec{r}t) = e^{-i\int_0^t dt'\, C(t')}\, \varphi(\vec{r}t)$$

It is clear that

$$\hat{n}(\vec{r}t) = |\tilde{\varphi}(\vec{r}t)|^2 = |\varphi(\vec{r}t)|^2 = n(\vec{r}t)$$

So potentials that differ by a purely time-dependent function produce the same density.

We will prove the Runge-Gross theorem later. Let us first see what the consequences are:

<u>Time-dependent Kohn-Sham theory</u>

The Runge-Gross theorem applies to systems with any two-particle interaction $\hat{W}$.
In particular we can take $\hat{W} = 0$.
There is therefore for a given initial state $\Phi_{s,0}$ and a given density $n(\vec{r}t)$ a noninteracting system with Hamiltonian $\hat{H}_s(t)$ such that

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

$$i\partial_t \Phi_s(t) = \hat{H}_s(t)\Phi_s(t) \quad , \quad \Phi_s(t=0) = \Phi_{s,0}$$

$$n(\vec{r}t) = \langle \Phi_s(t)|\hat{n}(\vec{r})|\Phi_s(t)\rangle$$

If the initial state $\Phi_{s,0}$ is a Slater determinant then also the time-dependent wave function $\Phi_s(\vec{r}t)$ is one (check!). In that case

$$\Phi_s(t) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1\sigma_1,t) & \cdots & \phi_1(\vec{r}_N\sigma_N,t) \\ \vdots & & \vdots \\ \phi_N(\vec{r}_1\sigma_1,t) & \cdots & \phi_N(\vec{r}_N\sigma_N,t) \end{vmatrix}$$

where

$$\begin{cases} i\partial_t \phi_i(\vec{r}\sigma,t) = h_s(\vec{r}t)\,\phi_i(\vec{r}\sigma,t) \\ h_s(\vec{r}t) = -\frac{1}{2}\nabla^2 + v_s(\vec{r}t) \\ n(\vec{r}t) = \sum_\sigma \sum_{i=1}^{N} |\phi_i(\vec{r}\sigma,t)|^2 \end{cases}$$

A main difference with the ground state theory is that there is no energy minimization principle.

There exists an action principle, however, since we do not need the action principle in the following discussion we shift the discussion of this to a later time.

We can define the xc-potential by

$$v_{xc}[n](\vec{r}t) = v_s[n](\vec{r}t) - v[n](\vec{r}t) - v_H[n](\vec{r}t)$$

Potential that yields $n(\vec{r}t)$ in a noninteracting system

Potential that yields $n(\vec{r}t)$ in an interacting system

$v_H[n](\vec{r}t) = \int d\vec{r}' \frac{n(\vec{r}'t)}{|\vec{r}-\vec{r}'|}$

Hartree potential

We cannot just time-propagate the KS-equations to obtain $n(\vec{r}t)$ as $v_s[n]$ is defined by the density. We have to tell the KS-system which density we are interested in. We do this by saying that

$$v[n](\vec{r}t) = v_0(\vec{r}t) \leftarrow \text{The external potential of the system of interest}$$

We then solve the KS-equations with the potential

$$v_{s,0}[n](\vec{r}) = v_0(\vec{r}) + v_H[n](\vec{r}t) + v_{xc}[n](\vec{r}t)$$

$$\left(-\frac{1}{2}\nabla^2 + v_{s,0}[n](\vec{r}t)\right)\phi_i(\vec{r}\sigma,t) = i\partial_t\,\phi_i(\vec{r}\sigma,t) \qquad (\Delta)$$

The equations (Δ) only have a self-consistent solution when

$$v_{s,0}[n](\vec{r}t) = v_s[n](\vec{r}t)$$

which implies $\quad v[n](\vec{r}t) = v_0(\vec{r}t) \Rightarrow n(\vec{r}t) = n_0(\vec{r}t)$

We therefore see that the exact time-dependent density can be obtained from solution of the time-dependent Kohn-Sham equations.

The only thing that remains is to find an accurate approximation for $V_{xc}[n](\vec{r}t)$.

A commonly used one is the adiabatic local density approximation (ALDA)

$$V_{xc}^{ALDA}(n(\vec{r}t)) = \left.\frac{d\,\epsilon_{xc}^{h}}{dn}\right|_{n=n(\vec{r}t)}$$

in which we simply insert the time-dependent density into the expression V_{xc}^{LDA} for the homogeneous electron gas.

Linear response Kohn-Sham theory

Linear response theory can be used to calculate excitation energies within time-dependent density functional theory.

Since $\quad V_S[n](1) = V[n](1) + V_H[n](1) + V_{xc}[n](1)$

$(1 = \vec{r}_1 t_1)$ it follows from differentiation with respect to the density that

$$\underbrace{\frac{\delta V_S(1)}{\delta n(2)}}_{\substack{=\ \chi_S^{-1}(1,2) \\ \Downarrow \\ \text{Inverse Kohn-Sham} \\ \text{density response function}}} = \underbrace{\frac{\delta V(1)}{\delta n(2)}}_{\substack{=\ \chi^{-1}(1,2) \\ \Downarrow \\ \text{Inverse density} \\ \text{response function}}} + \underbrace{\frac{\delta V_H(1)}{\delta n(2)}}_{=\ \frac{\delta(t_1 - t_2)}{|\vec{r}_1 - \vec{r}_2|}} + \underbrace{\frac{\delta V_{xc}(1)}{\delta n(2)}}_{\substack{=\ \text{The xc-kernel} \\ f_{xc}(1,2)}} \qquad (\text{II})$$

The equation (II) is readily converted to

$$\chi(1,2) = \chi_s(1,2) + \int d3 \int d4\, \chi_s(1,3) \left[\frac{\delta(t_3-t_4)}{|\vec{r}_3-\vec{r}_4|} + f_{xc}(3,4) \right] \chi(4,1)$$

or more explicitly

$$\chi(\vec{r}_1,\vec{r}_2;t_1-t_2) = \chi_s(\vec{r}_1 r_2, t_1-t_2)$$

$$+ \int d\vec{r}_3 \int dt_3 \int d\vec{r}_4 \int dt_4\, \chi_s(\vec{r}_1 r_3; t_1-t_3) \left[\frac{\delta(t_3-t_4)}{|\vec{r}_3-\vec{r}_4|} + f_{xc}(\vec{r}_3 r_4; t_3-t_4) \right] \chi(\vec{r}_4 \vec{r}_2; t_4-t_2)$$

which can be simplified by Fourier transforming this equation

$$\chi(\vec{r}_1 r_2;\omega) = \chi_s(\vec{r}_1 r_2;\omega)$$

$$+ \int d\vec{r}_3 \int d\vec{r}_4\, \chi_s(\vec{r}_1 r_3;\omega) \left[\frac{1}{|\vec{r}_3-\vec{r}_4|} + f_{xc}(\vec{r}_3 \vec{r}_4;\omega) \right] \chi(\vec{r}_4 \vec{r}_2;\omega) \qquad (\text{III})$$

The form of the KS response function χ_s is known in terms of the KS-orbitals and eigenvalues.

Further $f_{xc}(r_1 t_1, r_2 t_2) = \dfrac{\delta v_{xc}(\vec{r}_1 t_1)}{\delta n(\vec{r}_2 t_2)}$

is known wherever we propose an explicit approximation for $v_{xc}[n]$.

Therefore for a given choice of $v_{xc}[n]$ the density response function χ can be calculated from (III).
Its poles then give the excitation energies of the system of interest.

Let's look at Eq. (□□) more closely

$$\chi = \chi_s + \int \chi_s \left[w + f_{xc} \right] \chi$$

Poles at the true excitation energies

Poles at the Kohn-Sham eigenvalue differences

f_{xc} is responsible for shifting the KS-poles towards the true excitation energies

In the adiabatic local density approximation (ALDA) one has

$$f_{xc}^{ALDA}(\vec{r}t, \vec{r}'t') = \frac{\delta v_{xc}^{LDA}(\vec{r}t)}{\delta n(\vec{r}'t')} = \left.\frac{d^2 \epsilon_{xc}}{dn^2}\right|_{n=n_0(\vec{r})} \delta(\vec{r}-\vec{r}')\delta(t-t')$$

local in space and time

So $$f_{xc}^{ALDA}(\vec{r},\vec{r}',\omega) = \left.\frac{d^2 \epsilon_{xc}}{dn}\right|_{n=n_0} \delta(\vec{r}-\vec{r}')$$

The ALDA - kernel is frequency - independent.

If the KS - eigenvalues are a good first order starting point to the true excitation energies then from (□□) one can derive the correction

$$\Omega_s = \epsilon_k - \epsilon_l + $$
$$+ 2\,\mathrm{Re} \int d\vec{r} \int d\vec{r}' \; \phi_k^*(\vec{r}) \phi_l(\vec{r}) f_{xc}(\vec{r},\vec{r}'; \epsilon_k - \epsilon_l) \phi_k(\vec{r}') \phi_l^*(\vec{r}')$$

(See: M. Petersilka, U. J. Gossmann and E. K. U. Gross)

In the case that the xc-kernel f_{xc} is approximated to be frequency - independent (as in the ALDA) then there are as much KS - excitations are true excitations.

However, in general there are more many-body excitations than KS - excitations

These many-body excitations are described by doubly- and higher excited Slater determinants.

The description of such states requires a frequency-dependence of the xc-kernel.

This corresponds to memory in the xc-potential als

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

implies that

$$\delta v_{xc}(\vec{r}t) = \int dt' \int d\vec{r}\,' \, f_{xc}(\vec{r},\vec{r}\,';t-t') \, \delta n(\vec{r}\,'t')$$

The change in the xc-potential at time t, requires knowledge of the density at all earlier times.

The argument above shows that memory is induced by electron-correlation effects beyond the single-particle excitations.

Foundations of time-dependent density functional theory
(Lecture 9)

Overview

1) Hohenberg-Kohn generalization:
   The Runge-Gross theorem (,).
2) Beyond Runge-Gross
   - Extension to Laplace-transformable potentials
   - The extended Runge-Gross theorem and existence of the Kohn-Sham system

The Runge-Gross theorem (Phys. Rev. Lett 52, 997 (1984))

Given an initial state Ψ_0 and a time-dependent density $n(\vec{r}t)$ then there is a unique potential $v(\vec{r}t)$ (modulo a pure time-dependent function $C(t)$) that produces density $n(\vec{r}t)$.

Proof. Consider two different time-dependent system

$$\hat{H}_1(t) = \hat{T} + \hat{V}_1(t) + \hat{W}$$
$$\hat{H}_2(t) = \hat{T} + \hat{V}_2(t) + \hat{W}$$

$$i\partial_t \Psi_1(t) = \hat{H}_1(t)\Psi_1(t) \quad , \quad i\partial_t \Psi_2(t) = \hat{H}_2(t)\Psi_2(t)$$

and $\Psi_1(t_0) = \Psi_2(t_0) = \Psi_0$

We assume that $v_1(\vec{r}t)$ an $v_2(\vec{r}t)$ have a Taylor expansion around t_0, i.e.

$$v_1(\vec{r}t) = \sum_{j=0}^{\infty} v_1^{(j)}(\vec{r})\frac{(t-t_0)^j}{j!} \qquad v_1^{(j)}(\vec{r}) = \partial_t^j v(\vec{r}t)\Big|_{t=t_0}$$
$$v_2(\vec{r}t) = \sum_{j=0}^{\infty} v_2^{(j)}\frac{(t-t_0)^j}{j!} \qquad v_2^{(j)}(\vec{r}) = \partial_t^j v(\vec{r}t)\Big|_{t=t_0}$$

Since $v_1 \neq v_2 + C(t)$ there must be an integer m such that

$$v_1^{(m)}(\vec{r}) \neq v_2^{(m)}(\vec{r})$$

Let k be the smallest of such integers.

We will first show that both systems have different currents.

To do this we consider the equation of motion for the current. We have

$$\partial_t j_1(\vec{r}t) = -i\,\partial_t \langle \Psi_1(t)|\hat{j}(\vec{r})|\Psi_1(t)\rangle$$

$$= -i\,\langle \Psi_1(t)|[\hat{j}(\vec{r}),\hat{H}_1(t)]|\Psi_1(t)\rangle$$

$$\partial_t j_2(\vec{r}t) = -i\,\partial_t \langle \Psi_2(t)|\hat{j}(\vec{r})|\Psi_2(t)\rangle$$

$$= -i\,\langle \Psi_2(t)|[\hat{j}(\vec{r}),\hat{H}_2(t)]|\Psi_2(t)\rangle$$

Since $\Psi_1(t_0)=\Psi_2(t_0)=\Psi_0$ we then have

$$\partial_t j_1(\vec{r}t)\Big|_{t=t_0} = -i\,\langle \Psi_0|[\hat{j}(\vec{r}),\hat{H}_1(t_0)]|\Psi_0\rangle$$

$$\partial_t j_2(\vec{r}t)\Big|_{t=t_0} = -i\,\langle \Psi_0|[\hat{j}(\vec{r}),\hat{H}_2(t_0)]|\Psi_0\rangle$$

$$\Rightarrow \partial_t\big(j_1(\vec{r}t)-j_2(\vec{r}t)\big)\Big|_{t=t_0} = -i\,\langle \Psi_0|[\hat{j}(\vec{r}),\hat{H}_1(t_0)-\hat{H}_2(t_0)]|\Psi_0\rangle$$

$$= -i\,\langle \Psi_0|[\hat{j}(\vec{r}),\hat{V}_1(t_0)-\hat{V}_2(t_0)]|\Psi_0\rangle \qquad (*)$$

If $\hat{V}_1(t_0)=V_2(t_0)$ $(k>0)$ the righthand side of the equation $(*)$ will be zero. In that case we take additional time-derivatives of the current

$$\partial_t^2 j_1(\vec{r}t) = -i\,\partial_t \langle \Psi_1|[\hat{j}(\vec{r}),\hat{H}_1(t)]|\Psi_1\rangle$$

$$= (-i)^2\,\langle \Psi_1|[\hat{j}(\vec{r}),[\hat{j}(\vec{r}),\hat{H}_1(t)]]|\Psi_1\rangle$$

$$-i\,\langle \Psi_1|\partial_t[\hat{j}(\vec{r}),\hat{H}_1(t)]|\Psi_1\rangle$$

with a similar expression for $j_2(\vec{r}t)$

At $t=t_0$ we have

$$\partial_t^2 j_1(\vec r t)\Big|_{t=t_0} = (-i)^2 \langle \Psi_0 | [\hat j(\vec r), [j(\vec r), \hat H_1(t_0)]] | \Psi_0 \rangle$$

$$-i \langle \Psi_0 | [j(\vec r), \partial_t V_1(t_0)] | \Psi_0 \rangle$$

with a similar expression for $\partial_t^2 j_2(\vec r t)\Big|_{t=t_0}$.

Since $\hat H_1(t_0) = \hat H_2(t_0)$ (otherwise we would not have taken the extra time-derivative) we find

$$\partial_t^2 (j_1(\vec r t) - j_2(\vec r t))\Big|_{t=t_0} = -i \langle \Psi_0 | [\hat j(\vec r), \partial_t \hat V_1(t_0) - \partial_t V_2(t_0)] | \Psi_0 \rangle \qquad (**)$$

If $\partial_t \hat V_1(t_0) = \partial_t \hat V_2(t_0)$ then the righthand side of Eq. (**) is zero. In that case we take an additional time-derivative and calculate

$$\partial_t^3 j_1(\vec r t) = (-i)^2 \partial_t \langle \Psi_1 | [\hat j(\vec r), [j(\vec r), \hat H_1(t)]] | \Psi_1 \rangle$$

$$(-i)\ \partial_t \langle \Psi_1 | [j(\vec r), \partial_t \hat H_1(t)] | \Psi_1 \rangle$$

$$= (-i)^3 \langle \Psi_1 | [j(\vec r), [j(\vec r), [j(\vec r), \hat H_1(t)]]] | \Psi_1 \rangle$$

$$+ (-i)^2 \langle \Psi_1 | \partial_t [j(\vec r), [j(\vec r), H_1(t)]] | \Psi_1 \rangle$$

$$+ (-i)^2 \langle \Psi_1 | [j(\vec r), [j(\vec r), \partial_t H(t)]] | \Psi_1 \rangle$$

$$-i \langle \Psi_1 | \partial_t [j(\vec r), \partial_t H(t)] | \Psi_1 \rangle$$

$$= (-i)^3 \langle \Psi_1 | [j(\vec r), [j(\vec r), [j(\vec r), H_1(t)]]] | \Psi_1 \rangle$$

$$+ 2(-i)^2 \langle \Psi_1 | [j(\vec r), [j(\vec r), \partial_t H_1(t)]] | \Psi_1 \rangle$$

$$+ (-i) \langle \Psi_1 | [j(\vec r), \partial_t^2 \hat H_1(t)] | \Psi_1 \rangle$$

With a similar equation for $\partial_t^3 j_2(\vec r t)$

At $t=t_0$ we have

$$\partial_t^3 j_1(\vec{r}t)\Big|_{t=t_0} = (-i)^3 \langle \Psi_0 | [j(\vec{r}), [j(\vec{r}), [j(\vec{r}), \hat{H}_1(t_0)]]] | \Psi_0 \rangle$$

$$+ 2(-i)^2 \langle \Psi_0 | [j(\vec{r}), [j(\vec{r}), \partial_t \hat{H}(t_0)]] | \Psi_0 \rangle$$

$$-i \quad \langle \Psi_0 | [j(\vec{r}), \partial_t^2 H_1(t_0)] | \Psi_0 \rangle$$

with a similar equation for $\partial_t^3 j_2(\vec{r}t)\Big|_{t=t_0}$

Since $H_1(t_0) = H_2(t_0)$, $\partial_t H_1(t_0) = \partial_t H_2(t_0)$ we find by subtraction that

$$\partial_t^3 (j_1(\vec{r}t) - j_2(\vec{r}t))\Big|_{t=t_0} = -i \langle \Psi_0 | [j(\vec{r}), \partial_t^2 \hat{V}_1(t_0) - \partial_t^2 \hat{V}_2(t_0)] | \Psi_0 \rangle \quad (\times\times)$$

If $\partial_t^2 V_1(t_0) = \partial_t^2 V_2(t_0)$ $(k > 2)$ then the righthand side of the equation is again zero and we have to take another time-derivative of $j_1(\vec{r}t)$. The general case is now clear. (check yourself!)

If $\partial_t^j V_1(t_0) = \partial_t^j V_2(t_0)$ for $j = 1 \ldots k-1$ then:

$$\partial_t^{k+1} (j_1(\vec{r}t) - j_2(\vec{r}t))\Big|_{t=t_0} = -i \langle \Psi_0 | [j(\vec{r}), \partial_t^k V_1(t_0) - \partial_t^k V_2(t_0)] | \Psi_0 \rangle \quad (\Delta)$$

We now use Eq. (Δ) for the smallest integer k such that $\partial_t^k \hat{V}_1(t_0) \neq \partial_t^k \hat{V}_2(t_0)$

We now evaluate the righthand side of (Δ) in more detail

$$\hat{V}_1(t) = \int d^3\vec{r} \; n(\vec{r}) \, v_1(\vec{r}t)$$

$$\Rightarrow \quad \partial_t^k V_1(t_0) = \int d^3\vec{r} \; \hat{n}(\vec{r}) \, \partial_t^k v_1(\vec{r}t_0)$$

and similarly for $\partial_t^k \hat{V}_2(t_0)$

Then

$$-i \langle \Psi_0 | [j(\vec r), \partial_t^k \hat V_1(t_0) - \partial_t^k V_2(t_0)] | \Psi_0 \rangle$$

$$= -i \int d^3\vec r' \; \langle \Psi_0 | [j(\vec r), \hat n(\vec r')] | \Psi_0 \rangle \; (\partial_t^k v_1(\vec r' t_0) - \partial_t^k v_2(\vec r t_0)) \qquad (\Delta\Delta)$$

So now we need to calculate the commutator

$$[\hat j(\vec r), \hat n(\vec r')] = \hat j(\vec r)\hat n(\vec r') - \hat n(\vec r')\hat j(\vec r)$$

$$= \left(\frac{1}{2i} \sum_j^N \delta(\vec r - \vec r_j)\nabla_j + \nabla_j \delta(\vec r - \vec r_j) \right) \sum_i^N \delta(\vec r' - \vec r_i)$$

$$- \sum_i^N \delta(\vec r' - r_i) \left(\frac{1}{2i} \sum_j \delta(\vec r - \vec r_j)\nabla_j + \nabla_j \delta(\vec r - \vec r_j) \right)$$

$$= \frac{1}{2i} \sum_{ij} \delta(\vec r - \vec r_j)(\nabla_j \delta(\vec r' - \vec r_i)) + \delta(\vec r - \vec r_j)(\nabla_j \delta(\vec r' - \vec r_i))$$

$$= -i \sum_j \delta(\vec r - \vec r_j)(\nabla_j \delta(\vec r' - \vec r_j))$$

Therefore $[j(\vec r), \hat V(t)] = \int d^3\vec r' \; [j(\vec r), \hat n(\vec r')] v(\vec r' t)$

$$= -i \sum_j \delta(\vec r - \vec r_j) \nabla_j \int d^3\vec r' \; \delta(\vec r' - \vec r_j) v(\vec r' t)$$

$$= -i \sum_j \delta(r - \vec r_j) \nabla_j v(\vec r_j t) =$$

$$= -i \sum_j \delta(\vec r - \vec r_j) \nabla_{\vec r} v(\vec r t) = \underline{-i \hat n(\vec r) \nabla_{\vec r} v(\vec r t)}$$

So Eq. $(\Delta\Delta)$ becomes

$$-i \langle \Psi_0 | [j(\vec r), \partial_t^k \hat V_1(t_0) - \partial_t^k \hat V_2(t_0)] | \Psi_0 \rangle$$

$$= - \langle \Psi_0 | \hat n(\vec r) | \Psi_0 \rangle \nabla_{\vec r} \cdot (\partial_t^k v_1(\vec r t_0) - \partial_t^k v_2(r t_0))$$

$$= - n_0(\vec r) \nabla_r (v_1^{(k)}(\vec r) - v_2^{(k)}(\vec r))$$

So finally we have

$$\partial_t^{k+1} \left(j_1(\vec{r}t) - j_2(\vec{r}t) \right) \Big|_{t=t_0} = - n(\vec{r}t_0) \nabla_{\vec{r}} \left(v_1^{(k)}(\vec{r}) - v_2^{(k)}(\vec{r}) \right)$$

Since $v_1^{(k)}(\vec{r}) \neq v_2^{(k)}(\vec{r})$ and $\vec{r}$ - dependent we find

$$\partial_t^{k+1} j_1(\vec{r}t_0) \neq \partial_t^{k+1} j_2(\vec{r}t_0)$$

So, if the k-th time-derivates at $t = t_0$ of v_1 and v_2 are different, then the (k+1)-th derivatives of the currents $j_1(\vec{r}t)$ and $j_2(\vec{r}t)$ become different

$$\Rightarrow \quad j_1(\vec{r}t) \neq j_2(\vec{r}t)$$

This establishes the first part of the Runge-Gross proof.

The second part of the proof consists of proving the densities to be different as well

To show this we use the continuity equation

$$\partial_t n(\vec{r}t) + \nabla j(\vec{r}t) = 0$$

$$\Rightarrow \quad \partial_t^{k+2} n(\vec{r}t) + \nabla \partial_t^{k+1} j(\vec{r}t) = 0$$

So for systems 1 and 2 we have

$$\partial_t^{k+2} \left(n_1(\vec{r}t) - n_2(\vec{r}t) \right) \Big|_{t=t_0} = \nabla_{\vec{r}} \, \partial_t^{k+1} \left(j_1(\vec{r}t) - j_2(\vec{r}t) \right) \Big|_{t=t_0}$$

$$= - \nabla \left(n(\vec{r}t_0) \nabla \left(v_1^{(k)}(\vec{r}) - v_2^{(k)}(\vec{r}) \right) \right)$$

Therefore to show that

$$\partial_t^{k+2} (n_1(\vec{r}t) - n_2(\vec{r}t))\Big|_{t=t_0} \neq 0$$

we have to show that

$$\nabla (n(\vec{r}t_0) \nabla f(\vec{r})) \neq 0 \qquad f(\vec{r}) = v_1^{(k)}(\vec{r}) - v_2^{(k)}(\vec{r})$$

However

$$\int d^3\vec{r}\ f(\vec{r}) \nabla (n(\vec{r}t_0) \nabla f(\vec{r}))$$

$$= \int d^3\vec{r} \left[\nabla \cdot \{ f(\vec{r})\, n(\vec{r}t_0) \nabla f(\vec{r}) \} - n(\vec{r}t_0)(\nabla f(\vec{r}))^2 \right]$$

$$= \underbrace{\oint f(\vec{r})\, n(\vec{r}t_0) \nabla f(\vec{r}) \cdot d\vec{S}}_{\substack{\text{surface integral at} \\ \text{infinity vanishes for} \\ \text{finite systems, and} \\ \text{for potentials } f(\vec{r}) \text{ generated} \\ \text{by bounded charge} \\ \text{distributions}}} - \int n(\vec{r}t_0)(\nabla f(\vec{r}))^2 d^3\vec{r}$$

So $\nabla (n(\vec{r}t_0) \nabla f(\vec{r})) = 0$ would lead to

$$0 = -\int d^3\vec{r}\ n(\vec{r}t_0) (\nabla f(\vec{r}))^2$$

This is, however, in contradiction to $\nabla f \neq 0$
since $n(\vec{r}t_0) > 0$

Therefore $\partial_t^{k+2} (n_1(\vec{r}t) - n_2(\vec{r}t))\Big|_{t=t_0} \neq 0$

This proves the Runge-Gross theorem.

The case of potentials that do not have a Taylor-expansion.

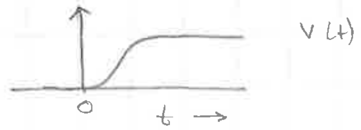
The Runge-Gross proof assumes that the potentials $v(\vec{r}t)$ have a Taylor-expansion for $t \geq t_0$

$$v(\vec{r}t) = \sum_{j=0}^{\infty} v^{(j)}(\vec{r}) \frac{(t-t_0)^j}{j!}$$

However, there exist infinitely differentiably functions $v(t)$ that have a Taylor-series with convergence radius of zero.

For example:

$$v(t) = \begin{cases} e^{-\frac{1}{t}} & t > 0 \\ 0 & t \leq 0 \end{cases}$$



One has $\lim_{t \to 0} \partial_t^k v(t) = 0 \quad \forall \, k \in \mathbb{N}$

This function can therefore not be distinguished from the function $v(t) \equiv 0$ by its Taylor expansion around $t = 0$.

However, one can design a Runge-Gross-type of proof that does not use the Taylor-expansion. The proof is, however, restricted to systems that are initially in a ground state.

This is done by proving that the density response function, $\chi(\vec{r}t, \vec{r}'t')$ has an inverse.

We prove the following: (R van Leeuwen, Int. J Mod. Phys. B15, 1969 (2001))

$$\delta n(\bar{r}_1 t_1) = \int_0^{+\infty} dt_2 \int d^3\bar{r}_2 \; \chi(r_1 t_1, \bar{r}_2 t_2)\, \delta v(\bar{r}_2 t_2) = 0$$

$$\Rightarrow \quad \delta v(\bar{r}_2 t_2) = C(t_2) \qquad (\mathrm{II})$$

In other words, only purely time-dependent functions yields zero density variations

So if two potentials yield the same density variation

$$\rightarrow \qquad \begin{aligned} \delta n_1 &= \int \chi\, \delta v_1 \\ \delta n_2 &= \int \chi\, \delta v_2 \end{aligned} \qquad \text{and} \qquad \delta n_1 = \delta n_2$$

then $\quad 0 = \delta n_1 - \delta n_2 = \int \chi\, (\delta v_1 - \delta v_2)$

$$\Rightarrow \quad \delta v_1 - \delta v_2 = C(t) \quad \Rightarrow \quad \delta v_1 = \delta v_2 + C(t)$$

Let us prove (II):

$$\chi(r_1 t_1, \bar{r}_2 t_2) = i\, \theta(t-t') \sum_n e^{i\Omega_n (t-t')} f_n^*(\bar{r}) f_n(\bar{r}')$$
$$- i\, \theta(t-t') \sum_n e^{-i\Omega_n (t-t')} f_n(\bar{r}) f_n^*(\bar{r}')$$

$f_n(\bar{r}) = \langle \Psi_0 | \hat{n}(\bar{r}) | \Psi_n \rangle$ n-th excited state of the unperturbed system

$\Omega_n = E_n - E_0$

We can therefore write (II) as

$$\delta n(\bar{r}_1 t_1) = i \sum_{n=1}^{\infty} \int_0^{t_1} dt_2 \int d^3\bar{r}_2 \; e^{i\Omega_n (t_1 - t_2)} f_n^*(r_1) f_n(\bar{r}_2)\, \delta v(\bar{r}_2 t_2) + c.c.$$

complex conjugate

Note that n=0 does not contribute in this sum

This can be written as

$$\delta n(\vec{r}_1 t_1) = i \sum_{n=1}^{\infty} f_n^*(\vec{r}_1) \int_0^{t_1} dt_2\, a_n(t_2)\, e^{i\Omega_n(t_1 - t_2)} + c.c. \qquad (\Box\Box)$$

where we defined $\quad a_n(t) = \int d^3r\, f_n(\vec{r})\, \delta v(\vec{r}t)$

The integral $(\Box\Box)$ is of a convolution form

$$(f * g)(t) = \int_0^t dt'\, f(t')\, g(t'-t)$$

This type of convolution integrals can be deconvoluted using Laplace transforms

$$\mathcal{L}f(s) = \int_0^{\infty} dt\, e^{-st} f(t)$$

$$\mathcal{L}(f*g)(s) = \mathcal{L}f(s)\, \mathcal{L}g(s)$$

Since for $f(t) = e^{i\Omega_n t}$;

$$(\mathcal{L}f)(s) = \int_0^{\infty} dt\, e^{(-s+i\Omega_n)t} = \frac{1}{s - i\Omega_n}$$

we see that Eq. $(\Box\Box)$ becomes

$$\mathcal{L}(\delta n)(\vec{r}_1 s) = i \sum_{n=1}^{\infty} f_n^*(r_1) \frac{1}{s - i\Omega_n} (\mathcal{L}a_n)(s) + c.c. \qquad (\Box\Box\Box)$$

where $\quad (\mathcal{L}a_n)(s) = \int d\vec{r}\, f_n(\vec{r})\, (\mathcal{L}\,\delta v)(\vec{r}\, s)$

If we multiply both sides of Eq. $(\Box\Box\Box)$ with $(\mathcal{L}\,\delta v)(\vec{r}_1 s)$ and integrate over $\vec{r}_1$ we obtain

$$\int d^3\vec{r}_1\, (\mathcal{L}\,\delta v)(\vec{r}_1, s)(\mathcal{L}\,\delta n)(\vec{r}_1, s)$$

$$= i \sum_{n=1}^{\infty} \frac{|(\mathcal{L}a_n)(s)|^2}{s - i\Omega_n} + c.c.$$

$$= \sum_{n=1}^{\infty} |(\mathcal{L}a_n)(s)|^2 \left\{ \frac{i}{s - i\Omega_n} - \frac{i}{s + i\Omega_n} \right\} = -2 \sum_{n=1}^{\infty} \frac{|\mathcal{L}a_n(s)|^2\, \Omega_n}{s^2 + \Omega_n^2}$$

If we therefore suppose that $\delta n(\vec{r},t) = 0$ then also $(\mathcal{L}\delta n)(\vec{r},s) = 0$ and consequently

$$0 = -2 \sum_{n=1}^{\infty} \frac{\Omega_n}{s^2+\Omega_n^2} |\mathcal{L}a_n(s)|^2$$

Since $\Omega_n = E_n - E_0 > 0$ (we consider nondegenerate systems)

it follows that

$$(\mathcal{L}a_n)(s) = 0 \qquad \text{for all} \quad n = 1, 2, \ldots$$

$$\Rightarrow \quad a_n(t) = 0 \qquad n = 1, 2, \ldots$$

But this implies that with $\delta\hat{V}(t) = \int d^3r\, \hat{n}(\vec{r})\, \delta v(\vec{r},t)$

$$\delta\hat{V}(t)\,|\Psi_0\rangle = \sum_{n=0}^{\infty} |\Psi_n\rangle\langle\Psi_n|\delta\hat{V}(t)|\Psi_0\rangle$$

$$= \sum_{n=0}^{\infty} |\Psi_n\rangle \int d^3r\, \underbrace{\langle\Psi_n|\hat{n}(\vec{r})|\Psi_0\rangle}_{f_n^*(\vec{r})}\, \delta v(\vec{r},t)$$

$$= \sum_{n=0}^{\infty} a_n^*(t)\,|\Psi_n\rangle = a_0^*(t)\,|\Psi_0\rangle$$

$$a_0^* = a_0 = \langle\Psi_0|\delta\hat{V}(t)|\Psi_0\rangle$$

So we find

$$\sum_{i=1}^{N} \delta v(\vec{r}_i,t)\,\Psi_0 = a_0(t)\,\Psi_0$$

$$\Rightarrow \quad \delta v(\vec{r}t) = \frac{a_0(t)}{N} = c(t)$$

So only purely time-dependent potentials yield zero density variations.

This proves (II)

The proof that we presented was valid for all Laplace-transformable potentials.

In particular it includes potential with a temporal behavior:

$$v(t) = e^{-1/t} \qquad t > 0$$

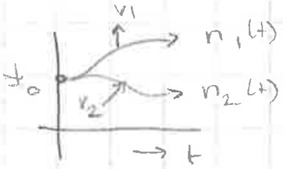
which has Laplace transform

$$(\mathcal{L}v)(s) = \int_0^\infty dt \; e^{-s(t+\frac{1}{t})}$$

The extended Runge-Gross theorem

(R. von Leeuwen, Phys. Rev. Lett. 82, 3863 (1999))

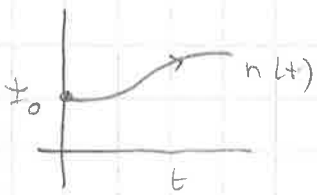
In the Runge-Gross theorem we had the following situation



True system

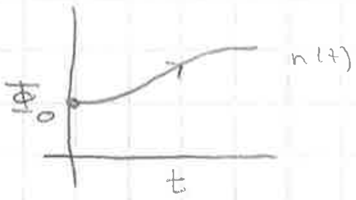
$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

However, in practice we want to use the following situation



True system

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



Kohn-Sham system

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

The Kohn-Sham system has a different initial state and different two-particle interactions (zero).

We can therefore ask ourselves the following question

Suppose we have solved the time-dependent Schrödinger equation

$$i\partial_t \Psi(t) = \hat{H}(t)\Psi(t) \qquad \Psi(t_0) = \Psi_0$$

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

and obtained density $n(\vec{r}t) = \langle \Psi(t) | \hat{n}(\vec{r}) | \Psi(t) \rangle$.

Does there exist a different system with external potential $\hat{V}'(t)$, interaction $\hat{W}'$ and initial state Φ_0, such that

$$i\partial_t \Phi(t) = \hat{H}'(t)\Phi(t)$$

$$\hat{H}'(t) = \hat{T} + \hat{V}'(t) + \hat{W}' \quad , \quad \Phi(t_0) = \Phi_0$$

and

$$n(\vec{r}t) = \langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle$$
$$= \langle \Psi(t) | \hat{n}(\vec{r}) | \Psi(t) \rangle \quad ?$$

In other, words: Can the same density $n(\vec{r}t)$ be reproduced in a different system, with different external potential, interactions and initial state ?

We will prove that this is possible

To prove this we start from the equation of motion for the current :

$$\partial_t j(\vec{r}t) = -i \langle \Psi(t) | [\hat{j}(\vec{r}), \hat{H}(t)] | \Psi(t) \rangle$$

$$= -i \langle \Psi(t) | [j(\vec{r}), \hat{V}(t)] | \Psi(t) \rangle$$

$$- i \langle \Psi(t) | [j(\vec{r}), \hat{T} + \hat{W}] | \Psi(t) \rangle$$

We already proved that

$$[\hat{j}(\vec{r}), \hat{V}(t)] = -i\,\hat{n}(\vec{r})\,\nabla v(\vec{r}t)$$

Then the equation of motion for the current can be written as

$$\partial_t \vec{j}(\vec{r}t) = -\langle \Psi(t)|\hat{n}(r)|\Psi(t)\rangle \nabla v(\vec{r}t)$$

$$-i\,\langle \Psi(t)|\,[\hat{j}(\vec{r}), \hat{T}+\hat{W}]\,|\Psi(t)\rangle$$

$$= -n(\vec{r}t)\nabla v(\vec{r}t) \quad -i\,\langle \Psi(t)|\,[\hat{j}(\vec{r}), \hat{T}+\hat{W}]\,|\Psi(t)\rangle$$

If we further consider the continuity equation

$$\partial_t n + \nabla\cdot\vec{j} = 0$$

We obtain

$$\partial_t^2 n = -\nabla\,\partial_t j = \nabla\left(n(\vec{r}t)\nabla v(\vec{r}t)\right) +$$

$$-i\,\langle \Psi|\,\nabla_r\cdot[\hat{j}(\vec{r}), \hat{T}+\hat{W}]\,|\Psi(t)\rangle$$

So we find

$$\partial_t^2 n(\vec{r}t) = \nabla\left(n(\vec{r}t)\nabla v(\vec{r}t)\right) + q(\vec{r}t) \qquad (\nabla)$$

Where we defined

$$\hat{q}(\vec{r}) = -i\,\nabla_{\vec{r}}\cdot[\hat{j}(\vec{r}), \hat{T}+\hat{W}]$$

and $q(\vec{r}t) = \langle \Psi(t)|\hat{q}(\vec{r})|\Psi(t)\rangle$

(We will not work out the explicit form of $\hat{q}(\vec{r})$ here. You can try it yourself, it will correspond to the stress-momentum tensor of the system).

We have a similar equation for the system with Hamiltonian $\hat{H}'$

$$\partial_t^2 n'(\vec{r}t) = \nabla(n'(\vec{r}t)\nabla v'(\vec{r}t)) + q'(\vec{r}t) \qquad (\nabla\nabla)$$

$$q'(\vec{r}t) = \langle \Phi(t) | \hat{q}'(\vec{r}t) | \Phi(t) \rangle$$

$$\hat{q}'(\vec{r}t) = -i\nabla_{\vec{r}} \cdot [\hat{j}(\vec{r}), \hat{T} + \hat{W}']$$

We are now going to construct $v'(\vec{r}t)$ such that $n'(\vec{r}t) = n(\vec{r}t)$

If $n(\vec{r}t) = n'(\vec{r}t)$ then also

$$\partial_t^k n(\vec{r}t)\Big|_{t=t_0} = \partial_t^k n'(\vec{r}t)\Big|_{t=t_0} \qquad \forall k$$

For those systems the initial states cannot be arbitrary. We must have

$$n(\vec{r}t_0) = \langle \Psi_0 | \hat{n}(\vec{r}) | \Psi_0 \rangle = \langle \Phi_0 | \hat{n}(\vec{r}) | \Phi_0 \rangle$$

and $$\partial_t n(\vec{r}t)\Big|_{t=t_0} = -\langle \Psi_0 | \nabla \cdot \hat{j}(\vec{r}) | \Psi_0 \rangle = -\langle \Phi_0 | \nabla \cdot \hat{j}(\vec{r}) | \Phi_0 \rangle$$

If we demand that $n'(\vec{r}t) = n(\vec{r}t)$ then Eq. $(\nabla\nabla)$ becomes

$$\partial_t^2 n(\vec{r}t) = \nabla(n(\vec{r}t)\nabla v'(\vec{r}t)) + q(\vec{r}t)$$

Subtracting this from (∇) gives

$$0 = \nabla(n(\vec{r}t)\nabla(v(\vec{r}t) - v'(\vec{r}t))) + q(\vec{r}t) - q'(\vec{r}t)$$

$$\Rightarrow \quad \underline{\nabla(n(\vec{r}t)\nabla w(\vec{r}t)) = \zeta(\vec{r}t)} \qquad (\nabla\nabla\nabla)$$

$$w(\vec{r}t) = v'(\vec{r}t) - v(\vec{r}t)$$

$$\zeta(\vec{r}t) = -(q'(\vec{r}t) - q(\vec{r}t))$$

We can now use ($\nabla\nabla\nabla$) to solve for $w(rt)$
Let us take $t = t_0$ then we have

$$\nabla(n(\vec{r}t_0)\nabla w(\vec{r}t_0)) = \zeta(\vec{r}t_0) = q(\vec{r}t_0) - q'(\vec{r}t_0) \qquad (\nabla\nabla\nabla\nabla)$$

$$= \langle \Psi_0 | \hat{q}(\vec{r}) | \Psi_0 \rangle - \langle \Phi_0 | \hat{q}(\vec{r}) | \Phi_0 \rangle$$

Since the righthand side of this equation is known, as well as $n(\vec{r}t_0)$, we can solve for $w(\vec{r}t_0)$.

If we specify the boundary condition $w(\vec{r}t_0) \to 0$ (for $|\vec{r}| \to \infty$ then ($\nabla\nabla\nabla\nabla$) has a unique solution.
We have therefore determined

$$w(\vec{r}t_0) = v'(rt_0) - v(\vec{r}t_0)$$

$$\Rightarrow \quad v'(\vec{r}t_0) = w(\vec{r}t_0) + v(\vec{r}t_0)$$

Our next goal is to determine the first derivative $\partial_t v'(t_0)$. To do this we take the first derivative of ($\nabla\nabla\nabla$) in t_0. This gives

$$\nabla(n^{(1)}(\vec{r})\nabla w^{(0)}(\vec{r})) + \nabla(n^{(0)}(\vec{r})\nabla w^{(1)}(\vec{r})) = \zeta^{(1)}(\vec{r})$$

where used the notation : $f^{(k)}(\vec{r}) = \partial_t^k f(\vec{r}t)\Big|_{t=t_0}$

We can write this as

$$\nabla(n^{(0)}(\vec{r})\nabla w^{(1)}(\vec{r})) = \zeta^{(1)}(\vec{r}) - \nabla(n^{(1)}(\vec{r})\nabla w^{(0)}(\vec{r}))$$

All quantities on the righthand side are known since $n^{(1)}(\vec{r}) = \partial_t n(\vec{r}t)\Big|_{t=t_0}$ is known and $w^{(0)}(\vec{r}) = v'(rt_0) - v(\vec{r}t_0)$ we just determined.
Furthermore

$$\zeta^{(1)}(\vec{r}) = \partial_t \zeta(rt)\Big|_{t=t_0} = \partial_t q(\vec{r}t)\Big|_{t_0} - \partial_t q'(rt)\Big|_{t_0}$$

$$= -i \langle \Psi_0 | [\hat{q}(\vec{r}), \hat{H}(t_0)] | \Psi_0 \rangle + i \langle \Phi_0 | [\hat{q}(\vec{r}), \hat{H}'(t_0)] | \Phi_0 \rangle$$

Since we know Ψ_0 and Φ_0 and we determined $H'(t_0)$ already also $\varsigma^{(1)}(\vec{r})$ is known.

We can therefore solve for $w^{(1)}(\vec{r})$ and obtain

$$v^{(1)'}(\vec{r}) = \partial_t v'(\vec{r}t)\Big|_{t=t_0} = w^{(1)}(\vec{r}) + \partial_t v(\vec{r}t)\Big|_{t=t_0}$$

To obtain $\partial_t^2 v'\Big|_{t_0}$ we differentiate $(\nabla V \nabla)$ twice and find

$$\nabla(n^{(2)}(\vec{r})\nabla w^{(0)}(\vec{r})) + 2\nabla(n^{(1)}(\vec{r})\nabla w^{(1)}(\vec{r})) + \nabla(n^{(0)}(\vec{r})\nabla w^{(2)}(\vec{r})) = \varsigma^{(2)}(\vec{r})$$

This equation can be rewritten as

$$\nabla(n^{(0)}(\vec{r})\nabla w^{(2)}(\vec{r})) = \varsigma^{(2)}(\vec{r}) - 2\nabla(n^{(1)}\nabla w^{(1)}) - \nabla(n^{(2)}\nabla w^{(0)})$$

Again all quantities on the righthand side are known: $w^{(0)}, w^{(1)}$ are determined earlier and $\varsigma^{(2)}(\vec{r})$ can be calculated from

$$\begin{aligned}\varsigma^{(2)}(\vec{r}) &= \partial_t^2 g(\vec{r}t)\Big|_{t=t_0} - \partial_t^2 g'(\vec{r}t)\Big|_{t=t_0} \\ &= (-i)^2 \langle\Psi_0|[\hat{q}(\vec{r}),[\hat{q}(\vec{r}),\hat{H}(t_0)]]|\Psi_0\rangle \\ &\quad - (-i)^2 \langle\Phi_0|[\hat{q}(\vec{r}),[\hat{q}(\vec{r}),\hat{H}'(t_0)]]|\Phi_0\rangle \\ &\quad + (-i)\langle\Psi_0|[\hat{q}(\vec{r}),\partial_t\hat{H}(t_0)]|\Psi_0\rangle \\ &\quad - (-i)\langle\Phi_0|[\hat{q}(\vec{r}),\partial_t\hat{H}'(t_0)]|\Phi_0\rangle\end{aligned}$$

which is determined since Ψ_0, Φ_0, and $H'(t_0)$, $\partial_t\hat{H}(t_0)$ are known.

We can therefore solve for $w^{(2)}(\vec{r})$ and we obtain

$$\partial_t^2 v'(\vec{r}t_0) = w^{(2)}(\vec{r}) + \partial_t^2 v(\vec{r}t_0)$$

The procedure is now clear.
If we differentiate $(\nabla V \nabla)$ k times we find

$$\sum_{l=0}^{k} \binom{k}{l} \nabla \cdot \left(n^{(k-l)}(\bar r) \nabla \omega^{(l)}(\bar r) \right) = \zeta^{(k)}(\bar r)$$

which yields the equation

$$\nabla \left(n^{(0)}(\bar r) \nabla \omega^{(k)}(\bar r) \right) = \zeta^{(k)}(\bar r) - \sum_{l=0}^{k-1} \binom{k}{l} \nabla \left(n^{(k-l)}(\bar r) \nabla \omega^{(l)}(\bar r) \right)$$

All the terms on the righthand side are known. $\omega^{(l)}$, $l=1,..k-1$ are determined earlier and

$$\zeta^{(k)}(\bar r) = \partial_t^k g(\bar r t_0) - \partial_t^k g(\bar r t_0)$$

= an expression in terms of multiple commutators of $\hat g(\bar r)$, involving derivatives of the Hamiltonian $\partial_t^l \hat H'(t_0)$ for $l=1..k-1$ an evaluated between states Ψ_0 and Φ_0

So also $\zeta^{(k)}(\bar r)$ is known.
We can therefore solve for $\omega^{(k)}(\bar r)$ and find

$$\partial_t^k v'(\bar r t_0) = \omega^{(k)}(\bar r) + \partial_t^k v(\bar r t_0)$$

In this way we have constructed all coefficients $\partial_t^k v'(\bar r t_0)$ and can thus construct

$$v'(\bar r t) = \sum_{k=0}^{\infty} \partial_t^k v'(\bar r t_0) \frac{(t-t_0)^k}{k!}$$

This proves the theorem

(For further discussion see also:

G.F. Giuliani and G. Vignale,
Quantum Theory of the Electron Liquid,
Cambridge University Press, 2005)

Let us now consider a few special cases:

a) $\hat{W}' = 0$ (existence of the Kohn-Sham scheme)

Given Ψ_0, $n(\vec{r}t)$ of an interacting system there is a unique (modulo $c(t)$) potential $\hat{V}'(t)$ in a noninteracting system such that

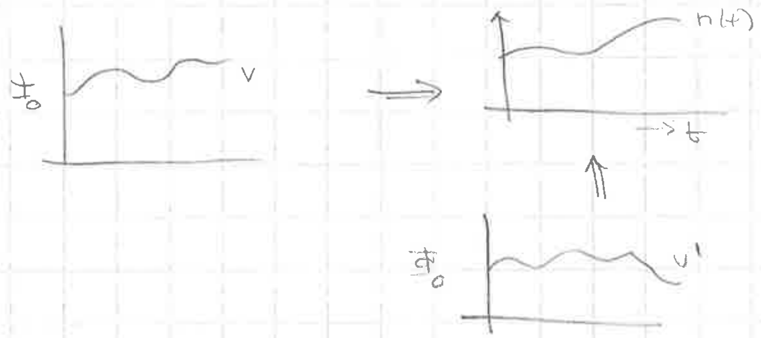
$$i\partial_t \Phi(t) = (\hat{T} + \hat{V}'(t))\Phi(t) \qquad \Phi(t_0) = \Phi_0$$

$$n(\vec{r}t) = \langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle$$

b) $\hat{W} = \hat{W}'$, $\Psi_0 \neq \Phi_0$

Given $n(\vec{r}t)$, Ψ_0, Φ_0 being initial states, then there is a unique potential $v'(\vec{r}t)$ (modulo $c(t)$) such that

$$\langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle = \langle \Psi(t) | \hat{n}(\vec{r}) | \Psi(t) \rangle$$



Two different potentials with two different initial states yield the same density

c) $\hat{W} = \hat{W}'$, $\Psi_0 = \Phi_0$

The proof yields $v(\vec{r}t) = v'(\vec{r}t)$

This corresponds to the usual Runge-Gross theorem.

Concluding remarks:

We have now given a detailed discussion of the foundations of time-dependent density-functional theory an established

- ⇒ The Runge-Gross mapping
- ⇒ Extension to non-Taylorexpandable potentials
- ⇒ Proved the extended Runge-Gross theorem and proved the existence of the Kohn-Sham system (which solves the time-dependent v-representability problem)

Another topic that we did not discuss is the action principle.

For a detailed discussion of these and other topics we refer to

"Time-Dependent Density Functional Theory"

Lecture Notes in Physics, Vol. 706
(Springer) Berlin, 2006

Eds. M.A.L. Marques et al.

and the textbook

"Time-Dependent Density-Functional Theory: Concepts and Applications"

C.A. Ullrich, Oxford University Press (2011)

Beyond the adiabatic local density approximation (Lecture 10)

We can study be linear response equation of TDDFT for the case of a homogeneous electron gas:

$$\chi(\vec{r}_1\vec{r}_2,\omega) = \chi_s(\vec{r}_1\vec{r}_2,\omega) + \int d\vec{r}_3 d\vec{r}_4\, \chi_s(\vec{r}_1\vec{r}_3;\omega)$$

$$\times \left[\frac{1}{|\vec{r}_3-\vec{r}_4|} + f_{xc}(\vec{r}_3\vec{r}_4;\omega) \right] \chi(\vec{r}_4\vec{r}_2;\omega) \qquad (*)$$

In a homogeneous system $\chi(\vec{r}_1\vec{r}_2;\omega) = \chi(|\vec{r}_1-\vec{r}_2|;\omega)$ as a consequence of translational invariance. We can therefore Fourier transform

$$\chi(\vec{q},\omega) = \int d\vec{r}\, \chi(|\vec{r}-\vec{r}'|;\omega)\, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}')}$$

and write $(*)$ as

$$\chi(\vec{q},\omega) = \chi_s(\vec{q},\omega) + \chi_s(\vec{q},\omega)\left[v(\vec{q}) + f_{xc}(\vec{q},\omega)\right]\chi(\vec{q},\omega)$$

or

$$f_{xc}(\vec{q},\omega) = \frac{1}{\chi_s(\vec{q},\omega)} - \frac{1}{\chi(\vec{q},\omega)} - v(\vec{q})$$

where $v(\vec{q}) = \frac{4\pi}{|\vec{q}|^2}$ is the Fourier transform of $\frac{1}{|\vec{r}|}$.

Therefore, by studying the density response function of the homogeneous electron gas, we can construct approximations for $f_{xc}(\vec{q},\omega)$

We can then go back to real space and find

$$f_{xc}^{hom}(n_0;|\vec{r}-\vec{r}'|,\omega) = \int \frac{d^3\vec{q}}{(2\pi)^3}\, f_{xc}^{hom}(n_0,\vec{q},\omega)\, e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}$$

where n_0 is the homogeneous density of the electron gas.

We can now make a local density type of approximation for the xc-kernel f_{xc}

We consider a slowly varying system and we replace

$$f_{xc}^{hom}(n_0; |\vec{r}-\vec{r}'|, \omega) \quad \text{by} \quad f_{xc}^{hom}(n_0(\vec{r}); |\vec{r}-\vec{r}'|, \omega)$$

$n_0(\vec{r})$

The linear response to this slowly varying system is then given by

$$\begin{aligned}
\delta v_{xc}(\vec{r}\omega) &\simeq \int d\vec{r}' \, f^{hom}(n_0(\vec{r}); |\vec{r}-\vec{r}'|, \omega) \, \delta n(\vec{r}'\omega) \\
&\simeq \delta n(\vec{r}\omega) \int d\vec{r}' \, f^{hom}(n_0(\vec{r}); |\vec{r}-\vec{r}'|, \omega) \\
&\simeq \delta n(\vec{r}\omega) \, f_{xc}^{hom}(\underline{\vec{q}}=0, \omega)
\end{aligned}$$

where we assumed that $f(|\vec{r}-\vec{r}'|, n_0(\vec{r}))$ has a short range.

This approximation corresponds to the so-called Gross-Kohn kernel (Phys. Rev. Lett. 55, 2850, (1985))

$$f_{xc}^{GK}(\vec{r}, \vec{r}'; \omega) = \delta(\vec{r}-\vec{r}') \, f_{xc}^{hom}(\underline{\vec{q}}=0, \omega, n_0(\vec{r}))$$

This approximation may seem to improve on the simpler ALDA. However, the approximation violates some conservation laws. So we will look at bit further into this.

The zero-force theorem

Let us look at the position operator

$$\hat{r} = \int d^3\vec{r}\ \vec{r}\ \hat{n}(\vec{r}) = \int d^3\vec{r}\ \vec{r} \sum_i^N \delta(\vec{r}-\vec{r}_i) = \sum_i^N \vec{r}_i$$

and calculate its time-derivative

$$\frac{d}{dt}\langle\hat{r}\rangle(t) = -i\langle[\hat{r},\hat{H}(t)]\rangle = -i\langle[\hat{r},\hat{T}+\hat{V}(t)+\hat{W}]\rangle$$

$$= -i\langle[\hat{r},\hat{T}]\rangle$$

as $\hat{r}$ commutes with $\hat{V}(t)$ and $\hat{W}$. We further have

$$-i[\hat{r},\hat{T}] = -i(\hat{r}\hat{T} - \hat{T}\hat{r})$$

$$= -i\sum_j \vec{r}_i\left(-\frac{1}{2}\nabla_j^2\right) - \left(-\frac{1}{2}\nabla_j^2\right)\vec{r}_i$$

$$= \sum_j -i\nabla_j = \sum_j \hat{p}_j = \hat{P}$$

where $\hat{p}_j$ the momentum operator for a single particle and $\hat{P}$ the operator for the total momentum.

So $$\frac{d\langle\hat{r}\rangle}{dt} = \langle\hat{P}\rangle(t)$$

We further have

$$\frac{d}{dt}\langle\hat{P}\rangle(t) = -i\langle[\hat{P},\hat{H}(t)]\rangle = -i\langle[\hat{P},\hat{T}+\hat{V}(t)+\hat{W}]\rangle$$

Now

$$[\hat{P},\hat{T}] = \sum_j^N [\hat{p}_i, \frac{\hat{p}_j^2}{2}] = 0$$

$$[\hat{P},\hat{W}] = \sum_{\substack{ijk \\ j\neq k}}^N \frac{1}{2}[\hat{p}_i, w(|\vec{r}_j-\vec{r}_k|)] = -i\sum_{ijk}(\delta_{ji}-\delta_{ki})\frac{\partial w}{\partial r}(|r_j - r_j|)$$

$$= 0$$

$$[\hat{P},\hat{V}] = \sum_j^N [\hat{p}_i, v(\vec{r}_j t)] = -i\sum_j^N \nabla_{r_j} v(\vec{r}_j t)$$

So $[\hat{P}, \hat{V}] = -i \sum_{j=1}^{N} \nabla_{r_j} v(\vec{r}_j t)$

$$= -i \int d^3\vec{r}\ \hat{n}(\vec{r}) \nabla_{\vec{r}} v(\vec{r} t)$$

So we finally obtain

$$\frac{d^2 \langle \vec{r} \rangle}{dt^2} = \frac{d\langle \hat{P} \rangle}{dt} = -i \langle [\hat{P}, \hat{V}] \rangle$$

$$= - \int d^3\vec{r}\ n(\vec{r}t) \nabla_{\vec{r}} v(\vec{r}t)$$

Newton's second law.

Since $\langle \hat{r} \rangle = \int d^3\vec{r}\ \vec{r}\ n(\vec{r}t)$

this can also be written as

$$\int d^3\vec{r}\ \vec{r}\ \partial_t^2 n(\vec{r}t) = - \int d^3\vec{r}\ n(\vec{r}t) \nabla v(\vec{r}t) \qquad (*)$$

This was derived for any Hamiltonian. Therefore it is in particular true for the Kohn-Sham Hamiltonian.

$$\int d^3\vec{r}\ \vec{r}\ \partial_t^2 n(\vec{r}t) = - \int d^3\vec{r}\ n(\vec{r}t) \nabla v_s(\vec{r}t) \qquad (**)$$

Since the true and the Kohn-Sham system have (by definition) the same density we find by subtraction of $(*)$ and $(**)$ that

$$0 = \int d^3\vec{r}\ n(\vec{r}t) \nabla \left(v_s(\vec{r}t) - v(\vec{r}t) \right)$$

$$= \int d^3\vec{r}\ n(\vec{r}t) \nabla \left(v_H(\vec{r}t) + v_{xc}(\vec{r}t) \right) \qquad (***)$$

Now for the Hartree potential we find that

$$\int d^3\vec{r}\ n(\vec{r})\,\nabla v_H(\vec{r}) = \int d^3\vec{r}\ n(\vec{r})\,\nabla_{\vec{r}} \int d^3\vec{r}\,' \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$= \int d\vec{r}\, d\vec{r}\,' \ -\frac{(\vec{r}-\vec{r}\,')}{|\vec{r}-\vec{r}\,'|^3}\, n(r)\, n(r') = 0$$

We therefore obtain from (xxx)

Zero-Force Theorem:

$$0 = \int d^3\vec{r}\ n(\vec{r}t)\,\nabla v_{xc}(\vec{r}t) \qquad (\Delta)$$

This tells us that the xc-potential does not exert any force on the KS system.

If we differentiate (Δ) with respect to the density we obtain:

$$0 = \frac{\delta}{\delta n(\vec{r}\,'t')} \int d^3\vec{r}\ n(\vec{r}t)\,\nabla v_{xc}(\vec{r}t)$$

$$= \nabla v_{xc}(\vec{r}\,'t') + \int d^3\vec{r}\ n(\vec{r}t)\,\nabla \frac{\delta v_{xc}(\vec{r}t)}{\delta n(\vec{r}\,'t')}$$

$$= \nabla v_{xc}(\vec{r}\,'t') - \int d^3\vec{r}\ \nabla n(\vec{r}t)\, f_{xc}(\vec{r}t, \vec{r}\,'t')$$

This leads to the equation (we take the derivative at ground state density $n_0(\vec{r})$)

$$\int d^3\vec{r}\ \nabla n_0(\vec{r})\, f_{xc}(\vec{r}\vec{r}\,'; t-t') = \nabla v_{xc}([n_0], \vec{r}\,')$$

Fourier transforming gives

$$\int d^3\vec{r}\ \nabla n_0(\vec{r})\, f_{xc}(\vec{r}\vec{r}\,'; \omega) = \nabla v_{xc}([n_0]; \vec{r}\,') \qquad (\Delta\Delta)$$

We see that the righthand side is frequency-independent. So integration over $\vec{r}$ on the lefthand side washes out the ω-dependence!

If we insert the GK xc-kernel we see that we obtain the contradiction

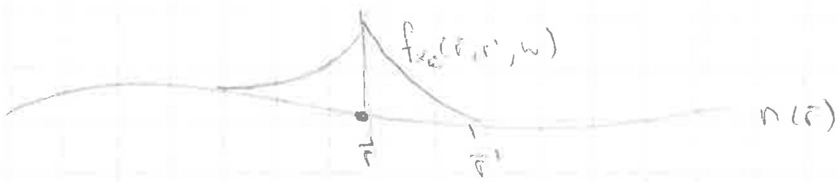
$$\nabla n_0(\vec r)\, f_{xc}^{hom}(n_0(\vec r), \vec q = 0, \omega) = \nabla v_{xc}(\vec r)$$

Frequency-dependent Frequency independent

The GK-approximation violates the zero-force theorem.

This can be turned into a general argument.

Suppose $f_{xc}(\vec r, \vec r\,'; \omega)$ is and has a range shorter than distances on which the density changes considerably, i.e.



$\nabla n(\vec r) \approx \nabla n(\vec r\,')$

Then

$$\nabla v_{xc}(\vec r) = \int d\vec r\,'\, f_{xc}(\vec r, \vec r\,'; \omega)\, \nabla n_0(\vec r\,')$$

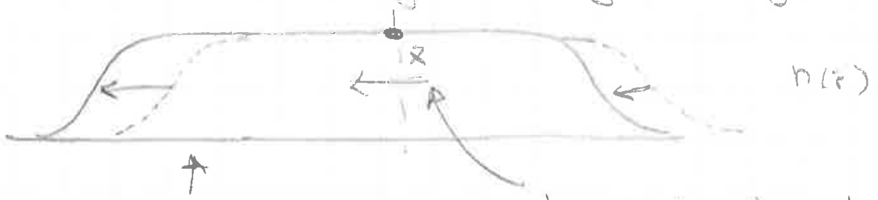
$$\simeq \nabla n_0(\vec r) \int d\vec r\,'\, f_{xc}(\vec r, \vec r\,', \omega)$$

$$\simeq \nabla n_0(\vec r)\, f_{xc}(\vec q = 0, \omega)$$

Contradiction!

Functionals that are nonlocal in time must also be nonlocal in space in order to satisfy the zero-force theorem!

We can also understand this more physically.
Consider the following density change



A rigid translation

Local density at $\vec{x}$ does not change

A local functional does not notice the motion at $\vec{x}$. (however, a local current density functional would!)

So in order to go beyond ALDA we need functionals that are nonlocal in space and time!

<u>Nonlocal</u> f_{xc}

A nonlocal f_{xc} has been developed that works well for absorbtion spectra in solids, including so-called excitonic phenomena.

It is based on many-body perturbation theory and satisfies the equation

$$\int \chi_s(1,2)\, f_{xc}(2,3)\, \chi_s(3,4)\, d2\, d3 = Q\left[\{\phi_i, \epsilon_i\}, 1, 3\right]$$

Orbital functional

(For more details see:
U. von Barth, N.E. Dahlen, R van Leeuwen, G. Stefanucci
Phys. Rev. B72, 235109 (2005))