Time-dependent current-density-functional theory for metals
Romaniello, Pina

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DFT and its Progeny

To describe completely the quantum-mechanical behaviour of a stationary system of $N$ interacting electrons it is necessary to calculate its many-electron wavefunction. In principle this may be obtained from the time-independent Schrödinger equation (in the relativistic case one has to solve the Dirac equation). However, since the motion of each electron is coupled to that of the other electrons in the system, in practice the equation is not solvable analytically and approximations are needed. This chapter is an introduction to the key concepts in the density functional formalism, from the fundamental Hohenberg-Kohn theorem for stationary systems, to its extension to treat time-dependent phenomena and transverse fields.

2.1 The main ideas behind DFT

The Schrödinger equation for a stationary system of $N$ interacting electrons can be written, in the Born-Oppenheimer approximation, as

$$\hat{H} \Psi(r_1\sigma_1, r_2\sigma_2, ..., r_N\sigma_N) = E \Psi(r_1\sigma_1, r_2\sigma_2, ..., r_N\sigma_N). \quad (2.1)$$

Here $E$ is the energy of the system, and $\Psi(r_1\sigma_1, r_2\sigma_2, ..., r_N\sigma_N)$ is the electronic wavefunction, with $r_i$ and $\sigma_i$ the space and spin coordinates of the electron $i$. The Hamiltonian of the system is defined as

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} + \sum_i v(r_i). \quad (2.2)$$

We will use atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) throughout the thesis. The first term on the right-hand side of expression (2.2) is the kinetic energy operator $\hat{T}$, the
second term represents the Coulomb electron-electron interaction energy operator $\hat{W}$, and the last term is the potential energy operator $\hat{V}$ of the electrons in the external potential $v(r)$. The Hamiltonian is parametrized by the external potential $v(r)$, thus the energies $E = \langle \Psi | \hat{H}_v | \Psi \rangle$ and the electronic wavefunctions $\Psi$, which satisfy the Schrödinger equation (2.1), can be considered functionals of this external potential. We will denote $\Psi = \Psi[v]$ and $E = E[v]$. We can now introduce the electron density $\rho(r)$ of the system through

$$\rho(r) = \langle \Psi | \hat{\rho}(r) | \Psi \rangle = N \int |\Psi(r_1, r_2, \ldots, r_N, \sigma_N)|^2 dr_1 \ldots dr_N d\sigma_1 \ldots d\sigma_N,$$

(2.3)
in which the density operator $\hat{\rho}(r)$ is defined as

$$\hat{\rho}(r) = \sum_i \delta(r - r_i).$$

(2.4)

Using this density operator, we can write the potential energy due to the external potential $\hat{V}$ as

$$V = \langle \Psi | \hat{V} | \Psi \rangle = \langle \Psi | \int \rho(r) v(r) dr | \Psi \rangle = \int \rho(r) v(r) dr.$$

(2.5)

In the next section we will show that there is a one-to-one mapping between the external potential $v(r)$ and the ground-state density $\rho(r)$. These two quantities can now be considered to be conjugate variables in the meaning of a Legendre transform,

$$\frac{\delta E_0[v]}{\delta v(r)} = \langle \Psi_0[v] | \hat{H}_v | \Psi_0[v] \rangle + \langle \Psi_0[v] | \hat{W} | \Psi_0[v] \rangle = \delta \rho(r),$$

(2.6)

where we have used that the wavefunction $\Psi_0[v]$ is normalized and the ground-state eigenfunction of the Hamiltonian $\hat{H}_v$ with energy $E_0[v]$. We can use the density as basic variable by defining a Legendre transform

$$\mathcal{F}[\rho] = E_0[\rho] - \int \rho(r) v(r) dr = \langle \Psi_0[v] | \hat{W} + \hat{V} | \Psi_0[v] \rangle,$$

(2.7)

where $v(r)$ must be regarded as a functional of $\rho(r)$. The uniqueness of this functional is guaranteed by the one-to-one mapping between the external potential and the ground-state density. The functional $\mathcal{F}[\rho]$ is defined for so-called $v$-representable densities, i.e., ground-state densities for a Hamiltonian with external potential $v$ [4].

By using the chain rule of differentiation and the result in Eq. (2.6), it immediately follows that

$$\frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} = \int \frac{\delta E_0[\rho]}{\delta v(r')} \frac{\delta v(r')}{\delta \rho(r)} dr' - \int \rho(r') \frac{\delta v(r')}{\delta \rho(r')} dr' = -v(r).$$

(2.8)
2.1. The main ideas behind DFT

2.1.1 The Hohenberg-Kohn theorems

The main objective of density functional theory is to replace the many-body electronic wavefunction with the electronic ground-state density as basic quantity [5]. Whereas the many-body wavefunction is dependent on $3N$ spatial variables and $N$ spin variables, the density is a function of only three variables and is a simpler quantity to deal with both conceptually and practically. Besides this, a deeper reason for a density functional formulation is given by Eq. (2.6). The method is in principle exact and is firmly based on two theorems derived and proved by Hohenberg and Kohn in 1964 [6]. The first theorem shows that the density $\rho$ of a nondegenerate ground state uniquely determines the external potential $v(r)$ (up to an arbitrary constant) to which the many-electron system is subjected. Consequently the density determines the electronic wavefunction of the system and thus all the electronic properties of the ground state. The proof of the theorem is rather simple. First we notice that the external potential $v(r)$ defines a mapping $v \rightarrow \rho$, where $\rho(r)$ is the corresponding nondegenerate ground-state density from the Schrödinger equation. The inverse mapping $\rho \rightarrow v$ can be proved by reductio ad absurdum. First we show that if two potentials $v(r)$ and $v'(r)$ differ by more than a constant they will not lead to the same wavefunction $\Psi$. From the Schrödinger equation (2.1) we have for the two potentials,

$$
\left(\hat{T} + \hat{V} + \hat{W}\right) |\Psi_0\rangle = E_0 |\Psi_0\rangle,
$$

$$
\left(\hat{T} + \hat{V}' + \hat{W}\right) |\Psi'_0\rangle = E'_0 |\Psi'_0\rangle.
$$

If $\Psi_0$ and $\Psi'_0$ were to be the same, then by subtracting (2.10) from (2.9) one would get

$$
\left(\hat{V} - \hat{V}'\right) |\Psi_0\rangle = (E_0 - E'_0) |\Psi_0\rangle,
$$

where $\hat{V}$ and $\hat{V}'$ appear to differ only by a constant if $\Psi_0$ does not vanish. However, for “reasonably well behaved” potentials, i.e., potentials which do not exhibit infinite barriers, etc., $\Psi_0$ cannot vanish on a set with nonzero measure by the unique continuation theorem [7]. So we obtain a contradiction with our initial assumption, and hence we can conclude that $\Psi_0 \neq \Psi'_0$. We can now prove that two potentials $v(r)$ and $v'(r)$ with corresponding Hamiltonians $\hat{H}$ and $\hat{H}'$ and nondegenerate ground-state wavefunctions $\Psi_0$ and $\Psi'_0$ yield two different densities $\rho(r)$ and $\rho'(r)$. By using the

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variational principle we have that

\[ E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{H}' + \hat{V} - \hat{V}' | \Psi'_0 \rangle, \]  

so that

\[ E_0 < E'_0 + \int \rho'(r)[v(r) - v'(r)]dr. \]  

(2.13)

Similarly, interchanging primed and unprimed quantities, one finds

\[ E'_0 < E_0 + \int \rho(r)[v'(r) - v(r)]dr. \]  

(2.14)

If \( \rho(r) \) and \( \rho'(r) \) were to be the same, the addition of (2.13) and (2.14) would lead to the inconsistency

\[ E_0 + E'_0 < E_0 + E'_0, \]  

(2.15)

and consequently we conclude that there cannot exist two different external potentials \( v(r) \) and \( v'(r) \) corresponding to the same density \( \rho(r) \). This defines our mapping \( \rho \rightarrow v \), and thus the one-to-one mapping \( v \rightarrow \rho \) is constructed. We can then conclude that the mapping between \( v, \Psi_0 \), and \( \rho \) is one-to-one. The immediate result is that the total energy of a (Coulomb) many-electron system in an external static potential can be expressed in terms of the potential energy due to this external potential and of an energy functional \( \mathcal{F}[\rho] \) of the ground-state density,

\[ E_0[\rho] = \langle \Psi_0[\rho] | \hat{H} | \Psi_0[\rho] \rangle = \int \rho(r)v(r)dr + \mathcal{F}[\rho], \]  

(2.16)

with \( \mathcal{F}[\rho] \) defined in Eq. (2.7). Note that this functional is defined independently of the external potential \( v(r) \), and thus it is a universal functional of the density. This means that, if the explicit form is known, it can be used for any system. The second Hohenberg-Kohn theorem states that the exact ground-state density of a system in a particular external potential \( v(r) \) minimizes the energy functional

\[ E_0 = \min_{\rho} \left\{ \mathcal{F}[\rho] + \int \rho(r)v(r)dr \right\}, \]  

(2.17)

where \( E_0 \) is the ground-state energy for the system in an external potential \( v(r) \). The proof uses the variational principle. The previous theorem assures that a trial density \( \tilde{\rho}(r) \), such that \( \tilde{\rho}(r) \geq 0 \) and \( \int \tilde{\rho}(r)dr = N \), with \( N \) a number of electrons, determines its own potential \( \tilde{v}(r) \), Hamiltonian \( \tilde{H} \), and wavefunction \( \tilde{\Psi} \). This wavefunction can
be taken as trial function for the problem of interest having external potential \( v(\mathbf{r}) \).

The variational principle asserts that

\[
\langle \hat{\Psi} | \hat{H} | \hat{\Psi} \rangle = \mathcal{F}[\bar{\rho}] + \int \bar{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \geq \mathcal{F}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r},
\]

which proves the second Hohenberg-Kohn theorem. Assuming differentiability of \( \{\mathcal{F}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}\} \), this theorem requires that the ground-state density satisfies the Euler-Lagrange equations

\[
0 = \frac{\delta}{\delta \rho(\mathbf{r})} \left\{ \mathcal{F}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} - \mu \left( \int \rho(\mathbf{r}) d\mathbf{r} - N \right) \right\},
\]

where we have introduced the Lagrange multiplier \( \mu \) to satisfy the constraint that the density integrates to the correct number of electrons. Although exact, this method requires in fact approximations to the universal functional, for which no explicit expressions in terms of the density are known.

### 2.1.2 The Kohn-Sham equations

A practical scheme to approximate the energy functional has been proposed by Kohn and Sham who re-introduced the orbitals in the density functional framework [8]. They introduced an auxiliary noninteracting electron system in an effective external potential \( v_s(\mathbf{r}) \), which reproduces the same ground-state density as in the corresponding interacting system. If \( v_s(\mathbf{r}) \) exists, then the first Hohenberg-Kohn theorem ensures its uniqueness. In other words the interacting density is assumed to be noninteracting-\( v \)-representable. Like for the interacting system, we can define the energy functional \( E_s[v_s] \) and its Legendre transform \( \mathcal{F}_s[\rho] \) along the same lines described above by putting \( \hat{W} \) to zero. We obtain

\[
E_s[v_s] = \langle \Psi_s[v_s] | \hat{T} + \hat{V}_s | \Psi_s[v_s] \rangle,
\]

\[
\mathcal{F}_s[\rho] = E_s[v_s] - \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} = \langle \Psi_s[v_s] | \hat{T} | \Psi_s[v_s] \rangle,
\]

with the derivatives

\[
\frac{\delta E_s[v_s]}{\delta v_s(\mathbf{r})} = \rho(\mathbf{r}),
\]

\[
\frac{\delta \mathcal{F}_s[\rho]}{\delta \rho(\mathbf{r})} = -v_s(\mathbf{r}).
\]

We can now introduce the exchange-correlation energy functional \( E_{xc}[\rho] \), which relates the functionals \( \mathcal{F}[\rho] \) and \( \mathcal{F}_s[\rho] \) of the interacting and the corresponding noninteracting
systems in the following way,

$$\mathcal{F}[\rho] = \mathcal{F}_s[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho], \quad (2.24)$$

where the second term on the right-hand side represents the classical Hartree electron-electron interaction energy. By differentiating this expression with respect to the density $\rho(\mathbf{r})$, the following relation between the external potential and the effective Kohn-Sham potential can be obtained,

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}), \quad (2.25)$$

where

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (2.26)$$

Since the state $\Psi_s[\rho]$ is the ground state for a system of noninteracting particles, it can be written as a single Slater determinant of one-electron orbitals $\psi_i$,

$$\Psi_s(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, ..., \mathbf{r}_N \sigma_N) = \frac{1}{\sqrt{N!}} \left( \begin{array}{c} \psi_1(\mathbf{r}_1 \sigma_1) & \cdots & \psi_N(\mathbf{r}_1 \sigma_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N \sigma_N) & \cdots & \psi_N(\mathbf{r}_N \sigma_N) \end{array} \right), \quad (2.27)$$

where $\psi_i$ satisfy the self-consistent Kohn-Sham equations

$$\left( -\frac{\nabla^2}{2} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.28)$$

in which the ground-state density is to be obtained by occupying the $N$ one-electron orbitals that are lowest in energy,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \quad (2.29)$$

Within the Kohn-Sham scheme one has to approximate, instead of $\mathcal{F}[\rho]$, only a small part of it, $E_{xc}[\rho]$ (and $v_{xc}[\rho]$), which contains all the many-body effects. A huge effort is put into finding approximations for the xc energy and potential that can describe with increasing accuracy the physical and chemical properties of an electronic system. The existing approximations are for example based on the uniform electron gas model (local density approximation) [8] or on the slowly varying electron gas expansion (generalized gradient approximations) [9–12]. Despite their simplicity, these approximations work very well for many properties and systems, although some problematic cases exist, which require more advanced approximations.
2.2 Time-dependent DFT

The many-electron wavefunction of a nonrelativistic many-electron system in a time-dependent external potential \( v(\mathbf{r}, t) \) must satisfy the time-dependent Schrödinger equation,

\[
\hat{H}(t)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = i\frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t),
\]

(2.30)

where the time-dependent Hamiltonian takes the form

\[
\hat{H}(t) = -\frac{1}{2} \sum_i \nabla^2_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v(\mathbf{r}_i, t).
\]

(2.31)

Analogously to the stationary case, we have the kinetic energy operator \( \hat{T} \), the Coulombic electron-electron interaction energy operator \( \hat{W} \), and the potential energy operator \( \hat{V}(t) \) of the electrons in the time-dependent potential \( v(\mathbf{r}, t) \). In 1984 Runge and Gross [13] derived the analog of the Hohenberg-Kohn theorem for time-dependent systems by establishing a one-to-one mapping between time-dependent densities and time-dependent potentials for a given initial state.

2.2.1 The Runge-Gross proof

The theorem states that the densities \( \rho(\mathbf{r}, t) \) and \( \rho'(\mathbf{r}, t) \), evolving from the same initial state \( \Psi_0 = \Psi(t = t_0) \) under the influence of the two potentials \( v(\mathbf{r}, t) \) and \( v'(\mathbf{r}, t) \) (both expandable in Taylor series around the initial time \( t = t_0 \)), are always different provided that the two potentials differ by more than a pure function of time,

\[
v(\mathbf{r}, t) - v'(\mathbf{r}, t) \neq c(t).
\]

(2.32)

In this case there is a one-to-one mapping between densities and potentials, and one can construct a time-dependent version of density functional theory. We give the essential steps of the demonstration of the theorem, by closely following Ref. [13]. We will consider the time-dependent density and current-density as

\[
\rho(\mathbf{r}, t) = \langle \Psi(t)|\hat{\rho}(\mathbf{r})|\Psi(t)\rangle,
\]

(2.33)

\[
\mathbf{j}(\mathbf{r}, t) = \langle \Psi(t)|\hat{\mathbf{j}}(\mathbf{r})|\Psi(t)\rangle,
\]

(2.34)

in which the density operator \( \hat{\rho}(\mathbf{r}) \) has been given in (2.4) and the current-density operator \( \hat{\mathbf{j}}(\mathbf{r}) \) is defined as

\[
\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2} \sum_i \{ -i\nabla, \delta(\mathbf{r} - \mathbf{r}_i) \},
\]

(2.35)
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where \{\hat{A}, \hat{B}\} = (\hat{A}\hat{B} + \hat{B}\hat{A}) denotes the anticommutator of two operators \(\hat{A}\) and \(\hat{B}\). We first show that the current-densities \(j(r, t)\) and \(j'(r, t)\) corresponding to the two different external potentials \(v(r, t)\) and \(v'(r, t)\) must differ for \(t > t_0\). To prove this we use the condition that the potentials \(v(r, t)\) and \(v'(r, t)\) can be expanded in Taylor series around \(t_0\),

\[
v(r, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(r)(t - t_0)^k,
\]

with a similar expression for \(v'(r, t)\) with coefficients \(v'_k(r)\). Eq. (2.32) implies that there is a minimum value \(k > 0\) such that

\[
w_k(r) = v_k(r) - v'_k(r) = \frac{\partial^k}{\partial t^k}(v(r, t) - v'(r, t)) \Big|_{t=t_0} \neq \text{constant.} \tag{2.37}
\]

If now we use the quantum mechanical equation of motion for a Schrödinger operator \(\hat{A}(t)\),

\[
\frac{d}{dt} \langle \Psi(t) | \hat{A}(t) | \Psi(t) \rangle = \langle \Psi(t) | \frac{\partial}{\partial t} \hat{A}(t) - i[\hat{A}(t), \hat{H}(t)] | \Psi(t) \rangle, \tag{2.38}
\]

for the two current-densities we obtain

\[
\frac{\partial}{\partial t} (j(r, t) - j'(r, t)) \Big|_{t=t_0} = -i\langle \Psi_0 | [\hat{j}, \hat{H}(t_0) - \hat{H}'(t_0)] | \Psi_0 \rangle
\]

\[
= -\rho_0(r) \nabla (v_{\text{ext}}(r, t_0) - v'_{\text{ext}}(r, t_0)), \tag{2.39}
\]

where we have considered that the two Hamiltonians \(\hat{H}(t)\) and \(\hat{H}'(t)\) differ only in their external potentials. Here \(\rho_0(r) = \rho(r, t_0)\) is the initial density. One can repeatedly use the equation of motion such to arrive at [13]

\[
\frac{\partial^{k+1}}{\partial t^{k+1}} (j(r, t) - j'(r, t)) \Big|_{t=t_0} = -\rho_0(r) \nabla w_k(r) \neq 0. \tag{2.40}
\]

We can conclude that the two current-densities will differ infinitesimally later than \(t_0\), which proves the first part of the theorem. In the second part we extend the proof to the densities. We make use of the continuity equation,

\[
\frac{\partial}{\partial t} \rho(r, t) = -\nabla \cdot j(r, t), \tag{2.41}
\]

which, after differentiating \(k + 1\) times, gives for the density difference at \(t_0\)

\[
\frac{\partial^{k+2}}{\partial t^{k+2}} (\rho(r, t) - \rho'(r, t)) \Big|_{t=t_0} = \nabla \cdot (\rho_0(r) \nabla w_k(r)). \tag{2.42}
\]
2.2. Time-dependent DFT

The right-hand side of this expression can not vanish for the following arguments. We note that

\[ \int \rho_0(r)|\nabla w_k(r)|^2 dr = \int \rho_0(r) w_k(r) \nabla w_k(r) ds \]

\[ - \int w_k(r) \nabla \cdot (\rho_0(r) \nabla w_k(r)) dr, \quad (2.43) \]

where we have applied Gauss’ theorem. For finite systems the surface integral will vanish, since any realistic potential (i.e., potentials due to normalizable external charge densities) falls off at least as fast as $1/r$ at $r = \infty$, while the density will decay exponentially. Thus $\nabla \cdot (\rho_0(r) \nabla w_k(r))$ can not vanish everywhere otherwise the left-hand side of Eq. (2.43) would be zero. This in turn would imply that $|\nabla w_k(r)|^2 = 0$, which is in contradiction to the assumption that $w_k(r)$ is not a constant. This completes the proof of the theorem for finite systems. An important observation is that the density difference in Eq. (2.42) is linear in the $w_k(r)$, and thus it does not vanish already at first order in $v(r, t) - v'(r, t)$. In particular this implies that the linear density response function is invertible for switch-on processes.

2.2.2 The time-dependent Kohn-Sham equations

One can prove that the time-dependent density $\rho(r, t)$ obtained from a many-particle system with Hamiltonian $\hat{H}(t)$ and initial state $\Psi_0$ can be reproduced exactly in a different system evolving from a different initial state $\Psi'_0$ of finite momentum, under a different Hamiltonian $\hat{H}'(t)$, with different two-particle interaction and external potential, provided that the initial density and initial first derivative of the density are the same in both systems. The external potential of the second system is then uniquely determined up to a pure function of time. This theorem solves the noninteracting $\nu$-representability problem for the time-dependent case, provided we can find the appropriate initial state, although it is still unknown whether this initial state can be chosen to be the ground state for the noninteracting system [14]. It follows that, as in the stationary case, one can introduce an auxiliary system of noninteracting electrons which satisfies the time-dependent Kohn-Sham equations

\[ i \frac{\partial}{\partial t} \psi_i(r, t) = \left( -\frac{\nabla^2}{2} + v_s(r, t) \right) \psi_i(r, t), \quad (2.44) \]

and with density

\[ \rho(r, t) = \sum_{i=1}^{N} |\psi_i(r, t)|^2, \quad (2.45) \]
which is exactly that of the interacting system. The effective potential \( v_s(r, t) \) is uniquely determined up to a purely time-dependent function, and it can be decomposed in external, Hartree, and exchange-correlation contributions,

\[
v_s(r, t) = v(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' + v_{xc}(r, t).
\]

The time-dependent exchange-correlation potential \( v_{xc}(r, t) \) is not obtained as functional derivative of any action functional, but is implicitly defined by this relation. Indeed, attempts to base time-dependent density functional theory on the stationary action have led to paradoxes [15]. However, approximations for the exchange-correlation potentials can still be constructed based on exact constraints that the exchange-correlation potential has to satisfy [16]. In particular, the zero-force and zero-torque theorem, which states that the exchange-correlation potential cannot exert any net force or torque on the system, and the generalized translational invariance, which requires that a rigid translation of the current-density implies a rigid translation of the exchange-correlation potentials. Recently van Leeuwen has shown that the problems related to the formulation of TDDFT based on the action functional can be solved by using the Keldysh action functional [15]. This new kind of action functional is defined on the Keldysh contour [17], in which the physical time is parametrized by an underlying parameter \( \tau \), called pseudotime. In this case the Kohn-Sham potential can be obtained as functional derivative of the Keldysh action functional.

### 2.3 Time-dependent current-DFT

In the previous section we have shown that the second part of the Runge-Gross proof is valid under the conditions of a positive density \( \rho_0(r) \) and time-dependent potentials vanishing at the boundary. The proof becomes questionable for extended system in external longitudinal electric fields. In this case the ground-state density remains finite everywhere, and we can choose two electric fields \( E[v](r, t) = \nabla v(r, t) \) and \( E'[v'](r, t) = \nabla v'(r, t) \) so that

\[
E[v](r, t) - E'[v'](r, t) = \frac{c(t)}{\rho_0(r)},
\]

with \( c(t) \) an arbitrary function of time, expandable in Taylor series around \( t = t_0 \). This immediately follows from Eq. (2.40) in the proof of the Runge-Gross theorem. Although the potentials themselves are not finite, this kind of fields are finite everywhere, hence physically acceptable. They will lead to nonvanishing uniform current-densities, but to constant densities, since these currents are divergence free. The first
part of the Runge-Gross theorem still holds in this case, whereas the second part is not needed if one formulates a density functional theory in terms of the current-density as fundamental variable. In order to treat also magnetic fields in the time-dependent density functional framework, Ghosh and Dhara were the first to reformulate the theory in terms of the current-density [18,19]. Following the same line of the Runge-Gross proof, Ghosh and Dhara showed that the single-particle current-density uniquely determines, up to an arbitrary gauge transformation, the time-dependent scalar and vector potentials of the system, and hence the many-electron wavefunction. Recently Vignale has given an alternative formulation of the TDCDFT [20], which closely follow that one given by van Leeuwen for the TDDFT [14], and which is easier and more complete than the Ghosh-Dhara one. We give here the statement of the theorem and the essential steps of its proof, by closely following Ref. [20].

2.3.1 Mapping from current-densities to vector potentials

We consider an interacting many-particle system moving in a scalar and vector potentials \( v(\mathbf{r}, t) \) and \( \mathbf{A}(\mathbf{r}, t) \), which are analytic functions of time around \( t_0 \). The motion of the system is governed by the following Hamiltonian \( \hat{H}(t) \),

\[
\hat{H}(t) = \sum_i \left\{ \frac{1}{2}[-i \nabla_i + \frac{1}{c} \mathbf{A}(\mathbf{r}_i, t)]^2 + v(\mathbf{r}_i, t) \right\} + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j),
\]

(2.48)

where \( U(\mathbf{r}_i - \mathbf{r}_j) \) is a two-particle interaction. The density operator takes the same form as in Eq. (2.4) for the ordinary TDDFT, whereas the current-density operator is given in term of the velocity operator \( \dot{\mathbf{r}}_i = (-i \nabla_i + \mathbf{A}(\mathbf{r}_i, t)/c) \) as

\[
\hat{\mathbf{j}}(\mathbf{r}, t) = \frac{1}{2} \sum_i \{\dot{\mathbf{r}}_i(t), \delta(\mathbf{r} - \mathbf{r}_i)\}.
\]

(2.49)

If \( \rho(\mathbf{r}, t) \) and \( \hat{\mathbf{j}}(\mathbf{r}, t) \) are the time-dependent density and current-density, respectively, of the system, then one can prove that the same density and current-density can be reproduced by another many-particle system evolving under a different Hamiltonian \( \hat{H}'(t) \),

\[
\hat{H}'(t) = \sum_i \left\{ \frac{1}{2}[-i \nabla_i + \frac{1}{c} \mathbf{A}'(\mathbf{r}_i, t)]^2 + v'(\mathbf{r}_i, t) \right\} + \sum_{i<j} U'(\mathbf{r}_i - \mathbf{r}_j),
\]

(2.50)

from a different initial state \( \Psi'_0 \) which produces the same density and current-density as \( \Psi_0 \) at \( t = t_0 \) in the unprimed system. The potentials \( v'(\mathbf{r}, t) \) and \( \mathbf{A}'(\mathbf{r}, t) \) are uniquely determined by \( v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t), \Psi_0, \) and \( \Psi'_0 \) up to gauge transformations of
the form
\[ v'(r, t) \rightarrow v'(r, t) + \frac{\partial \Lambda(r, t)}{\partial t}, \]
\[ A'(r, t) \rightarrow A'(r, t) + \nabla \Lambda(r, t), \] (2.51)
with \( \Lambda(r, t) \) a regular function of \( r \) and \( t \). One can always make a gauge transformation of the form (2.51) to eliminate the scalar potential at all times. To obtain this, we choose \( (r, t) \) such that the scalar potential is always zero in both primed and unprimed systems, i.e., \( \partial \Lambda(r, t)/\partial t = -v(r, t) \) at all times, with the initial condition \( \Lambda(r, t_0) = 0 \). The current-density obeys the equation of motion
\[
\frac{dj(r, t)}{dt} = \frac{\partial j(r, t)}{\partial t} + i[H(t), j(r, t)] = \rho(r, t)\frac{1}{c} \frac{\partial A(r, t)}{\partial t} \\
- \frac{1}{c} j(r, t) \times [\nabla \times A(r, t)] + F(r, t) + \nabla \cdot \sigma(r, t),
\] (2.52)
with \( 1/c \partial A(r, t)/\partial t \) and \( \nabla \times A(r, t) \) the external electric and magnetic fields, respectively. The quantities \( F(r, t) \) and \( \sigma(r, t) \) represent the internal force density and the stress tensor, respectively, and are defined as
\[
F(r, t) = -\left\langle \sum_i \delta(r - r_i) \sum_{j \neq i} \nabla_{r_i} U(r_i - r_j) \right\rangle,
\] (2.53)
\[
\sigma_{\alpha\beta}(r, t) = -\left\langle \frac{1}{4} \sum_i \{ \hat{\epsilon}_\alpha, \{ \hat{\epsilon}_\beta, \delta(r - r_i) \} \} \right\rangle.
\] (2.54)
The brackets \( \langle ... \rangle \) represent the expectation value in the unprimed system at time \( t \). An expression analogue to Eq. (2.52) can be written also for the primed system: the external electric and magnetic fields, the internal force, and the stress tensor become now primed. By assumption \( \rho(r, t) = \rho'(r, t) \) and \( j(r, t) = j'(r, t) \), thus taking the difference of the two equations we arrive at
\[
\rho(r, t) \frac{1}{c} \frac{\partial \Delta A(r, t)}{\partial t} = \frac{1}{c} j(r, t) \times [\nabla \times \Delta A(r, t)] + Q(r, t) - Q'(r, t),
\] (2.55)
where \( \Delta A(r, t) \equiv A'(r, t) - A(r, t) \) and
\[
Q(r, t) \equiv F(r, t) + \nabla \cdot \sigma(r, t).
\] (2.56)
\( Q'(r, t) \) is the analogue of \( Q(r, t) \) in the primed system. If solved, this equation can give the vector potential \( A'(r, t) \) which produces the same current-density as the vector potential \( A(r, t) \) in the unprimed system. However, since \( A'(r, t) \) enters the
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equation also implicitly through $Q'(r, t)$, it is not immediate to verify the existence and uniqueness of the solution of this equation. To overcome this difficulty one can follow an alternative approach. By hypothesis both $A(r, t)$ and $A'(r, t)$ are expandable in Taylor series around $t = t_0$, and the Taylor series of their difference is given by

$$
\Delta A(r, t) = \sum_{k=0}^{\infty} \Delta A_k(r)(t - t_0)^k, \tag{2.57}
$$

with

$$
\Delta A_k(r) = \frac{1}{k!} \frac{\partial^k \Delta A(r, t)}{\partial t^k} \bigg|_{t=t_0}. \tag{2.58}
$$

Substituting this expansion in Eq. (2.55) and equating the $l$th term of the Taylor expansion on each side of it, we arrive at the final result

$$
\rho_0(r)(l + 1)\frac{1}{c}\Delta A_{l+1}(r) = - \sum_{k=0}^{l-1} \rho_{l-k}(r)(k + 1)\frac{1}{c}\Delta A_{k+1}(r) + \frac{1}{c} \sum_{k=0}^{l} \{\mathbf{j}_{l-k}(r) \times [\nabla \times \Delta A_k(r)]\} + [Q(r, t)]_l - [Q'(r, t)]_l. \tag{2.59}
$$

Here we have considered that all the quantities appearing in Eq. (2.55) admit Taylor expansion in the neighbourhood of $t = t_0$, as consequence of the analyticity of the vector potential and the time-dependent Schrödinger equation. In general $[f(r, t)]_l$ indicates the $l$th coefficient (a function of $r$ alone) in the Taylor expansion of the function $f(r, t)$. Moreover, we have used the relation $[\partial \Delta A(r, t)/\partial t]_k = (k + 1)\Delta A(r)_{k+1}$. One can show that Eq. (2.59) is a recursion relation for the coefficients $\Delta A_k(r)$ of the Taylor expansion of $\Delta A(r, t)$. This means that the coefficient $\Delta A_{l+1}(r)$ can be expressed in terms of $\Delta A_k(r)$, with $k \leq l$. In order this to be true, the right-hand side of Eq. (2.59) must depend only on the coefficient $\Delta A_k(r)$, with $k \leq l$. This is immediately clear for the terms in which this coefficient appears explicitly. There are also $\Delta A_k(r)$s that enter the equation implicitly through the coefficients of the expansion of the expectation value of the stress tensor. However, the time-dependent Schrödinger equation, which is of first order in time, assures that the $l$th coefficient of the Taylor expansion of the quantum states $\Psi(t)$ and $\Psi'(t)$ is entirely determined by the coefficients of order $k < l$ in the expansion of the vector potentials $A_k(r, t)$ and $A'_k(r, t)$, respectively. We can then conclude that all the quantities on the right-hand side of Eq. (2.59) are completely determined by the coefficients $\Delta A_k(r)$, with $k \leq l$. To use the
recursion relation we also need to know the initial state $\Delta A_0(r) = A'(r, t_0) - A(r, t_0)$. This can be retrieved from the equality of densities and current-densities of the primed and unprimed systems,

$$\langle \Psi(t_0) | \hat{j}(r) | \Psi(t_0) \rangle = \langle \Psi'(t_0) | \hat{j}(r) | \Psi'(t_0) \rangle,$$

which leads to the following expression,

$$\rho(r, t_0) \Delta A_0(r) = \langle \Psi'(t_0) | \hat{j}_p(r) | \Psi'(t_0) \rangle - \langle \Psi(t_0) | \hat{j}_p(r) | \Psi(t_0) \rangle, \quad (2.60)$$

where $\hat{j}_p(r) = 1/2 \sum_i \{-i\nabla_i, \delta(r - r_i)\}$ is the paramagnetic current-density operator. The recursion equation (2.59), together with the initial condition (2.60), completely determine the Taylor expansion of the vector potential $A_0(r)$ which produces in the primed system the same current-density that $A(r, t)$ produces in the unprimed system. The knowledge of these coefficients uniquely defines the potential $A_0(r)$ provided that the series itself converges within a nonvanishing convergence radius $t_c > 0$. Physically, the possibility of a vanishing radius can be safely discounted [20]. Under this assumption, the potential can be computed up to $t_c$ and then the process can be iterated taking $t_c$ as initial time.

Two special cases can now be discussed.

In the case in which the unprimed and primed systems are such that $U = U'$ and $\Psi(t_0) = \Psi'(t_0)$, Eq. (2.60) implies that $\Delta A_0(r) = 0$. From Eq. (2.59) it then follows that $\Delta A_k(r) = 0$ for all $k$, i.e., $A(r, t) = A'(r, t)$ at all times. This result is the analogue of the Runge-Gross theorem for the TDCDFT: two vector potentials that produce the same current-density in two systems evolving from the same initial state must be the same up to a gauge transformation. In other words the map between vector potentials and current-densities is invertible.

In the case in which the primed system is a noninteracting one, i.e., $U' = 0$, then the current-density produced in an interacting system under a vector potential $A(r, t)$ can be also reproduced in a noninteracting system evolving under a suitable vector potential $A'(r, t)$. This is possible if $\Psi'(t_0)$ is a Slater determinant which produces the initial density and current-density. It becomes clear that in this case we have a solid basis for the use of a time-dependent Kohn-Sham formalism. The time-dependent one-electron Kohn-Sham equations take the form

$$\left\{ \frac{1}{2} [-i \nabla + \frac{1}{e} A_s(r, t)]^2 + v_s(r, t) \right\} \psi_i(r, t) = i \frac{\partial}{\partial t} \psi_i(r, t). \quad (2.61)$$

The effective potentials are uniquely determined up to a gauge transformation. In the Coulomb gauge ($\nabla \cdot A = 0$), they can be decomposed in external, classical, and
exchange-correlation potentials as follows,
\[ v_s(r, t) = v(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' + v_{xc}(r, t), \] (2.62)
\[ A_s(r, t) = A(r, t) + \frac{1}{c} \int \frac{j_T(r', t - |r - r'|/c) dr'}{|r - r'|} + A_{xc}(r, t), \] (2.63)
where we have assumed the two-particle interaction to be the repulsive Coulomb potential. The vector potential defined in terms of the transverse current-density \( j_T(r, t) \) accounts for the properly retarded contribution to the total current and for the retardation effects which have not been included in the instantaneous Coulomb potential [21]. The density of the real system can be obtained in a similar way as in TDDFT by using Eq. (2.45). The current is obtained as
\[ j(r, t) = -\frac{i}{2} \sum_{i=1}^{N} \left( \psi_i^*(r, t) \nabla \psi_i(r, t) - \nabla \psi_i^*(r, t) \psi_i(r, t) \right) + \frac{1}{c} \rho(r, t) A_s(r, t). \] (2.64)
Here the first and the second terms on the right-hand side represent the paramagnetic and diamagnetic currents, respectively. The time-dependent density and current-density are related \( \text{via} \) the continuity equation, whereas the initial values are fixed by the initial state.

### 2.4 Linear response

One of the main applications of time-dependent (current)-density-functional theory is the study of the dynamics of a system, initially in the ground state, when an external small perturbation is applied. In the linear regime one considers only terms which are linear in the perturbation and neglects higher order ones. We consider a system which at \( t \leq t_0 \) is in the ground state \( \Psi_0 \) of the Hamiltonian \( \hat{H}_0 \). At \( t = t_0 \) we apply a small perturbation \( \delta \hat{h}(t) \) and we study the linear response for an arbitrary physical observable \( \hat{O} \) of the system as
\[ \delta \langle \hat{O} \rangle(t) = \langle \Psi(t)|\hat{O}|\Psi(t)\rangle - \langle \Psi_0|\hat{O}|\Psi_0\rangle. \] (2.65)
Here \( \Psi(t) \) is the solution of the time-dependent Schrödinger equation
\[ i \frac{\partial}{\partial t} \Psi(t) = [\hat{H}_0 + \delta \hat{h}(t)]\Psi(t). \] (2.66)
This equation is better treated in the Heisenberg picture relative to \( \hat{H}_0 \), in which wavefunctions and operators are related to the corresponding wavefunctions and operators.
in the Schrödinger picture by an unitary transformation as follows,

\[
\Psi_H(t) = e^{i(t-t_0)\hat{H}_0} \Psi(t), \quad (2.67)
\]

\[
\hat{O}_H(t) = e^{i(t-t_0)\hat{H}_0} \hat{O} e^{-i(t-t_0)\hat{H}_0}. \quad (2.68)
\]

The wavefunction \(\Psi_H(t)\) satisfies the following equation of motion,

\[
i \frac{\partial}{\partial t} \Psi_H(t) = \delta \hat{H}(t) \Psi_H(t), \quad (2.69)
\]

which can be reformulated as an integral equation

\[
\Psi_H(t) = \Psi(t_0) - i \int_{t_0}^{t} \delta \hat{H}(t') \Psi_H(t') dt'. \quad (2.70)
\]

Here the causality constraint is automatically incorporated. Note that at \(t = t_0\) the wavefunctions in the Heisenberg and Schrödinger pictures are the same. This integral equation can be solved by iteration. The solution up to the terms linear in the perturbation is given already by a single iteration, so that, together with Eq. (2.67), we obtain

\[
\Psi(t) = e^{-i(t-t_0)\hat{H}_0} \left[ 1 - i \int_{t_0}^{t} \delta \hat{H}(t') dt' \right] \Psi_0 + O(\delta \hat{H}_0^2). \quad (2.71)
\]

From this, the linear response equation (2.65) for the observable \(\hat{O}\) becomes

\[
\delta \langle \hat{O} \rangle (t) = -i \int_{t_0}^{t} \langle \Psi_0 | \left[ \hat{O}_H(t), \delta \hat{H}(t') \right] | \Psi_0 \rangle dt', \quad (2.72)
\]

where \([\hat{a}, \hat{b}]\) is the commutator of the operators \(\hat{a}\) and \(\hat{b}\). If we consider the perturbation \(\delta \hat{H}(t)\) to be

\[
\delta \hat{H}(t) = \sum_i \hat{O}_i(t) \varphi_i(t), \quad (2.73)
\]

with \(\varphi_i(t)\) arbitrary time-dependent variables, then the linear response for the operators \(\hat{O}_i\) is given as

\[
\delta \langle \hat{O}_i \rangle (t) = -i \int_{t_0}^{t} \langle \Psi_0 | \left[ \hat{O}_i H(t), \sum_j \hat{O}_j H(t') \varphi_j(t') \right] | \Psi_0 \rangle dt' \\
= \sum_j \int_{t_0}^{\infty} \chi_{ij}(t,t') \varphi_j(t') dt'. \quad (2.74)
\]

Here \(\chi_{ij}(t,t')\) represent the response functions and are defined as

\[
\chi_{ij}(t,t') = -i \Theta(t - t') \langle \Psi_0 | \left[ \hat{O}_i H(t), \hat{O}_j H(t') \right] | \Psi_0 \rangle. \quad (2.75)
\]
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The Heaviside step-function \( \Theta(\tau) \) (\( \Theta(\tau > 0) = 1, \Theta(\tau \leq 0) = 0 \)) assures the causality of the response functions, since the system should not respond to the perturbation before this is applied. If the set \( |\Psi_n\rangle \) is the complete set of eigenstates of \( \hat{H}_0 \), we may use the closure relation \( \sum_n |\Psi_n\rangle \langle \Psi_n| = 1 \) and write

\[
\chi_{ij}(t, t') = -i\Theta(t - t') \sum_n \left\{ \langle \Psi_0|\hat{O}_i\hat{H}(t)|\Psi_n\rangle \langle \Psi_n|\hat{O}_j\hat{H}(t')|\Psi_0\rangle - \langle \Psi_0|\hat{O}_j\hat{H}(t')|\Psi_n\rangle \langle \Psi_n|\hat{O}_i\hat{H}(t)|\Psi_0\rangle \right\}. \tag{2.76}
\]

Using (2.68) we can write,

\[
\langle \Psi_0|\hat{O}_i\hat{H}(t)|\Psi_n\rangle \langle \Psi_n|\hat{O}_j\hat{H}(t')|\Psi_0\rangle = \langle \Psi_0|e^{i(t-t_0)\hat{H}_0}\hat{O}_i e^{-i(t-t_0)\hat{H}_0} |\Psi_n\rangle \times \\
\langle \Psi_n|e^{i(t'-t_0)\hat{H}_0}\hat{O}_j e^{-i(t'-t_0)\hat{H}_0} |\Psi_0\rangle = e^{i(E_0-E_n)(t-t')} \langle \Psi_0|\hat{O}_i|\Psi_n\rangle \langle \Psi_n|\hat{O}_j|\Psi_0\rangle \tag{2.77}
\]

with \( E_0 \) and \( E_n \) the eigenvalues corresponding to the eigenstates \( \Psi_0 \) and \( \Psi_n \), respectively, of the Hamiltonian \( \hat{H}_0 \). A similar expression can be written for the other term of the commutator in Eq. (2.76). The response functions (2.76) depend thus only on the difference \( (t - t') \) as follows,

\[
\chi_{ij}(t - t') = -i\Theta(t - t') \sum_n \left\{ e^{i(E_0-E_n)(t-t')} \langle \Psi_0|\hat{O}_i|\Psi_n\rangle \langle \Psi_n|\hat{O}_j|\Psi_0\rangle - e^{-i(E_0-E_n)(t-t')} \langle \Psi_0|\hat{O}_j|\Psi_n\rangle \langle \Psi_n|\hat{O}_i|\Psi_0\rangle \right\}. \tag{2.78}
\]

Note that this is only true if the operators \( \hat{O}_i \) and \( \hat{O}_j \) are time-independent. By using the following expression for the Heaviside step-function \( \Theta(\tau) \),

\[
\Theta(\tau) = -\frac{1}{2\pi i} \lim_{\eta \to 0^+} \int_{-\infty}^{\infty} \frac{e^{-i\omega\tau}}{\omega + i\eta} d\omega, \tag{2.79}
\]

we can arrive at

\[
\chi_{ij}(t - t') = \lim_{\eta \to 0^+} \int_{-\infty}^{\infty} \frac{1}{2\pi} e^{-i\omega(t-t')} \chi_{ij}(\omega), \tag{2.80}
\]

where

\[
\chi_{ij}(\omega) = \lim_{\eta \to 0^+} \sum_n \left\{ \frac{\langle \Psi_0|\hat{O}_i|\Psi_n\rangle \langle \Psi_n|\hat{O}_j|\Psi_0\rangle}{\omega - (E_n - E_0) + i\eta} - \frac{\langle \Psi_0|\hat{O}_j|\Psi_n\rangle \langle \Psi_n|\hat{O}_i|\Psi_0\rangle}{\omega + (E_n - E_0) + i\eta} \right\}. \tag{2.81}
\]

represent the response functions in the frequency domain. The limit in (2.81) can be rewritten as

\[
\lim_{\eta \to 0^+} \frac{1}{\omega - (E_n - E_0) + i\eta} = P \left( \frac{1}{\omega - (E_n - E_0)} \right) - i\pi \delta(\omega - (E_n - E_0)), \tag{2.82}
\]

where

\[
P(\omega) = \text{Principal value of } \frac{1}{\omega - (E_n - E_0)}.
\]
where $P$ represents the principal value of the limit. If the system has time-reversal invariance, then one can choose the quantities $\langle \Psi_0 | \hat{O}_i | \Psi_n \rangle$ real, so that the real and imaginary parts of the response functions are given by

\[
\Re \{ \chi_{ij} (\omega) \} = \sum_n \langle \Psi_0 | \hat{O}_i | \Psi_n \rangle \langle \Psi_n | \hat{O}_j | \Psi_0 \rangle \times \left\{ P \left( \frac{1}{\omega - (E_n - E_0)} \right) - P \left( \frac{1}{\omega + (E_n - E_0)} \right) \right\},
\]

\[
\Im \{ \chi_{ij} (\omega) \} = -\pi \sum_n \langle \Psi_0 | \hat{O}_i | \Psi_n \rangle \langle \Psi_n | \hat{O}_j | \Psi_0 \rangle \times \left\{ \delta (\omega - (E_n - E_0)) - \delta (\omega + (E_n - E_0)) \right\}.
\] (2.83)

**2.4.1 Linear response in TDCDFT**

Within the TDCDFT framework we can now describe the response of an interacting many-electron system to a time-dependent external perturbation in terms of the response functions of the corresponding noninteracting Kohn-Sham systems. We consider as initial state the ground state of the stationary Kohn-Sham system corresponding to the external potentials $v_0 (r) = v(r, t_0)$ and $A_0 (r) = A(r, t_0) = 0$. The first-order perturbation of the ground state is governed by the perturbation Hamiltonian $\hat{h}(r, t)$ containing all terms linear in the field,

\[
\delta h(r, t) = \hat{\rho}(r) \delta v_s (r, t) + \frac{1}{c} \hat{j}(r) \cdot \delta A_s (r, t),
\] (2.85)

where $\hat{\rho}(r) = 1$ and $\hat{j}(r) = -i \left( \nabla - \nabla \right) / 2$. In chapter 4 we derive the equation of the linear response by including the spin of electrons as well. The Kohn-Sham perturbing potentials $\delta v_s (r, t)$ and $\delta A_s (r, t)$ are given by

\[
\delta v_s (r, t) = \delta v(r, t) + \int \frac{\delta \rho(r', t)}{|r - r'|} dr' + \delta v_{xc}(r, t),
\] (2.86)

\[
\delta A_s (r, t) = \delta A(r, t) + \frac{1}{c} \int \frac{\delta j_T(r', t - |r - r'|/c)}{|r - r'|} dr' + \delta A_{xc}(r, t).
\] (2.87)

The linear contributions to the exchange-correlation potentials depend on both the induced density and induced current-density. One can choose the gauge such that in the exchange-correlation scalar potential only terms linear in the induced density are retained, whereas all the terms linear in the induced current-density are gauge-transformed to the exchange-correlation vector potential. The terms linear in the induced density which contribute to the exchange-correlation vector potential can be considered as functional of the induced current-density, since density and current are related by the continuity equation (2.41). Thus the exchange-correlation vector
2.4. Linear response

potential is a functional of the induced current-density. In this gauge, the linear
contribution to the scalar exchange-correlation potential can be defined via a response
kernel $f_{xc}(\mathbf{r}, \mathbf{r}', t - t')$ as

$$
\delta v_{xc}(\mathbf{r}, t) = \int_{t_0}^{t} \int f_{xc}(\mathbf{r}, \mathbf{r}', t - t') \delta \rho(\mathbf{r}', t') d\mathbf{r}' dt'.
$$

(2.88)

The exchange-correlation contribution to the vector potential is given in terms of a
tensor kernel $f_{xc}(\mathbf{r}, \mathbf{r}', t - t')$ as

$$
\delta \mathbf{A}_{xc}(\mathbf{r}, t) = \int_{t_0}^{t} \int f_{xc}(\mathbf{r}, \mathbf{r}', t - t') \cdot \delta \mathbf{j}(\mathbf{r}', t') d\mathbf{r}' dt'.
$$

(2.89)

The exchange-correlation kernels are, as expected, very complicated functionals of the
density and current-density and need to be approximated. The induced density and
current-density are then obtained, in the linear regime and in the frequency domain, as

$$
\begin{align*}
\delta \rho(\mathbf{r}, \omega) &= \int \left\{ \chi_{s, \rho \rho}(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta v_{s}(\mathbf{r}', \omega) \\
&\quad + \frac{1}{c} \chi_{s, \rho \mathbf{j}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta \mathbf{A}_{s}(\mathbf{r}', \omega) \right\} d\mathbf{r}' \\
\delta \mathbf{j}(\mathbf{r}, \omega) &= \int \left\{ \chi_{s, \mathbf{j} \rho}(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta v_{s}(\mathbf{r}', \omega) \\
&\quad + \frac{1}{c} \left[ \chi_{s, \mathbf{j} \mathbf{j}}(\mathbf{r}, \mathbf{r}', \omega) + \rho_0(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right] \cdot \delta \mathbf{A}_{s}(\mathbf{r}', \omega) \right\} d\mathbf{r}',
\end{align*}
$$

(2.90)

where $\rho_0(\mathbf{r})$ is the density in the ground state. The term $\delta \mathbf{j}_d(\mathbf{r}, \omega) = \rho_0(\mathbf{r}) \delta \mathbf{A}_{s}(\mathbf{r}, t)/c$
is the diamagnetic contributions to the induced current-density, and can be related to
the current-current Kohn-Sham response function $\chi_{s, \mathbf{j} \mathbf{j}}(\mathbf{r}, \mathbf{r}', \omega)$ via the conductivity
sum rule

$$
\chi_{s, \mathbf{j} \mathbf{j}}(\mathbf{r}, \mathbf{r}', \omega = 0) + \rho_0(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') = 0.
$$

(2.92)

In this expression we neglect a purely transverse contribution which gives rise to the
weak Landau diamagnetism [1]. In the next chapter we give a detailed description of
this sum-rule. The set of equations (2.86)-(2.91) needs to be solved self-consistently.
To do this we need to approximate the exchange-correlation kernels.

2.4.2 The Adiabatic Local Density Approximation

The simplest approximation to the time-dependent exchange-correlation potentials is
the adiabatic local density approximation (ALDA) [22], which is a straightforward
extension of the local density approximation used in the stationary case. Within this
approximation one neglects the exchange-correlation vector potential and evaluates
the LDA expression for the ground-state exchange-correlation scalar potential at the
time-dependent local density,
\[ v_{xc}(\mathbf{r}, t) = v_{xc}^{\text{hom}}(\rho(\mathbf{r}, t)) = \frac{d}{d\rho}(\rho e_{xc}^{\text{hom}}(\rho)) \bigg|_{\rho(\mathbf{r}, t)}, \quad (2.93) \]
where \( e_{xc}^{\text{hom}}(\rho) \) is the exchange-correlation energy per particle of the homogeneous
electron gas with density \( \rho \). The main characteristic of the ALDA is that it is lo-
cal in time as well as in space. This approximation can be expected to be valid in
nearly homogeneous systems in which densities change very slowly in time; in practice,
however, it works quite well also beyond this domain of applicability. When the adia-
batic approximation is used in the linear response approach, the exchange-correlation
response kernel
\[ f_{xc}(\mathbf{r}, \mathbf{r}', t, t') = \frac{d}{d\rho}(\rho e_{xc}^{\text{hom}}(\rho)) \bigg|_{\rho(\mathbf{r}, t)} \quad (2.94) \]
The kernel is real and local in space and time. When Fourier-transformed, the lo-
cality in time implies that \( f_{xc}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', t, t') \) is frequency-independent. In order to improve
this approximation one can incorporate the frequency-dependence of the exchange-
correlation kernel. But it has been rigorously proved that the frequency-dependent
\( f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \) is long range in space and that frequency-dependence and locality are in-
compatible in an exchange-correlation potential that is expressed as functional of the
density alone [23]. Vignale and Kohn showed that a consistent local approximation
can be constructed if the theory is formulated in terms of the current-density as dyna-
nical basic variable, with the vector potential as conjugate variable [24]. The main
result is that one obtains a local current approximation for the exchange-correlation
kernel for the vector potential.

### 2.4.3 The Vignale-Kohn functional

The exchange-correlation vector potential can be approximated as a local functional
of the current by using the expression derived by Vignale and Kohn [21,24],
\[ \frac{i\omega}{c} \delta A_{xc,i}(\mathbf{r}, \omega) = -\frac{1}{\rho_0(\mathbf{r})} \sum_j \partial_j \sigma_{xc,ij}(\mathbf{r}, \omega). \quad (2.95) \]
Here \( \sigma_{xc,ij}(\mathbf{r}, \omega) \) has the structure of a symmetric viscoelastic stress tensor,
\[ \sigma_{xc,ij} = \eta_{xc} \left( \partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} \sum_k \partial_k u_k \right) + \zeta \delta_{ij} \sum_k \partial_k u_k, \quad (2.96) \]
with \( \mathbf{u}(\mathbf{r}, \omega) = \delta \mathbf{j}(\mathbf{r}, \omega)/\rho_0(\mathbf{r}) \) the velocity field. The coefficients \( \bar{\eta}_{xc}(\mathbf{r}, \omega) \) and \( \bar{\zeta}_{xc}(\mathbf{r}, \omega) \) depend on the exchange-correlation energy \( e_{xc}(\rho_0) \) and on the transverse and longitudinal exchange-correlation kernels \( f_{xcT}(\rho_0(\mathbf{r}), \omega) \) and \( f_{xcL}(\rho_0(\mathbf{r}), \omega) \) of the homogeneous electron gas with density \( \rho_0(\mathbf{r}) \). In chapter 7 we give a more detailed discussion on this functional and we show the performance in the linear response of noble metals.