5 Current density functional theory

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5.1 Introduction

The nonlocality of the exchange-correlation (xc) potential, i.e., the fact that the xc potential at a certain position depends on the global distribution of the particle density in space, is the curse of density functional theory. It is mainly because of this fact that, even after years of intensive studies, the exact form of the xc potential as a functional of the density remains unknown. Nevertheless, it is true that many accurate and useful results can be obtained from the use of an approximation – the local density approximation (LDA) – which ignores the problem altogether. Apparently, the nonlocal dependence of the Kohn-Sham orbitals on the density is sufficient in many cases to give the right quantum chemistry. Furthermore, a number of successful strategies have been designed to go beyond the LDA when needed: in one such approach (the generalized gradient approximation – GGA) one goes beyond the LDA by including the dependence of the xc potential on the gradient of the local density; in another one expresses the xc potential as a functional of the Kohn-Sham orbitals, and, finally, in the “meta-GGA” approach one fights the problem by including additional local variables, such as the kinetic energy density.

In this chapter we are going to see that the nonlocality problem affects in a more severe form the time-dependent density functional theory. This complication arises as a consequence of memory (see Chapter 4). The xc potential at a time \( t \) (now) depends on the density at earlier times \( t' \). But at these earlier times a small volume element of the system, which is now located at \( \mathbf{r} \), was located at a different position \( \mathbf{r}' \). Retardation in time thus implies nonlocality in space (see Chapter 8). We will see that, when retardation is taken into account, the local density approximation breaks down even in the limit of slowly varying density. We will refer to this feature of the time-dependent theory as ultranonlocality, to distinguish it from the ordinary nonlocality, which becomes harmless in the limit of slowly varying density. Furthermore, we will see that “ultranonlocality” is not related to the presence of a long-range interaction between the particles, but, more in depth, implies that the particle density is not a well-chosen variable (although, in principle a legitimate one) for the description of effects that involve retardation in time. It is also evident that the inclusion of additional variables might cure the
“disease”: for example, by looking at the current density of an infinitesimal volume element of the fluid at position \( r \) at a certain time we might be able to estimate its position at an earlier time, and thus arrive at a local or quasi-local expression for the retarded xc potential. These general ideas will be explored in some detail in the following sections.

### 5.2 First hints of ultranonlocality: the harmonic potential theorem

Historically, the first hint of ultranonlocality in TDDFT came from the work of John Dobson [Dobson 1994a] on the collective dynamics of electrons in parabolic quantum wells. Under the action of a uniform time-dependent electric field the density of such system oscillates back and forth without changing its shape, i.e., one has \( n(r, t) = n_{\text{GS}}(r - R(t)) \) where \( n_{\text{GS}}(r) \) is the ground-state density and \( R(t) \) is the position of the center of mass of the system. The latter moves exactly as a single classical particle of mass \( m \) and charge \(-e\) under the action of the external electric field: this is the content of the “harmonic potential theorem” (HPT). It is easy to see that the exact TDDFT satisfies the HPT for, according to the translational invariance condition (11.19) (see also Appendix to this chapter), the xc potential created by the oscillating density \( n_{\text{GS}}(r - R(t)) \) is given by \( v_{xc}(r, t) = v_{xc, \text{GS}}(r - R(t)) \), where \( v_{xc, \text{GS}}(r) \) is the xc potential in the ground-state. In an accelerated frame of reference that moves together with the center of mass of the system, the external electric field is cancelled by the inertial force while the xc potential has exactly the form that is needed to preserve the ground-state density distribution.

Dobson observed that a naïve application of the local density approximation, including a local but retarded xc potential [Gross 1985], leads to results that are in conflict with the HPT. For example, one finds a density-dependent shift in the frequency of the oscillatory motion of the center of mass, and this motion becomes “damped”. The reason for this difficulty is that the local density approximation is unable to distinguish between a situation in which the density variation is due to local compression/rarefaction of the electron liquid (as in the case of a long-wavelength plasmon) and the present one, in which this variation is due to a global translation of a system, without compression or rarefaction. The “obvious” choice of [Gross 1985] amounts to choosing the first option in both cases: thus introducing fictitious dissipative processes when none is present.

From a mathematical point of view, the link between ultranonlocality and the HPT can be seen as follows [Vignale 1998]. First of all, notice that the translational invariance identity (11.19) (which ensures satisfaction of the HPT) is intimately related to the zero-force theorem, Eq. (11.11a), (and Eq. 5.25 in the Appendix), which in turn implies that the exact xc kernel of
any system must satisfy the equation
\begin{equation}
\int d^3 r' f_{xc}(r, r', \omega) \nabla n_{GS}(r') = \nabla v_{xc, GS}(r),
\end{equation}
(5.1)

where \(n_{GS}(r)\) and \(v_{xc, GS}(r)\) are the density and the \(xc\) potential in the ground-state. Notice that the quantity on the right hand side of this equation is frequency-independent, implying that the integral over \(r'\) on the left hand side must somehow “wash out” the frequency dependence of the integrand. Now assume that \(f_{xc}\) has a finite range in the sense that the integral
\begin{equation}
\int d^3 r' f_{xc}(r, r', \omega)
\end{equation}
(5.2)
is finite. Indeed, this condition is satisfied by the \(xc\) kernel of a strictly homogeneous electron liquid, since it is known that the Fourier transform \(f_{xc}(k, \omega)\) of the homogeneous \(xc\) kernel has finite limit for \(k \to 0\) (see discussion in Sect. 5.5). Suppose now that \(n_{GS}(r)\) is very slowly varying on the scale of the range of \(f_{xc}(r, r', \omega)\). Then we can pull \(\nabla n_{GS}(r')\) out of the integral of Eq. (5.1) and get
\begin{equation}
\nabla n_{GS}(r) \int d^3 r' f_{xc}(r, r', \omega) = \nabla v_{xc, GS}(r).
\end{equation}
(5.3)

In the limit that the density approaches uniformity, the integral on the left hand of this expression ought to converge (if it converges at all) to the \(k \to 0\) limit of the homogeneous electron gas kernel \(f_{xc}(k, \omega)\), which, as we have just stated, is a function of frequency. Since the right hand side of the expression is still frequency-independent we have arrived at a contradiction. This proves the fallacy of the initial assumption, namely, the finiteness of the integral (5.2) in a weakly inhomogeneous system. Indeed, the divergence of the integral (5.2) is the mathematical signature of what we have dubbed “the ultranonlocality problem”. Notice that, unlike ordinary nonlocality, this problem is present in systems that are arbitrarily close to a homogeneous electron liquid, and has nothing to do with the range of the interaction.

### 5.3 TDDFT and hydrodynamics

Looking at TDDFT with hindsight one can easily understand why the description of many-body forces as gradients of a density-dependent potential led to the difficulties described in the previous section. It is not by accident that the two major classical theories of the dynamics of continuous media, namely, elasticity, for solids, and hydrodynamics, for fluids, express the many-body forces not as gradients of a scalar potential, but as divergences of a stress tensor, which is a local functional of the displacement or
the velocity field. For example, in hydrodynamics the current density, \( j(r, t) \), satisfies the Navier-Stokes equation [Landau 1987]

\[
m \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{j}(r, t) = \mathbf{F}(r, t) + \nabla \cdot \mathbf{\sigma}(r, t), \tag{5.4}\]

where the velocity field, \( \mathbf{v}(r, t) \), is defined as the ratio of the current density to the particle density, i.e., \( \mathbf{v}(r, t) \equiv \mathbf{j}(r, t)/n(r, t) \). Here \( \mathbf{F}(r, t) \) is the external volume force density (in which we also include the force density generated by the Hartree potential) while the second term on the right-hand side is the contact force exerted on the volume element by the surrounding medium.

The stress tensor is given by

\[
\sigma_{ij}(r, t) = -p \delta_{ij} + \eta \left( \frac{\partial v_i}{\partial r_j} + \frac{\partial v_j}{\partial r_i} - \frac{2}{d} \nabla \cdot \mathbf{v} \delta_{ij} \right) + \zeta \nabla \cdot \mathbf{v} \delta_{ij}, \tag{5.5}\]

where \( p \) is the equilibrium pressure associated with the local instantaneous density (and temperature), \( d \) is the number of spatial dimensions, and the coefficients \( \eta \) and \( \zeta \) are, respectively, the shear viscosity and the bulk viscosity of the fluid.

Notice that, by expressing the force density as the divergence of a stress tensor, the Navier-Stokes equation is guaranteed to satisfy Newton’s third law. Indeed, the net contact force exerted on a certain volume \( V \) of the fluid by the fluid that surrounds it is given by

\[
\int_V d^3r \nabla \cdot \mathbf{\sigma}(r, t) = \int_{\partial V} d\Omega \mathbf{e}_n \cdot \mathbf{\sigma}(r, t), \tag{5.6}\]

where the integral on the right hand side is done over the boundary surface \( S \) of the volume under consideration and \( \mathbf{e}_n \) is the unit vector normal to this surface. The surface integral vanishes when \( V \) encloses the whole system because \( \mathbf{\sigma} \) vanishes at infinity: this is another way of saying that the system, or each of its parts, does not exert a net force upon itself (the corresponding result for the torque can be shown to follow from the symmetry relation \( \sigma_{ij} = \sigma_{ji} \), see [Landau 1987]).

In comparison to hydrodynamics, TDDFT seems to take a “back step” since it attempts to represent the contact force density \( \mathbf{F}_{xc} \) in terms of a scalar exchange-correlation potential, i.e., \( \mathbf{F}_{xc} = -n(r, t) \nabla v_{xc}(r, t) \), where \( v_{xc} \) is a functional of the density. This is admissible in principle, but may lead to a violation of Newton’s third law when an approximate form of \( v_{xc} \) is used.

To understand why it might be better to formulate the theory in terms of the current density (and its conjugate field, the vector potential), consider the continuity equation

\[
\frac{\partial n(r, t)}{\partial t} = -\nabla \cdot \mathbf{j}(r, t), \tag{5.7}\]
Fig. 5.1. Diagram showing the relation between current density functional theory and density functional theory. The nonlocal relation between \( n \) and \( v_{xc} \) is transformed into a local relation between \( j \) and \( A_{xc} \) by means of two non-local transformations from \( n \) to \( j \) and from \( v_{xc} \) to \( A_{xc} \).

which expresses the local conservation of particle number. Starting from this equation it is relatively easy to get \( n(r, t) \) from \( j(r, t) \) by taking the divergence of the latter and integrating over time. But the inverse problem, getting \( j(r, t) \) from \( n(r, t) \), is far more difficult and does not possess a unique solution (we can always add to the solution the curl of an arbitrary vector field, i.e., a purely transverse vector field). Only the longitudinal part of \( j \) is determined by the continuity equation and even this involves an integration over the whole space, i.e., one has

\[
j_L(r, t) = \int d^3r' \frac{\partial n(r', t)}{\partial t} \nabla_r \frac{1}{4\pi|r-r'|}.
\]

(5.8)

This relation is highly nonlocal (as is the corresponding relation between a scalar potential and the equivalent longitudinal vector potential, see Eq. (5.11) below), and this is why we expect to be able to drastically reduce the nonlocality of the density-dependent scalar potential by re-expressing it as a current-dependent vector potential. The idea is schematically depicted in Fig. 5.1. As a byproduct, the formulation in terms of \( j \) gives also direct access to the transverse component of the current density. This is important because the transverse current cannot be reliably extracted from the Kohn-Sham orbitals.

The path in front of us is now clear. In the next three sections we will develop a time-dependent current-density functional theory (TD-CDFT) in which the basic variable is the current density and the ordinary xc potential is replaced by an xc vector potential. We will see that in this theory the exchange-correlation force density has the form of the contact force density of hydrodynamics, i.e., it is the divergence of a stress tensor, and that this stress tensor can be safely approximated as a local functional of the current density.
This theory will enable us to calculate not only the density but also the current density from an effective Kohn-Sham equation. In order to accomplish this we will have to generalize Eq. (5.5) by endowing the viscosity constants \( \eta \) and \( \zeta \) with both real and imaginary parts (the latter representing the dynamical bulk and shear moduli of the liquid) and making them functions of the frequency as well as the local particle density.

Our discussion will be restricted to the linear response regime. By this we mean that the time dependent density has the form

\[
n(r, t) = n_{\text{GS}}(r) + \delta n(r)e^{-i\omega t} + \text{c.c.},
\]

where \( n_{\text{GS}}(r) \) is the ground-state (equilibrium) density, and \( \delta n(r) \ll n_{\text{GS}}(r) \). It will also be assumed that the frequency is high in the sense that \( \omega \gg qv_F \) and \( \omega \gg k_F \) where \( q^{-1} \) is the characteristic length scale for density variations in the ground-state, \( k \) is the wave vector of the external field, and \( v_F \) is the local Fermi velocity.

### 5.4 Current density functional theory

In time-dependent CDFT we consider a broader class of Hamiltonians than those considered in the original Runge-Gross formulation, namely Hamiltonians of the form

\[
\hat{H} = \sum_i \left\{ \frac{1}{2m} \left( p_i + e A_{\text{ext}, i} \right)^2 + v_{\text{ext}, i} \right\} + \hat{V}_{\text{ee}},
\]

where \( A_{\text{ext}, i} \) is the external vector potential evaluated at the position \( r_i \) of the \( i \)th particle, \( v_{\text{ext}, i} \) is the scalar potential at the position of the \( i \)th particle, and \( \hat{V}_{\text{ee}} \) represents the electron-electron interaction. The reason why this is a proper generalization of the Runge-Gross (RG) Hamiltonian is that every scalar potential \( v(r) \) can be represented as a *longitudinal* vector potential \( A_v(r) \) by choosing the latter as the solution of the equation

\[
\frac{e}{c} \frac{\partial A_v(r, t)}{\partial t} = \nabla v(r, t).
\]

Of course, *transverse* vector potential represents different physics (magnetic fields).

It can be easily proved that for Hamiltonians of the form (5.10) the time-dependent current density, together with the initial state, uniquely determine the scalar and the vector potential, up to a gauge transformation that leaves the initial state unchanged. A first proof of this generalized RG theorem was provided by Ghosh and Dhara [Ghosh 1988], and I have recently found a simpler proof [Vignale 2004]. Therefore, following the usual arguments, one expects to be able to construct, uniquely, a Kohn-Sham hamiltonian, \( \hat{H}_{\text{KS}} \).
that produces the correct current of the many-body system. This Hamiltonian will have the form

$$\hat{H}_{KS} = \sum_i \left\{ \frac{1}{2m} \left( \mathbf{p}_i + \frac{e}{c} \mathbf{A}_{KS,i} \right)^2 + v_{KS,i} \right\}, \quad (5.12)$$

and notice that the effective vector potential \( \mathbf{A}_{KS} \) will have in general longitudinal and transverse components even though the original external vector potential \( \mathbf{A}_{ext} \) was purely longitudinal. This equation (unlike the Kohn-Sham equation of ordinary TDDFT) determines in principle the whole current – not just its longitudinal component. The particle density is, of course, an immediate by-product of the longitudinal current.

So far goes the formalism. Now in order to find a concrete expression for \( \mathbf{A}_{KS} = \mathbf{A}_{ext} + \mathbf{A}_{xc} \) we resort to linear response theory; namely we assume that we are close to equilibrium and therefore \( \mathbf{A}_{xc} \) can be approximated as a linear functional of the current, with coefficients that depend on the equilibrium density. In other words we assume that \( \mathbf{A}_{xc} \) has the form

$$\mathbf{A}_{xc}(\mathbf{r}, \omega) = \int d^3 r' \mathbf{f}_{xc}(\mathbf{r}, \mathbf{r'}, \omega) \cdot \mathbf{j}(\mathbf{r'}, \omega), \quad (5.13)$$

where the tensor kernel \( \mathbf{f}_{xc} \) is a generalization of the scalar xc kernel of TDFT. We will discuss its structure in the next section. It must be borne in mind, however, that after doing the linear response approximation on \( \mathbf{A}_{xc} \), we lose control on the terms proportional to \( A_{xc}^2 \), which arise from the expansion of the kinetic energy operator in the Kohn-Sham equation.

### 5.5 The xc vector potential for the homogeneous electron liquid

Let us first consider the tensor exchange-correlation kernel \( \mathbf{f}_{xc}(\mathbf{r}, \mathbf{r'}, \omega) \) in a homogeneous electron liquid of density \( n \). Translational invariance makes \( \mathbf{f}_{xc}(\mathbf{r}, \mathbf{r'}, \omega) \) a function of \( \mathbf{r} - \mathbf{r'} \) and we will therefore focus on its Fourier transform

$$\mathbf{f}_{xc}(\mathbf{k}, \omega) = \int d^3 r \mathbf{f}_{xc}(\mathbf{r}, \omega) e^{i \mathbf{k} \cdot \mathbf{r}}. \quad (5.14)$$

Furthermore, we make use of rotational invariance to express the full kernel in terms of just two independent scalar functions of \( k = |\mathbf{k}| \), the longitudinal component \( f_{xc, L}(k, \omega) \) and the transversal component \( f_{xc, T}(k, \omega) \):

$$[\mathbf{f}_{xc}(\mathbf{k}, \omega)]_{\alpha\beta} = \left[ f_{xc, L}(k, \omega) \mathbf{k}_\alpha \mathbf{k}_\beta + f_{xc, T}(k, \omega)(\delta_{\alpha\beta} - \mathbf{k}_\alpha \mathbf{k}_\beta) \right] \frac{ck^2}{e\omega^2}, \quad (5.15)$$

where \( \mathbf{k} \) is the unit vector in the direction of \( \mathbf{k} \). The factor \( ck^2/e\omega^2 \) is introduced here as a matter of convenience, in order to make \( f_{xc, L}(k, \omega) \) coincide with the xc kernel of the ordinary density functional theory.
Fig. 5.2. The imaginary and the real parts of $f_{xc,L}(\omega)$ (in units of $\hbar\omega_p/n$) in a homogeneous electron liquid at $r_s = 3$. The short-dashed line (NCT) is the result of a mode-coupling calculation [Nifosi 1998]. The long-dashed line (GK) [Gross 1985] and the solid line (QV) [Qian 2002] are interpolation formulas based on exact limiting forms.

Given the kernels $f_{xc,L}$ and $f_{xc,T}$ it is easy to construct the linear response of the homogeneous electron liquid to an external vector potential $A_{ext}(\mathbf{k}, \omega)$. As discussed in the previous section, this is just the response of the non-interacting electron gas (at the same density $n$) to the effective field $A_{ext}(\mathbf{k}, \omega) + A_{dw}(\mathbf{k}, \omega)$. (Once again, the “external” field $A_{ext}$ is assumed to include the Hartree potential $A_H(\mathbf{k}, \omega) = 4\pi e^2 \mathbf{k}/\omega^2$ in three dimensions.)

The connection between the xc kernels and the linear response functions of the electron liquid is the basis of the microscopic calculation of $f_{xc,L}$ and $f_{xc,T}$ [Nifosi 1998, Qian 2002, Qian 2003]. These calculations are too technical to be described here, but the following features should be noted:

(i) Both $f_{xc,L}(k, \omega)$ and $f_{xc,T}(k, \omega)$ tend to finite limits, denoted by $f_{xc,L}(\omega)$ and $f_{xc,T}(\omega)$, when $k \to 0$ at finite $\omega$ (this is a consequence of translational invariance, as it implies that the electron liquid accelerates uniformly in response to a uniform electric field)

(ii) The $k = 0$ kernels $f_{xc,L}(\omega)$ and $f_{xc,T}(\omega)$ have both real and imaginary parts. The real parts have finite limiting values at $\omega = 0$ and $\omega = \infty$ and may have either sign; the imaginary parts are negative at all frequencies and tend to zero linearly for $\omega \to 0$ and as $\omega^{-d/2}$ for $\omega \to \infty$: the coefficients of these asymptotic behaviors are known analytically.

Representative plots of the longitudinal kernel $f_{xc,L}(\omega)$ and of the transverse kernel $f_{xc,T}(\omega)$ vs $\omega$ are shown in Fig. 5.2 and Fig. 5.3.

Let us now return to the full xc vector potential. Combining the longitudinal and transverse components, and making use of the existence of the $k \to 0$ limit of $f_{xc,L(T)}(k, \omega)$ we see that, up to order $k^2$, the xc vector potential can
Fig. 5.3. Same as the previous figure for the imaginary and real parts of $f_{\text{sc},\tau}(\omega)$ at $r_s = 3$.

be written as

$$
\frac{e}{c} A_{\text{xc}}(\mathbf{k}, \omega) = \left[ f_{\text{sc},1}(\omega) \mathbf{k} \cdot \mathbf{j} - f_{\text{sc},\tau}(\omega) \mathbf{k} \times (\mathbf{k} \times \mathbf{j}) \right] \frac{k^2}{\omega^2}.
$$

(5.16)

From this we want to separate the adiabatic LDA contribution. Recall that in the adiabatic LDA the xc potential is just the xc component of the chemical potential, $\mu_{\text{xc}}$, evaluated at the instantaneous local density $n = n_{\text{GS}} + n_1 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] + \text{c.c.}$ Thus, in the linear response approximation we have

$$
v_{\text{xc}}^{\text{ALDA}}(\mathbf{k}, \omega) = \mu_{\text{xc}}'(n_{\text{GS}}) n(\mathbf{k}, \omega),
$$

(5.17)

where the prime denotes a derivative with respect to $n$. Making use of the continuity equation $n(\mathbf{k}, \omega) = \mathbf{k} \cdot \mathbf{j}(\mathbf{k}, \omega)/\omega$, and recasting $v_{\text{xc}}^{\text{ALDA}}$ as a longitudinal vector potential according to the formula

$$
\frac{e}{c} A_{\text{xc}}^{\text{ALDA}}(\mathbf{k}, \omega) = \frac{k}{\omega} v_{\text{xc}}^{\text{ALDA}}(\mathbf{k}, \omega),
$$

(5.18)

we arrive at

$$
\frac{e}{c} A_{\text{xc}}(\mathbf{k}, \omega) = \frac{e}{c} A_{\text{xc}}^{\text{ALDA}}(\mathbf{k}, \omega)
$$

$$
+ \left( f_{\text{sc},1}(\omega) - \mu_{\text{xc}}'(\mathbf{k}) \mathbf{k} \cdot \mathbf{j} - f_{\text{sc},\tau}(\omega) \mathbf{k} \times (\mathbf{k} \times \mathbf{j}) \right) \frac{k^2}{\omega^2}.
$$

(5.19)

We are now very close to the promised hydrodynamic form. All that remains to be done is to Fourier-transform the expression for $A_{\text{xc}}$ back to real space, keeping in mind that under this transformation $i \mathbf{k}$ becomes the $\nabla$ operator. It is also convenient to focus on the force exerted by the vector potential on the volume element rather than the vector potential itself: this is given by $F_{\text{xc}}(\mathbf{k}, \omega) = -ne \mathbf{E}_{\text{xc}}(\mathbf{k}, \omega) = -i\omega n_1 \mathbf{j} A_{\text{xc}}(\mathbf{k}, \omega)$. (This is strictly speaking only the electric force. The magnetic Lorentz force is neglected, being of higher
order in both $j$ and $k$). Thus, after some straightforward algebra we arrive at the following expression for the force density:

$$F_{xc}(\mathbf{r}, \omega) = F_{xc}^{\text{ALDA}}(\mathbf{r}, \omega) - \nabla \cdot \tilde{\sigma}_{xc}(\mathbf{r}, t),$$  \hspace{1cm} (5.20)

where

$$[\tilde{\sigma}_{xc}(\mathbf{r}, t)]_{\alpha\beta} = \tilde{\eta} \left( \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} - \frac{2}{d} \nabla \cdot \mathbf{v} \delta_{\alpha\beta} \right) + \tilde{\zeta} \nabla \cdot \mathbf{v} \delta_{\alpha\beta},$$  \hspace{1cm} (5.21)

and $\tilde{\eta}$, $\tilde{\zeta}$ are generalized viscosities that depend on the density and the frequency and are related to the $k \to 0$ limit of the xc kernel in the following manner:

$$\tilde{\eta} = -\frac{n^2}{k\omega} f_{xc, T}(\omega),$$  \hspace{1cm} (5.22a)

$$\tilde{\zeta} = -\frac{n^2}{k\omega} \left[ f_{xc, 1}(\omega) - \frac{2(1-d)}{d} f_{xc, T}(\omega) - \mu'_{xc} \right].$$  \hspace{1cm} (5.22b)

Notice that, at variance with the original hydrodynamic viscosities of Eq. (5.5), the generalized viscosities have both a real and an imaginary part:

$$\tilde{\eta}(\omega) = \eta(\omega) - \frac{S_{xc}(\omega)}{k\omega},$$  \hspace{1cm} (5.23a)

$$\tilde{\zeta}(\omega) = \zeta(\omega) - \frac{B_{xc}^{\text{dyn}}(\omega)}{k\omega},$$  \hspace{1cm} (5.23b)

where $\eta$, $\zeta$, $S_{xc}$, and $B_{xc}^{\text{dyn}}$ are all real quantities. Clearly $\eta(\omega)$ and $\zeta(\omega)$ describe the physical viscosity of the liquid. On the other hand, $S_{xc}(\omega)$ and $B_{xc}^{\text{dyn}}(\omega)$ describe the elasticity of the electron liquid [Conti 1999]; they are the dynamical shear modulus and the dynamical bulk modulus, respectively. Notice that there is no static shear modulus in a liquid, hence the superscript “dyn” is not needed for $S_{xc}$; on the other hand $B_{xc}^{\text{dyn}}(\omega)$ denotes the difference between the frequency-dependent bulk modulus, $B_{xc}(\omega)$ and its static value $B_{xc}(0)$. These elastic constants are absent in hydrodynamics because hydrodynamics deals with the collisional regime $\omega\tau \ll 1$ in which frequent collisions between the particles, (occurring at a rate $1/\tau$) create a situation of local equilibrium in a time that is short compared to the period of the oscillations. But at frequencies higher than $1/\tau$ the system is out of equilibrium, the Fermi surface is deformed, and there is an energy cost to pay for such a deformation. The elastic constants of the electron liquid are precisely the stiffnesses of the Fermi surface against deformations.

Based on the above discussion one could expect that $S_{xc}$ and $B_{xc}^{\text{dyn}}$ vanish in the $\omega \to 0$ limit. This expectation is borne out for the dynamical bulk modulus, but, surprisingly, not for the shear modulus. The reason is that even a very small frequency $\omega \ll \epsilon_F$ (where $\epsilon_F$ is the Fermi energy) is large in comparison with the inverse relaxation time from electron-electron collisions,
which vanishes as $T^2$ when the temperature, $T$, tends to zero. Indeed, since the real part of $f_{xc,T}^{\omega}(\omega)$ tends to a finite limit for $\omega \to 0$, while the imaginary part tends to zero, it turns out that the shear modulus is the dominant contribution to the xc field in the $\omega \to 0$ limit. It is precisely this term that makes the difference between CDFT and ordinary adiabatic LDA in the calculation of the polarizability of long polymer chains, which is described later in this book (Chapter 21). In any case, the lesson to be learned is that the $\omega \to 0$ limit of the time-dependent CDFT is not the same as the adiabatic ALDA, provided that the limit is taken in such a way that local equilibrium is not reached.

### 5.6 The xc vector potential for the inhomogeneous electron liquid

The main result of the previous section, Eq. (5.20), is written so that it can immediately be turned into a local density approximation for the xc electric field of an inhomogeneous electron liquid through the replacement $n \rightarrow n_{GS}(r)$, where $n_{GS}(r)$ is the ground-state density of the inhomogeneous liquid. Of course, the xc kernels must also be evaluated at the local density. The correctness of this procedure is confirmed by a careful study of the structure of the tensor exchange-correlation kernel of a weakly inhomogeneous electron liquid. This study was carried out by VK [Vignale 1996] and is reviewed in [Vignale 1997]. In [Vignale 1996] VK considered an electron liquid modulated by a charge-density wave of small amplitude $\gamma$ and small wave vector $q$. The wave vector $k$ of the external field and $q$ were assumed to be small not only in comparison to the Fermi wave vector $k_F$ but also in comparison to $\omega/\nu_F$ ($\nu_F$ being the Fermi velocity). The second condition ensures that the phase velocity of the density disturbance is higher than the Fermi velocity, so that no form of static screening can occur. Under these assumptions, all the components of the tensorial kernel $\vec{f}_{xc}$ could be calculated, up to first order in the amplitude of the charge density wave, and to second order in the wave vectors $k$ and $q$. The calculations were greatly facilitated by a set of sum rules which are mathematically equivalent to the zero-force and zero-torque requirements discussed in Chapter 11 and in the Appendix of this chapter. The result of the analysis was a rather complicated but regular expression for the various components of $f_{xc}$ in the limit of small $k$ and $q$. Finally, this expression could be rearranged [Vignale 1997, Ulrich 2002b] in the elegant form

$$\frac{e}{c} A_{xc}(r, \omega) = \frac{e}{c} A_{xc}^{ALDA}(r, \omega) - \frac{1}{i\omega n_{GS}(r)} \nabla \cdot \sigma_{xc}(r, t),$$

which is of course equivalent to Eq. (5.20).

As the occurrence of two spatial derivatives of the velocity field in the second term on the right hand side of this equation is dictated by general prin-
principles, Eq. (5.20), with the xc stress tensor given by Eq. (5.21), is expected to remain valid even for large values of the velocity, i.e., in the nonlinear regime, provided \( v \) and \( n \) are slowly varying. The argument goes as follows: Suppose we tried to extend Eq. (5.20) into the nonlinear regime by including terms of order \( v^2 \). Because the stress tensor must depend on first derivatives of \( v \), such corrections would have to go as \( (\nabla v)^2 \). But then the force density, given by the derivative of the stress tensor, would have to involve at least three derivatives. Thus, for sufficiently small spatial variation of the density and velocity fields, the nonlinear terms can be neglected. Since the ALDA is an intrinsically nonlinear approximation, VUC proposed that Eq. (5.20), written in the time domain, could provide an appropriate description of both linear and nonlinear response properties. A nonlinear, retarded expression for \( \delta v_{\text{xc}} \) was also proposed by Dobson et al. [Dobson 1997]. The two approximations coincide in “one-dimensional systems” (i.e., when one has a unidirectional current density field that depends only on one coordinate), but differ in the general case. More recently, Ilya Tokatly has developed a more general and beautiful theory, based on the use of Lagrangian coordinates, which is applicable also when the gradient of the velocity field is not small. An accessible presentation of his theory can be found in Chapter 8 of this book.

5.7 Applications

Several applications of time-dependent CDFT have appeared so far in the literature and are described in Chapters 18 and 19. Here I limit myself to a very brief summary, illustrating how new effects can be described which were not accessible by the standard TDDFT.

Collective excitations in semiconductor quantum wells – This is an ideal application, because the electronic density profile of semiconductor quantum wells is defined by electrostatic gating and is therefore slowly varying in space. A particularly important problem is the characterization of intersubband transitions, which take place between two different levels of quantized motion in the growth direction. These transitions are highly collective (i.e., they consist of a complex superposition of electron-hole pairs) and cannot be described within a single-particle picture. It turns out that the ordinary TDDFT, in the adiabatic approximation, does a reasonably good job of predicting the energy of these excitations. However, the calculation of the linewidth is completely beyond the power of ordinary TDF. Chapter 18 explains how the linewidth is calculated in TDCDFT, and how it can be brought to excellent agreement with experiment by the inclusion of extrinsic effects such as impurity scattering and surface roughness. Unfortunately, the excellent agreement found in simple quantum wells does not extend to more complex structures, such as the double quantum well (a single well split into two parts by a potential barrier). The non classical, low-density barrier
region is problematic because the velocity field has a large gradient there. Thus double-well systems expose some of the limitations of the local current density approximation.

Atoms – Ulrich and Burke[Ulrich 2004] have applied TDCDFT to the calculation of the excitation energies of divalent atoms. The results are mixed. For $1S \rightarrow 1S$ transitions they find a small improvement upon the ordinary DFT (in local density approximation), but for $1S \rightarrow 1P$ transitions things get worse. Furthermore, CDFT predicts a small but finite linewidth for all atomic excitations. This is an artifact of the theory, since the linewidth arises from the continuum excitation spectrum of the homogeneous electron gas to which the electronic cloud of the atom is locally assimilated.

Conjugated polymers – TDCDFT has been applied, in the zero-frequency limit, to the study of the static dielectric response of long insulating polymer chains (polyacetylene and other Pi-conjugated polymers). The interest and importance of the problem arises from the fact that the ordinary LDA-based DFT leads to a serious overestimation of the dielectric polarizability – an overestimation that grows with the length of the chain, and is due to the ultra-nonlocality of the xc functional. Indeed, Hartree-Fock calculations, in which the nonlocality of the potential is preserved, do not suffer from this problem (at least not in such a serious form). In applying the TD-CDFT one must keep in mind that the zero-frequency limit of this theory does not coincide with the naive LDA. There is an additional term, which arises from the elasticity of the electron liquid in the insulator, and this term is (within the local current density approximation) taken to be equal to the dynamical shear modulus of a uniform electron gas of the same density. The results are quite spectacular for polyacetylene and other polymer chains which have well extended electronic states at the top of the valence band: the new term corrects the overestimation of the dielectric constant and brings the result in excellent agreement with state-of-the-art wave function methods (MP2 perturbation theory). The method is not equally successful for other polymer chain (e.g., long $H_2$ chains) which are characterized by much more localized electronic states. In this case the improvement upon the LDA is marginal. It is of course expected that the local approximation should be less effective in dealing with systems that are further away from the homogeneous electron liquid. A more detailed discussion of these results is provided in Chapter 19.

Optical spectra of semiconductors – The problem of calculating the optical spectra of semiconductors (e.g. Si) is historically very important, for it exposes one of the main weaknesses of DFT: its lack of accuracy in predicting the value of the optical gap (LDA typically underestimates it by a significant fraction). Can TDCDFT solve the band-gap problem? I think the jury is still out on this important question. At the fundamental level the answer is probably no. Although TDCDFT does possess the two features which are
known to be necessary for a renormalization of the band gap, namely, a finite imaginary part and an infinite range in space of the xc kernel \( f_{xc} \), it appears that the uniform electron-gas approximation is not sufficient to produce a sharp change in the optical gap (in fact the present approximations predict a finite absorption coefficient at all frequencies). In practice, however, one could still obtain improved optical spectra, since the xc potential may alter the oscillator strength of transitions near the gap in such a way as to simulate an increase in the band gap. This is what seems to be happening in recent calculations of the optical spectra carried out by the Groningen group. These calculations, however, are still based on a frequency-independent exchange-correlation kernel. More details will be found in Chapter 19.

**Irreversible dynamics and transport** – Finally, I mention that the inclusion of the current in the xc potential makes the latter non-invariant under time reversal, and thus opens the way to a first principle treatment of irreversible effects, such as the relaxation of an excited state [Wijewardane 2005, D’Agosta 2005b]. It is remarkable that the irreversible behavior of a global variable (the current) can be computed without leaving the framework of the Kohn-Sham equation, i.e. within a pure-state description of the system. TDCDFT can also be applied to electrical transport problems, since it gives direct access to the current and therefore to the resistance. Recently it has been shown that the low-frequency viscosity gives a substantial contribution to the resistance of molecular junctions and quantum point contacts [Nasai 2005]. Remarkably, the term in the xc potential which causes this effect in a conductor is the same that modifies the dielectric polarizability in an insulator.

In conclusion, the time-dependent CDFT is a powerful and versatile tool for the study of optical, dielectric, transport, and relaxational properties of electronic system. However, the local approximation upon which xc functionals are based does have severe shortcomings, particularly in atomic systems. More research is needed to produce functionals that work in difficult situations.

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**Appendix – The zero force theorem and generalized translational invariance**

It is important to become familiar with the few known exact properties of the exchange-correlation potential in TDDFT since they provide insight into
the structure of the theory and are useful constraints on approximations. The simplest exact condition probably is the zero-force theorem, which states that

$$\int d^3r \ n(r, t) \nabla v_{xc}(r, t) = 0, \quad (5.25)$$

i.e., the net force exerted by the xc potential on the system is zero [Vignale 1995a]. This is a fairly obvious statement, following from Newton’s third law, and can be proved in a completely elementary manner [Gross 1996]. One simply notices that the average center of mass coordinate of a system of $N$ identical particles of mass $m$, defined as

$$R \equiv \frac{1}{N} \int d^3r \ n(r, t), \quad (5.26)$$

satisfies the equation of motion

$$N m \ddot{R}(t) = - \int d^3r \ n(r, t) \nabla v_{\text{ext}}(r, t), \quad (5.27)$$

where $v_{\text{ext}}(r, t)$ is the external potential and $\ddot{R}(t)$ denotes the second derivative of $R(t)$ with respect to time. The internal particle-particle interactions cancel out in pairs. Recalling that the Kohn-Sham system has precisely the same density (and therefore precisely the same center of mass coordinate) as the true many-particle system, we can also write

$$N m \ddot{R}(t) = - \int d^3r \ n(r, t) \nabla [v_{\text{ext}}(r, t) + v_{\text{HI}}(r, t) + v_{xc}(r, t)]. \quad (5.28)$$

Subtracting Eq. (5.27) from Eq. (5.28), and noting that the Hartree potential explicitly satisfies the zero-force theorem, we immediately arrive at Eq. (5.25).

The zero-force theorem can also be cast in a differential form which turns out to be useful in the analysis of linear response. To this end consider the linear response regime $n(r, t) = n_{\text{GS}}(r) + \delta n(r, t)$ and $v_{xc, \text{GS}}(r) + \delta v_{xc}(r, t)$, with $\delta n(r, t) \ll n_{\text{GS}}(r)$ and $v_{xc, \text{GS}}(r) \ll \delta v_{xc}(r, t)$, where $n_{\text{GS}}(r)$ is the ground-state density and $v_{xc, \text{GS}}(r)$ is the xc potential associated with it. Expanding Eq. (5.25) to first order in $\delta n$ we get

$$\int d^3r \ n_{\text{GS}}(r) \nabla \delta v_{xc}(r, t) + \int d^3r \ \delta n(r, t) \nabla v_{xc, \text{GS}}(r) = 0. \quad (5.29)$$

The first term on the left hand side can be integrated by parts yielding

$$\int d^3r \ \delta v_{xc}(r, t) \nabla n_{\text{GS}}(r) = \int d^3r \ \delta n(r, t) \nabla v_{xc, \text{GS}}(r). \quad (5.30)$$

We now express $\delta v_{xc}$ in terms of $\delta n$ according to the linear relation

$$\delta v_{xc}(r, t) = \int dt' \int d^3r' f_{xc}(r, r', t - t') \delta n(r', t') \quad (5.31)$$
where $f_{xc}$ is the xc kernel of the ground-state, which depends only on the difference $t - t'$ and vanishes for $t < t'$. Substituting this into Eq. (5.30) and Fourier-transforming both sides with respect to time we arrive at

$$\int d^3r \int d^3r' f_{xc}(r, r', \omega) \delta n(r', \omega) \nabla n_{GS}(r) = \int dr' \delta n(r', \omega) \nabla v_{xc, GS}(r').$$

(5.32)

Finally, taking into account the arbitrariness of $\delta n(r, \omega)$ we see that the above equation implies

$$\int d^3r f_{xc}(r, r', \omega) \nabla n_{GS}(r) = \nabla v_{xc, GS}(r').$$

(5.33)

Furthermore, since $f_{xc}(r, r', \omega)$ is symmetric under interchange of $r$ and $r'$ [Vignale 1998] we also have

$$\int dr' f_{xc}(r, r', \omega) \nabla n_{GS}(r') = \nabla v_{xc, GS}(r).$$

(5.34)

We make use of this form of the identity in the discussion of “ultranonlocality” in Chapter 5.

Deep down, the above conditions are consequences of the fact that we are free to choose an arbitrary reference frame to describe the time evolution of a many-particle system [Vignale 1995a]. Of course, the dynamics in some reference frames will be more complicated than in others. However, the transformation rules for the particle density and for the xc potential are easily worked out, and since the xc potential in one frame must be the same universal functional of the density (and initial state) that it is in any other frame, the knowledge of these transformation rules leads to exact constraints on the form of the functional.

For example consider the transformation

$$r = r' + R(t),$$

(5.35)

where $R(t)$ is an arbitrary time-dependent vector. Evidently, the particle density in the transformed frame is related to the particle density in the original frame by

$$n'(r', t) = n(r' + R(t), t).$$

(5.36)

and the initial state is transformed according the unitary transformation

$$|\psi'\rangle = \exp \left\{ -i \sum_{i=1}^{N} m r_i \cdot \hat{R}(0) \right\} \exp \left\{ i \sum_{i=1}^{N} p_i \cdot \hat{R}(0) \right\} |\psi\rangle,$$

(5.37)

where $r_i$ and $p_i$ are the position and momentum operators of the $i$-th particle. Then it can be shown [Vignale 1995a] that

$$v_{xc}[|\psi'\rangle, |\phi'\rangle, n'(r', t) = v_{xc}[|\psi\rangle, |\phi\rangle, n](r' + R(t), t),$$

(5.38)
where \( v_{xc}|\psi>, |\phi>, n(r, t) \) is the xc potential at position \( r \) and time \( t \) produced by the density \( n \) in a system that starts its evolution in the initial many-body state \( |\psi> \), with initial Kohn-Sham state \( |\phi> \) (see Sect. 11.4.4). \( |\varphi> \) and \( |\psi'> \) are related to \( |\phi> \) and \( |\psi> \) respectively by the transformation (5.37). Eq. (5.38) can be interpreted as a “generalized translational invariance condition”, telling us that the exchange-correlation potential “rides on top” of a globally accelerating density, remaining a constant functional of the instantaneous density. It can be shown that this leads to the zero-force theorem [Vignale 1995a].

A similar set of conditions is arrived at by considering global rotations of the system by an arbitrary time-dependent angle about an arbitrary axis. An example is the “zero torque theorem” given by Eq. (11.11b). All these theorems carry over to CDFT with the appropriate modifications. For example the tensor xc kernel of CDFT for a system in the ground-state withdensity \( n_{GS}(r) \) satisfies the identity

\[
\int d^3 r' f_{xc, \alpha\beta}(r, r', \omega)n_{GS}(r') = -\frac{\nabla_{\alpha} \nabla_{\beta} v_{xc, GS}(r)}{\omega^2}, \tag{5.39}
\]

where \( \alpha \) and \( \beta \) denote cartesian components. This is the generalization of Eq. (5.34) in CDFT. We refer the reader to [Vignale 1998] for a detailed derivation and discussion of these identities.