

11 Exact Conditions

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11.1 Introduction

In this chapter, we collect and discuss several of the exact conditions known about time-dependent density functional theory. The subject of TDDFT is still much less developed than its ground-state counterpart, and this is reflected in the number and usefulness of exact conditions known.

11.2 Review of the Ground State

In ground-state DFT, the unknown exchange-correlation energy functional, $E_{xc}[n]$, plays a crucial role. In fact, it is really this energy that we typically wish to approximate with some given level of accuracy and reliability, and *not* the density itself. Using such an approximation in a modern Kohn-Sham ground-state DFT calculation, we can calculate the total energy of any configuration of the nuclei of the system, and so extract the bond lengths and angles of molecules, and deduce the lowest energy lattice structure of solids. We can also extract forces in simulations, vibrational frequencies, phonons, and bulk moduli. We can also discover response properties to both external electric fields and magnetic fields (using spin DFT). The accuracy of the self-consistent density is irrelevant to most of these uses.

Given the central role of the energy, it makes sense to devote much effort to its study as a density functional. Knowledge of its behavior in various limits can be crucial to restraining and constructing accurate approximations, and to understanding their limitations. This task is greatly simplified by the fact that the total ground-state energy satisfies the variational principle. Many exact conditions use this in their derivation.

Let us quickly review some of the more prominent exact conditions. They almost all concern the energy functional, which, as mentioned above, is crucial for good KS-DFT calculations. We do not give original references here, but refer the interested reader to [Perdew 2003] for a thorough discussion.

11.2.1 Basic Conditions

These conditions are very elementary, and any sensible approximation should satisfy them.

- **Coordinate scaling:** By defining $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$, one can easily show

$$E_x[n_\gamma] = \gamma E_x[n]. \quad (11.1)$$

- **Virial theorem:**

$$E_{xc} + T_c = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}(\mathbf{r}), \quad (11.2)$$

where T_c is the kinetic contribution to the correlation energy.

- **Coupling constant:** In DFT, one imagines varying the strength of the electron-electron repulsion, while keeping the density fixed, and defines quantities as a function of λ . One finds:

$$E_{xc}^\lambda[n] = \lambda^2 E_{xc}[n_{(1/\lambda)}], \quad (11.3)$$

i.e., altering the coupling constant is simply related to scaling the density.

- **Adiabatic connection formula:** By using the Hellmann-Feynman theorem, one can show:

$$E_c[n] = \int_0^1 d\lambda U_c^\lambda[n]/\lambda, \quad (11.4)$$

where U_c^λ is the potential contribution to the correlation energy.

11.2.2 Finite Systems

The next set of conditions are derived for finite systems, just as the Hohenberg-Kohn theorem is.

- **Coordinate scaling:** Coordinate scaling of the correlation is less simple than exchange:

$$\begin{aligned} E_c[n_\gamma] &> \gamma E_c[n] && (\gamma > 1) \\ E_c[n_\gamma] &= E_c^{(2)}[n] + E_c^{(3)}[n]/\gamma + \dots && (\gamma \rightarrow \infty) \\ E_c[n_\gamma] &= \gamma B[n] + \gamma^{3/2} C[n] + \dots && (\gamma \rightarrow 0), \end{aligned} \quad (11.5)$$

where $E_c^{(2)}[n]$, $E_c^{(3)}[n]$, $B[n]$ and $C[n]$ are all scale-invariant functionals. Not all popular approximations satisfy these conditions.

- **Self-interaction:** For any one-electron system,

$$E_x[n] = -E_H[n], \quad E_c = 0 \quad (N = 1), \quad (11.6)$$

where E_H is the Hartree energy.

- **Asymptotic behavior of potential:** Far from a Coulombic system

$$v_{xc}(\mathbf{r}) \rightarrow -1/r \quad (r \rightarrow \infty), \quad (11.7)$$

and

$$\varepsilon_{\text{HOMO}} = -I, \quad (11.8)$$

where $\varepsilon_{\text{HOMO}}$ is the eigenenergy of the highest occupied KS molecular orbital, and I the ionization potential. These results are intimately related to the self-interaction of one electron.

- **Lieb-Oxford bound:** For any density,

$$E_{xc} \geq 2.273 E_x^{\text{LDA}}. \quad (11.9)$$

11.2.3 Uniform and Nearly Uniform Gas

This last set of conditions involve the properties of the uniform or nearly uniform electron gas.

- **Uniform density:** When the density is uniform, $E_{xc} = e_{xc}^{\text{unif}}(n) \mathcal{V}$, where $e_{xc}^{\text{unif}}(n)$ is the xc energy density of a uniform electron gas of density n , and \mathcal{V} is the volume.
- **Slowly varying density:** For slowly varying densities, E_{xc} should recover the gradient expansion.
- **Linear response of uniform gas:** Another generic limit is when a weak perturbation is applied to a uniform gas, and the resulting change in energy is given by the static response function, $\chi(q, \omega = 0)$. This function is known from accurate quantum Monte Carlo calculations [Moroni 1995], and approximations can be tested against it.

11.2.4 Finite Versus Extended Systems

Note the distinction above between extended systems (like the uniform gas or any bulk system) and finite systems. The basic theorems of DFT are proven for *finite* quantum mechanical systems, with densities that decay at large distances from the center. Their extension to extended systems, even those as simple as the uniform gas, requires careful thought. For ground-state properties, one can usually take results directly to the extended limit without change, but not always. For example, the high-density limit of the correlation energy in (11.5) fails for a uniform gas.

11.2.5 Types of Approximations

Despite a plethora of approximations [Perdew 2005], no present-day approximation satisfies all these conditions, and so one chooses which conditions to impose on a given approximate form. Nonempirical approaches attempt to

fix all parameters via exact conditions [Perdew 1996a, Perdew 1996b], while good empirical approaches might include one or two parameters that are fit to some data set [Becke 1988b, Lee 1988, Becke 1993b].

There are two basic flavors of approximations: pure density functionals, which are often designed to meet conditions on the uniform gas, and orbital-dependent functionals [Grabo 1998], which meet the finite-system conditions more naturally. The most sophisticated approximations being developed today use both [Tao 2003].

11.3 Conditions and Approximations

The time-dependent problem is much more diverse than the ground-state problem, making the known exact conditions more difficult to classify. We make the basic distinction between general time-dependent perturbations, of arbitrary strength, and weak fields, where linear response applies. The former give conditions on the xc potential for all time-dependent densities, the latter yield conditions directly on the xc kernel, which is a functional of the ground-state density alone. Of course, all of the former also yield conditions in the special case of weak fields.

11.3.1 Role of the Energy

In the time-dependent problem, we do not have the energy playing a central role. Formally, the action plays an analogous role (see Chap. 2), but in practice, we never evaluate the action in TDDFT calculations (as it is identically zero on the real time evolution). In TDDFT, our focus is truly the time-dependent density itself, and so, by extension, the potential determining that density. Thus many of our conditions are in terms of the potential.

Note also that most pure *density* functionals for the ground-state problem produce poor approximations for the details of the potential. Such approximations work well only for quantities integrated over space, such as the energy. Thus approximations that work well for ground-state energies are sometimes very poor as adiabatic approximations in TDDFT. For example their failure to satisfy (11.7) leads to large errors in the KS energies of higher-lying orbitals.

In place of the energy, there are a variety of physical properties that people wish to calculate. On the one hand, quantum chemists are most often focused on first few low-lying excitations, which might be crucial for determining the photochemistry of some biomolecule. Then the adiabatic generalization of standard ground-state approximations is often sufficient (see Chaps. 17, 22 and 23). At the other extreme, very often people who study matter in strong laser fields are very focused on ionization probabilities, and there the violation of (11.8) makes density approximations too crude, and requires orbital-dependent approximations instead.

11.3.2 Approximations

As we go through the various exact conditions, we will discuss whether the simplest approximations in present use satisfy them. The most important are:

- **ALDA:** Adiabatic local density approximation, the simplest pure density functional, commonly used in many calculations, and described in Chap. 1.
- **AA:** “Exact” adiabatic approximation, in which we imagine using the exact ground-state potential for a given density (see Chap. 1).
- **EXX:** Exact exchange, the orbital-dependent functional, treated as an implicit density functional (see Chap. 9).

A key aim of today’s methodological development is to build in correlation memory effects. Exact exchange (for more than two unpolarized electrons) has some memory when considered as a density functional. We will discuss two attempts at memory inclusion, both limited to the linear response regime:

- **GK:** The Gross-Kohn approximation is simply to use the local frequency-dependent kernel of the uniform gas, $f_{xc}^{\text{unif}}(q \rightarrow 0, \omega)$ instead of its adiabatic limit as used in ALDA.
- **VK:** The Vignale-Kohn approximation is simply the gradient expansion in the current density for a slowly-varying gas (see Chap. 5).

The approximations suggested in the rest of this Part (Chaps. 8 and 10) could be tested for satisfaction of the conditions below, and perhaps improved.

11.4 General Conditions

In this section, we discuss conditions that apply no matter how strong the time-dependent potential is.

11.4.1 Adiabatic Limit

The most essential exact condition in TDDFT is the adiabatic limit. For any finite system, or an extended system with a finite gap, the deviation from the instantaneous ground-state during a perturbation (of arbitrary strength) can be made arbitrarily small, by slowing down the time-evolution, i.e., if the perturbation is $v(t)$, replacing it by $v(t/\tau)$ and making τ sufficiently large. This is the adiabatic theorem of quantum mechanics.

Similarly, as the time-dependence becomes very slow (or equivalently, as the frequency becomes small), for such system the functionals reduce to their ground-state counterparts:

$$v_{xc}(\mathbf{r}, t) \rightarrow v_{xc}[n(t)](\mathbf{r}) \quad (\tau \rightarrow \infty) \quad (11.10)$$

where $v_{xc}[n](\mathbf{r})$ is the exact ground-state xc potential of density $n(\mathbf{r})$.

Clearly, any adiabatic approximation satisfies this theorem, and so also does EXX, by reducing to their ground-state analogs for slow variations. On the other hand, if an approximation to $v_{xc}(\mathbf{r}, t)$ were devised that was not based on ground-state DFT, this theorem could be used in reverse to *define* the corresponding ground-state functional.

11.4.2 Equations of Motion

In this section, we discuss some elementary conditions that any reasonable TDDFT approximation should satisfy. Because almost all approximations do satisfy these conditions, they are best applied as tests of propagation schemes (see Part III). Satisfaction of these conditions by propagation schemes can be used to interpret their quality. For schemes that do not automatically satisfy a given condition, then a numerical check of its validity provides a test on the accuracy of the solution. A simple analog is the check of the virial theorem in ground-state DFT in a finite basis.

These conditions are all found via a very simple procedure. They begin with some operator that depends only on the time-dependent density, such as the total force on the electrons. The equations of motion for the operator in both the interacting and the KS systems are written down, and subtracted. Since the time-dependent density is the same in both systems, the difference vanishes. Usually, the Hartree term also separately satisfies the resulting equation, and so can be subtracted from both sides, yielding a condition on the xc potential alone. This procedure is well-described in Chap. 5 for the zero xc force theorem.

Zero xc Force and Torque: These are very simple conditions saying that interaction among the particles cannot generate a net force [Vignale 1995a, Vignale 1995b]:

$$\int d^3r n(\mathbf{r}, t) \nabla v_{xc}(\mathbf{r}, t) = 0 \quad (11.11a)$$

$$\int d^3r n(\mathbf{r}, t) \mathbf{r} \times \nabla v_{xc}(\mathbf{r}, t) = \int d^3r \mathbf{r} \times \frac{\partial \mathbf{j}_{xc}(\mathbf{r}, t)}{\partial t}, \quad (11.11b)$$

where $\mathbf{j}_{xc}(\mathbf{r}, t)$ is the difference between the interacting current density and the KS current density [van Leeuwen 2001]. The second condition says that there is no net xc torque, *provided* the KS and true current densities are identical. This is not guaranteed in TDDFT (but is in TDCDFT).

xc Power and Virial: By applying the same methodology to the equation of motion for the Hamiltonian, we find [Hessler 1999]:

$$\int d^3r \frac{dn(\mathbf{r}, t)}{dt} v_{xc}(\mathbf{r}, t) = \frac{dE_{xc}}{dt}. \quad (11.12)$$

while another equation of motion yields the virial theorem, which intriguingly has the exact same form as in the ground state, (11.2):

$$E_{\text{xc}}[n](t) + T_{\text{c}}[n](t) = - \int d^3r n(\mathbf{r}, t) \mathbf{r} \cdot \nabla v_{\text{xc}}[n](\mathbf{r}, t). \quad (11.13)$$

These conditions are so basic that they are trivially satisfied by any reasonable approximation, including the ALDA, AA, and EXX. Thus they are more useful as detailed checks on a propagation scheme. The correlation contribution to the latter is very small, and makes a very demanding test. But because the energy does not play the same central role as in the ground-state problem (and the action is *not* simply the time-integral of the energy – see Chap. 2), that is all they are used for so far.

11.4.3 Self-Interaction

For any One-Electron System,

$$v_{\text{x}}(\mathbf{r}, t) = - \int d^3r' \frac{n(\mathbf{r}, t')}{|\mathbf{r} - \mathbf{r}'|}, \quad v_{\text{c}}(\mathbf{r}, t) = 0, \quad (N = 1). \quad (11.14)$$

These conditions are automatically satisfied by EXX, but are violated by ALDA, GK, and VK.

11.4.4 Initial State Dependence

There is a simple condition based on the principle that *any* instant along a given density history can be regarded as the initial moment [Maitra 2002b, Maitra 2005a] (see Chap. 4). This follows very naturally from the fact that the time-dependent Schrödinger equation is first order. When applied to both interacting and non-interacting systems, we find:

$$v_{\text{xc}}[n_{t'}, \Psi(t'), \Phi(t')](\mathbf{r}, t) = v_{\text{xc}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) \quad \text{for } t > t', \quad (11.15)$$

This is discussed in much detail in Chap. 4. Here we just mention that any adiabatic approximation, by virtue of its lack of memory and lack of initial-state dependence, automatically satisfies it. Interestingly, although EXX is instantaneous in the orbitals, it will have memory (and so initial-state dependence) as a density functional (when applied to more than two unpolarized electrons).

But this condition provides very difficult tests for any functional with memory. Consider any two known evolutions of an interacting system, which after some time, \tilde{t} , become identical. This result states they must have identical xc potentials at that time and forever after, even though they had different histories before then. An approximate functional with memory is unlikely, in general, to produce such identical potentials.

11.4.5 Coupling-Constant Dependence

Because of the lack of a variational principle for the energy, there is no simple analog of the adiabatic connection formula, (11.4), or definite results as limits are approached, (11.5). But there remains a simple connection between scaling and the coupling constant [Hessler 1999]. For exchange, analogous to (11.1), the relation is linear:

$$v_x[n_\gamma, \Phi_\gamma(0)](\mathbf{r}, t) = \gamma v_x[n, \Phi(0)](\gamma\mathbf{r}, \gamma^2t), \quad (11.16)$$

where $\Phi(0)$ is the initial state of the Kohn-Sham system and, for time-dependent densities,

$$n_\gamma(\mathbf{r}, t) = \gamma^3 n(\gamma\mathbf{r}, \gamma^2t). \quad (11.17)$$

There is no simple correlation scaling, but we can relate the coupling constant to scaling and find, analogous to (11.4):

$$v_c^\lambda[n, \Psi(0), \Phi(0)](\mathbf{r}, t) = \lambda^2 v_c[n_{(1/\lambda)}, \Psi_{(1/\lambda)}(0), \Phi_{(1/\lambda)}(0)](\lambda\mathbf{r}, \lambda^2t), \quad (11.18)$$

where $\Psi(0)$ is the initial state of the interacting system. It seems likely that, taking the limit $\lambda \rightarrow 0$, makes the exchange term dominant for finite systems (just as in the ground-state) [Hessler 2002], but this has yet to be proven.

11.4.6 Translational Invariance

Consider a rigid boost $\mathbf{R}(t)$ of a system starting in its ground state at $t = 0$, with $\mathbf{R}(0) = d\mathbf{R}/dt(0) = 0$. Then the exchange-correlation potential of the boosted density will be that of the unboosted density, evaluated at the boosted point, i.e.,

$$v_{xc}[n'](\mathbf{r}, t) = v_{xc}[n](\mathbf{r} - \mathbf{R}(t), t), \quad n'(\mathbf{r}, t) = n(\mathbf{r} - \mathbf{R}(t), t), \quad (11.19)$$

This condition is universally valid [Vignale 1995a], and played a crucial role in the development of the VK approximation.

11.5 Linear Response

In the special case of linear response, all information is contained in the kernel. All the general conditions of Sect. 11.4 also yield results for the xc kernel.

11.5.1 Adiabatic Limit

For any finite system, the exact kernel satisfies:

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega \rightarrow 0) \rightarrow \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \quad (11.20)$$

where E_{xc} is the exact xc energy. Obviously, any approximate functional satisfies this, with its corresponding ground-state approximation on the right.

11.5.2 Zero Force and Torque

The exact conditions on the potential of Sect. 11.4.2 also yield conditions on f_{xc} , when applied to an infinitesimal perturbation (see Chap. 5). Taking functional derivatives of (11.11a) yields

$$\int d^3r n(\mathbf{r}) \nabla f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\nabla' v_{xc}(\mathbf{r}') \quad (11.21)$$

and

$$\int d^3r n(\mathbf{r}) \mathbf{r} \times \nabla f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\mathbf{r}' \times \nabla' v_{xc}(\mathbf{r}'), \quad (11.22)$$

the latter again assuming no xc transverse currents.

Again, these are satisfied by ground-state DFT with the static xc kernel, so they are automatically satisfied by any adiabatic approximation. Similarly, in the absence of correlation, they hold for EXX.

The equations employing energies do not produce directly useful results in the linear response regime, because the functional derivative of the exact time-dependent xc energy is not the xc potential.

11.5.3 Self-Interaction Error

For one electron, functional differentiation of (11.14) yields:

$$f_x(\mathbf{r}, \mathbf{r}', \omega) = -\frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad f_c(\mathbf{r}, \mathbf{r}', \omega) = 0, \quad (N = 1) \quad (11.23)$$

These conditions are trivially satisfied by EXX, but violated by the density functionals ALDA, GK, and VK.

11.5.4 Initial-State Dependence

The initial-state condition, (11.15), leads to very interesting restrictions on f_{xc} for arbitrary densities. But the information is given in terms of the initial-state dependence, which is very difficult to find.

11.5.5 Coupling-Constant Dependence

The exchange kernel scales linearly with coordinates, as found by differentiating (11.16):

$$f_x[n_\gamma](\mathbf{r}, \mathbf{r}', \omega) = \gamma f_x[n](\gamma\mathbf{r}, \gamma\mathbf{r}', \omega/\gamma^2). \quad (11.24)$$

A functional derivative and Fourier-transform of (11.18) yields [Lein 2000b]

$$f_c^\lambda[n_{GS}](\mathbf{r}, \mathbf{r}', \omega) = \lambda^2 f_c[n_{0,(1/\lambda)}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2). \quad (11.25)$$

A similar condition has recently been derived for the coupling-constant dependence of the vector potential in TDCDFT [Dion 2005].

These conditions are trivial for EXX. They can be used to test the derivations of correlation approximations in cases where the coupling-constant dependence can be easily deduced. More often, they can be used to *generate* the coupling constant dependence when needed, such as in the adiabatic connection formula of (11.4).

11.5.6 Symmetry

Because the susceptibility is symmetric, so must also be the kernel:

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}', \mathbf{r}, \omega). \quad (11.26)$$

This innocuous looking condition is satisfied by any adiabatic approximation by virtue of the kernel being the second derivative of an energy, and is obviously satisfied by EXX.

11.5.7 Kramers-Kronig

The kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ is an analytic function of ω in the upper half of the complex ω -plane and approaches a real function $f_{xc}(\mathbf{r}, \mathbf{r}', \infty)$ for $\omega \rightarrow \infty$. Therefore, defining the function

$$\Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - f_{xc}(\mathbf{r}, \mathbf{r}', \infty), \quad (11.27)$$

we find

$$\Re \Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega} \quad (11.28)$$

$$\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Re \Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega}, \quad (11.29)$$

where \mathbb{P} denotes the principal part of the integral. Also, since $f_{xc}(\mathbf{x}, \mathbf{x}')$ is real-valued,

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}^*(\mathbf{r}, \mathbf{r}', -\omega). \quad (11.30)$$

The simple lesson here is that any adiabatic kernel (no frequency dependence) is purely real, and any kernel with memory has an imaginary part (or else is not sensible). Putting it the other way round, to produce a complex kernel requires memory.

Thus, any adiabatic approximation must have a real kernel, which they do. And EXX, to the extent that it has any frequency-dependence (for more than 2 electrons), must have a complex kernel. Both GK and VK have complex kernels satisfying these conditions.

11.5.8 Adiabatic Connection

A beautiful condition on the exact xc kernel is given simply by the adiabatic connection formula for the ground-state correlation energy:

$$-\frac{1}{2} \int d^3r \int d^3r' v_{ee}(\mathbf{r}', \mathbf{r}) \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{\pi} [\chi_\lambda(\mathbf{r}, \mathbf{r}', i\omega) - \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', i\omega)] = E_c \quad (11.31)$$

Combined with the Dyson-like equation of Chap. 1 for χ_λ as a function of χ_{KS} and f_{xc} , this is being used to generate new and useful approximations to the ground-state correlation energy (see Chaps. 28, 29 and 30), although at considerable computational cost.

But it provides an obvious exact condition on any approximate xc kernel for *any* system. Thus *every* system for which the correlation energy is known can be used to test approximations for f_{xc} . Note that, e.g., using ALDA for the kernel does *not* yield the corresponding $E_{\text{xc}}^{\text{LDA}}$, but rather a much more sophisticated functional. Even insertion of f_{x} yields correlation contributions to all orders in E_c . And lastly, even the exact adiabatic approximation, $f_{\text{xc}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', \omega = 0)$, does not yield the exact $E_{\text{xc}}[n_{\text{GS}}]$. In Chap. 28, this condition is used to test several approximations, but only for the uniform gas.

11.6 Finite Versus Extended Systems, and Currents

As mentioned in Sect. 11.2.4, care must be taken when extending exact ground-state DFT results to extended systems. This is even more the case for TDDFT. The first half of the RG theorem (Chap. 1) provides a one-to-one correspondence between potentials and *current* densities, but a surface condition must be invoked to produce the necessary correspondence with densities. With hindsight, this is very suggestive that time-dependent functionals may contain a non-local dependence on the details at a surface. As such, they are more amenable to local approximations in the current rather than the density.

As discussed elsewhere (Chap. 5) and first pointed out by Dobson [Dobson 1994a], the frequency-dependent LDA (GK approximation) violates the translational invariance condition of Sect. 11.4.6. One can trace this failure back to the non-locality of the xc functional in TDDFT. But, by going to a current formulation, everything once again becomes reasonable. The gradient expansion in the current, for a slowly varying gas, was first derived by Vignale and Kohn [Vignale 1996], and later simplified by Vignale, Ullrich, and Conti [Vignale 1997], and is discussed in much detail in Chap. 5.

For our purposes, the most important point is that, by construction, VK satisfies translational invariance. The frequency-dependence shuts off (it reduces to ALDA) when the motion is a rigid translation, but turns on when there is a true (non-translational) motion of the density [Vignale 1996].

11.6.1 Gradient Expansion in the Current

Any functional with memory should recover the VK gradient expansion in this limit, or justify why it does not. However, the VK approximation is *only* the gradient expansion. In the ground-state, the gradient expansion in the density was found to give poor results, and afterwards discovered to violate several important sum rules [Burke 1998a]. Fixing those sum-rules led to the development of generalized gradient approximations.

11.6.2 Response to Homogeneous Field

A decade ago, GGG [Gonze 1995b] caused a stir by pointing out that the periodic density in an insulating solid in an electric field is insufficient to determine the one-body potential, in apparent violation of the Hohenberg-Kohn theorem [Hohenberg 1964]. In fact, this effect appears straightforwardly in TDCDFT, and is even estimated by calculations using the VK approximation [van Faassen 2003a, Maitra 2003a]. When translated back to TDDFT language, one finds a $1/q^2$ dependence in f_{xc} , where q is the wavevector corresponding to $\mathbf{r} - \mathbf{r}'$ (see Chaps. 10 and 20). Thus this effect arises naturally in the static limit of TDCDFT (see Chaps. 5 and 19).

However, it implies a need for a kernel that has the same degree of non-locality as the Hartree kernel, and this is missed by any local or semilocal approximation, such as ALDA, but *is* built in to EXX [Kim 2002a] or AA and many-body derived kernels (see Chap. 10).

11.7 Odds and Ends

11.7.1 Functional Derivatives

A TDDFT result ought to come from a TDDFT calculation, but this is not always the case. By a TDDFT calculation, we mean the result of an evolution of the TDKS equations with some approximation for the xc potential that is a functional of the density. This implies that the xc kernel should be the functional derivative of some xc potential, which also reduces to the ground-state potential in the adiabatic limit.

All the approximations discussed here satisfy this rule. But calculations that intermix kernels with potentials in the solution of Casida's equations violate this condition, and run the risk of violating underlying sum-rules.

11.7.2 Infinite Lifetimes of Eigenstates

This may seem like an odd requirement. When TDDFT is applied to calculate a transition to an excited state, the frequency should be real. This is obviously true for ALDA and EXX, but not so clear when memory approximations are

used. As shown in Sect. 11.5.7, Kramers-Kronig relations mean that memory implies imaginary xc kernels, and these can yield imaginary contributions to the transition frequencies. Exactly these effects were seen in calculations using the VUC for atomic transitions [Ullrich 2004]. Indeed, very long lifetimes were found when VUC was working well, and much shorter ones occurred when VUC was failing badly.

11.7.3 Single-Pole Approximation for Exchange

This is another odd condition, in which two wrongs make something right. Using Görling-Levy perturbation theory [Görling 1993a], one can calculate the exact exchange contributions to excited state energies [Filippi 1997, Zhang 2004a]. To recover these results using TDDFT, one does *not* simply use f_x , and solve the Dyson-like equations. As noted in Sect. 11.5.8, the infinite iteration yields contributions to all orders in the coupling constant.

However, the single-pole approximation (SPA) truncates this series after one iteration, and so drops all other orders. Thus, the correct exact exchange results are recovered in TDDFT from the SPA solution to Casida's equations, and *not* by a full solution [Gonze 1999]. This procedure can be extended to the next order [Appel 2003].

11.8 Memory Correlation Approximations

The first approximation that went beyond adiabatic is the Gross-Kohn approximation, as mentioned above, which was replaced by the VK approximation, when it was realized that it violated translational invariance.

11.8.1 Double Excitations and Branch Cuts

Maitra et al. [Maitra 2004, Cave 2004] argued that a strong ω -dependence in f_{xc} allows double excitation solutions to Casida's equations. Similarly, the second ionization of the He atom implies a branch cut in its f_{xc} at the frequency needed [Burke 2005a]. Under limited circumstances, this frequency dependence can be estimated, but a generalization [Casida 2005] has been proposed. It would be interesting to check its compliance with the conditions listed in this chapter.

11.8.2 Beyond Linear Response

A major point of interest is to go beyond the linear response regime for non-adiabatic approximations. The first such attempt was the bootstrap approach of [Dobson 1997]. More recent attempts are described in Chap. 8 and in [Kurzweil 2004].

11.9 Summary

What lessons can we take away from this brief survey?

1. In the ground-state theory, the xc energy dominates, and many conditions are proven for that functional. This is not so for TDDFT.
2. The adiabatic approximation satisfies many exact conditions by virtue of its lack of memory. Inclusion of memory may lead to violations of conditions that adiabatic approximations satisfy. This is reminiscent of the ground-state problem, where the gradient expansion approximation violates several key sum rules respected by the local approximation. Explicit imposition of those rules led to the development of generalized gradient approximations.
3. Explicit density functionals have poor quality potentials, but it is the time-dependent density that counts. The potential is a far more sensitive functional of the density than vice versa. Thus, while we have enumerated many conditions on the xc potential, it is important to determine which conditions significantly affect the density.

As shown in several chapters in this book, many people are presently testing the limits of our simple approximations, and very likely, these or other exact conditions will provide guidance on how to go beyond them.

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