Exact conditions and their relevance in TDDFT*

Lucas O. Wagner,[†] Zeng-hui Yang, and Kieron Burke
Department of Physics and Astronomy
and Department of Chemistry,
University of California, Irvine, CA 92697, USA

CONTENTS

I. INTRODUCTION

This chapter is devoted to exact conditions in time-dependent density functional theory. Many conditions have been derived for the exact ground-state density functional, and several have played crucial roles in the construction of popular approximations. We believe that the reliability of the most fundamental approximation of any density functional theory, the local density approximation (LDA), is due to the exact conditions that it satisfies. Improved approximations should satisfy at least those conditions that LDA satisfies, plus others. (Which others is part of the art of functional approximation).

In the time-dependent case, as we shall see, the adiabatic LDA (ALDA) plays the same role as LDA in the ground-state case, as it satisfies many exact conditions. But we do not have a generally applicable improvement beyond ALDA that includes nonlocality in time. For TDDFT, we have a surfeit of exact conditions, but that only makes finding those that are useful to impose an even more demanding task.

Throughout this chapter, we give formulas for pure DFT for the sake of simplicity (e.g., $E_{\rm xc}[n]$), but in practice *spin* DFT is used (e.g. $E_{\rm xc}[n_\uparrow, n_\downarrow]$). We use atomic units everywhere ($e^2 = \hbar = m_{\rm e} = 1$), so energies are in units of Hartrees and distances are in Bohrs.

II. REVIEW OF THE GROUND STATE

In ground-state DFT, the unknown exchange-correlation energy functional, $E_{\rm xc}[n]$, plays a crucial role. In fact, it is 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 within the Born-Oppenheimer approximation. In this way we can extract the bond lengths and angles of molecules and deduce the lowest energy lattice structure of solids. We can also extract forces in simulations, and vibrational frequencies and phonons and bulk moduli. We can 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.

In this section we will 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 also refer the interested

---

* **Appearing in:**
Fundamentals of Time-Dependent Density Functional Theory, edited by M. Marques, *et al.* (Springer, 2012).
† lwagner@uci.edu

reader to [1] for a thorough discussion. First, we will go over some of the formal definitions in DFT.

II.1. Basic definitions

The xc energy as a functional of the density is written as [2, 3]

$$E_{\rm xc}[n] = \min_{\Psi\to n} \langle\Psi|\,\hat{T}+\hat{V}_{\rm ee}\,|\Psi\rangle - T_{\rm KS}[n] - E_{\rm H}[n]\,, \quad (1)$$

where Ψ is a correctly antisymmetrized electron wavefunction, the minimization of the kinetic and electron-electron repulsion energies is done over all such wavefunctions that yield the density $n(\boldsymbol{r})$, $T_{\rm KS}[n]$ is the minimum (non-interacting) kinetic energy of a system with density $n(\boldsymbol{r})$, and

$$E_{\rm H}[n] = \frac{1}{2}\int d^3r \int d^3r'\, \frac{n(\boldsymbol{r})\,n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \quad (2)$$

is the Hartree energy. The xc energy is usually split into an exchange piece, $E_{\rm x}$, and a correlation piece, $E_{\rm c} \equiv E_{\rm xc} - E_{\rm x}$. Exchange can be defined in a Hartree-Fock-like way in terms of the KS spin orbitals $\varphi_{i\sigma}(\boldsymbol{r})$:

$$E_{\rm x}[n] = -\frac{1}{2}\sum_{i,j,\sigma}^{\rm occ} \int d^3r \int d^3r'\, \frac{\varphi^*_{i\sigma}(\boldsymbol{r})\,\varphi^*_{j\sigma}(\boldsymbol{r}')\,\varphi_{i\sigma}(\boldsymbol{r}')\,\varphi_{j\sigma}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\,. \quad (3)$$

To perform the self-consistent calculations in the non-interacting system, we need the functional derivative of the xc energy,

$$v_{\rm xc}[n](\boldsymbol{r}) = \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})}\,. \quad (4)$$

This is called the xc potential, and it is the essential part of the multiplicative KS potential $v_{\rm KS}[n](\boldsymbol{r})$.

Orbital-dependent functionals: Some functionals are most naturally expressed in terms of the orbitals rather than the density. When varying the orbitals of these functionals, *nonlocal* potentials are obtained. For example, varying $\varphi_{i\sigma}$ in Eq. (3) leads to the nonlocal exchange term used in HF. There is a way to transform such orbital-dependent functionals into local potentials as in Eq. (4). This procedure is known as optimized effective potential (OEP) or optimized potential method (OPM) and is computationally expensive [4]. Using OEP for $E_{\rm x}$ results in the exact exchange approximation (EXX) for $E_{\rm xc}$ in KS-DFT. The Krieger, Li, and Iafrate (KLI) approximation is a way to approximately solve EXX [5]. An in-depth discussion of orbital-dependent functionals is found in Kümmel's Chapter 6.

Adiabatic connection: One can imagine smoothly connecting the interacting and non-interacting systems by multiplying the electron-electron repulsion term by λ, called the coupling-constant. Changing λ varies the strength of the interaction, and if we simultaneously change the external potential to keep the density fixed, we have a family of solutions for various interaction strengths. This makes all quantities (besides the density) functions of λ. When $\lambda = 0$, one has the non-interacting KS system, and when $\lambda = 1$, one has the fully interacting system. The following coupling-constant relations hold [1]:

- **xc energy λ dependence:** Altering the coupling-constant is simply related to scaling the density:

$$E^{\lambda}_{\rm xc}[n] = \lambda^2 E_{\rm xc}[n_{1/\lambda}]\,, \quad (5)$$

where $n_{1/\lambda}(\boldsymbol{r})$ is the scaled density

$$n_\gamma(\boldsymbol{r}) \equiv \gamma^3\, n(\gamma\boldsymbol{r})\,, \quad (6)$$

with $\gamma = 1/\lambda$.

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

$$E_{\rm xc}[n] = \int_0^1 \frac{d\lambda}{\lambda}\, U^{\lambda}_{\rm xc}[n]\,, \quad (7)$$

where $U^{\lambda}_{\rm xc}$ is the potential contribution to exchange-correlation energy ($U_{\rm xc} = V_{\rm ee} - E_{\rm H}$) at coupling-constant λ.

II.2. Standard approximations

Despite a plethora of approximations [6], no present-day approximation satisfies all the conditions mentioned in this chapter, as seen in tests on bulk solids and surfaces [7]. With that the case, one must choose which conditions to impose on a given approximate form. Non-empirical (ab initio) approaches attempt to fix all parameters via exact conditions [8, 9], while good empirical approaches might include one or two parameters that are fit to some data set [10–12].

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 [13], which meet the finite-system conditions more naturally. The most sophisticated approximations being developed today use both [14]. For a good discussion on what approximation is the right tool for the job, see [15].

- **LDA:** The local density approximation is the bread and butter of DFT. It is the simplest, being derived from conditions on the uniform gas [16]. Though it is too inaccurate for quantum chemistry (being off by about 1 eV or 30 kcal/mol), it is useful in solids and other bulk materials where the electrons almost look like a uniform gas. There can be only one LDA.

- **GGA:** The generalized gradient approximation came from trial and error when energies were allowed to depend on the gradient of the density. While more accurate than the LDA (getting errors down to 5 or 6 kcal/mol), and thus useful for quantum chemistry applications, there is no uniquely-defined GGA. BLYP is an empirical GGA that was designed to minimize the error in a particular data set. PBE is a non-empirical GGA designed to satisfy exact conditions.

- **Hybrid:** Hybrids have an exchange energy which is a mixture of GGA and HF, which attempts to get the best of both worlds:

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = E_{\mathrm{xc}}^{\mathrm{GGA}} + a\,(E_{\mathrm{x}} - E_{\mathrm{x}}^{\mathrm{GGA}})\,, \tag{8}$$

where E_{x} is defined in (3). The parameter a was argued to be 0.25 for the non-empirical PBE0, but is fitted for the empirical B3LYP.

II.3. Finite systems

The following conditions are derived for finite systems, just as the Hohenberg-Kohn theorem is. This list is by no means exhaustive; it is only meant to give an idea of some of the simpler and more useful conditions in ground-state DFT. As we will see, many of these conditions have analogs in TDDFT.

- **Signs of energy components:** From the variational principle and other elementary considerations, one can deduce

$$E_{\mathrm{xc}}[n] \le 0\,, \qquad E_{\mathrm{c}}[n] \le 0\,, \qquad E_{\mathrm{x}}[n] \le 0\,. \tag{9}$$

- **Zero xc force and torque theorem:** The xc potential cannot exert a net force or torque on the electrons [17]:

$$\int d^3r\, n(\boldsymbol{r})\, \nabla v_{\mathrm{xc}}(\boldsymbol{r}) = 0 \tag{10a}$$

$$\int d^3r\, n(\boldsymbol{r})\, \boldsymbol{r} \times \nabla v_{\mathrm{xc}}(\boldsymbol{r}) = 0\,. \tag{10b}$$

- **xc virial theorem:**

$$E_{\mathrm{xc}}[n] + T_{\mathrm{c}}[n] = -\int d^3r\, n(\boldsymbol{r})\, \boldsymbol{r}\cdot\nabla v_{\mathrm{xc}}(\boldsymbol{r})\,, \tag{11}$$

where $T_{\mathrm{c}} = T - T_{\mathrm{KS}}$ is the kinetic contribution to the correlation energy. The xc virial theorem as well as the zero xc force and torque theorem are satisfied by all sensible approximate functionals.

- **Exchange scaling:** By using the scaled density (6), one can easily show

$$E_{\mathrm{x}}[n_\gamma] = \gamma\, E_{\mathrm{x}}[n]\,. \tag{12}$$

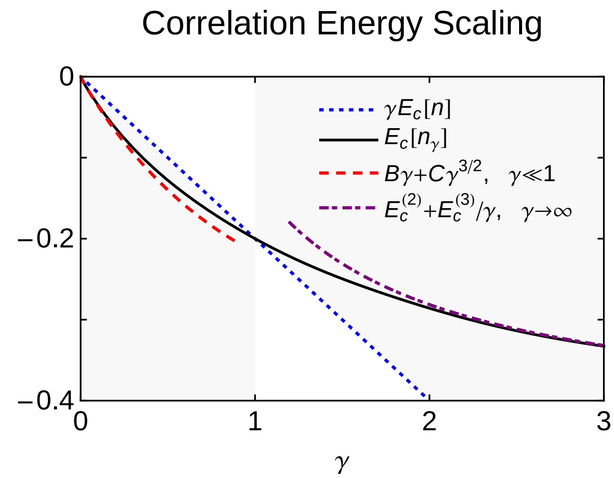

FIG. 1. Scaling of the correlation energy in ground state DFT, as well as the various conditions from Eq. (14). The first two relations are illustrated with the dotted line. For $\gamma < 1$, the exact curve (solid) must lie below this dotted line, and for $\gamma > 1$ the exact curve must lie above — in both cases within the shaded region of the graph. The high density limit is shown with the dot-dashed line, and the low density limit with the dashed line. It is believed that not only is $E_{\mathrm{c}}[n_\gamma]$ monotonic, but also its derivative with respect to γ.

- **Correlation scaling:** The scaling of correlation is less simple than exchange, and will depend on whether one is in the high density limit (γ large) or low density limit (γ small) [17, 18]:

$$E_{\mathrm{c}}[n_\gamma] < \gamma\, E_{\mathrm{c}}[n] \qquad (\gamma < 1) \tag{13a}$$

$$E_{\mathrm{c}}[n_\gamma] > \gamma\, E_{\mathrm{c}}[n] \qquad (\gamma > 1)\,. \tag{13b}$$

It is also possible to derive the following results

$$E_{\mathrm{c}}[n_\gamma] = E_{\mathrm{c}}^{(2)}[n] + E_{\mathrm{c}}^{(3)}[n]/\gamma + \cdots \qquad (\gamma \to \infty) \tag{14a}$$

$$E_{\mathrm{c}}[n_\gamma] = \gamma B[n] + \gamma^{3/2} C[n] + \cdots \qquad (\gamma \to 0)\,, \tag{14b}$$

where $E_{\mathrm{c}}^{(2)}[n]$, $E_{\mathrm{c}}^{(3)}[n]$, $B[n]$, and $C[n]$ are all scale-invariant functionals. These conditions are depicted in Fig. 1. Not all popular approximations satisfy these conditions.

- **Self-interaction:** For any one-electron system [19],

$$E_{\mathrm{x}}[n] = -E_{\mathrm{H}}[n], \qquad E_{\mathrm{c}} = 0 \qquad (N = 1)\,. \tag{15}$$

- **Lieb-Oxford bound:** For any density [20],

$$E_{\mathrm{xc}}[n] \ge 2.273\; E_{\mathrm{x}}^{\mathrm{LDA}}[n]\,. \tag{16}$$

In addition to conditions on E_{xc}, we also know some exact conditions on the xc potential and the KS eigenvalues.

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

$$v_{\rm xc}(\boldsymbol{r}) \to -1/r \qquad (r\to\infty)\,, \tag{17}$$

and

$$\varepsilon_{\rm HOMO} = -I\,, \tag{18}$$

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

II.4. Extended systems

The basic theorems of DFT (as discussed in the previous section) are proven for *finite* quantum mechanical systems, with densities that decay exponentially 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 in Eq. (14) of the correlation energy for a finite system is violated by a uniform gas. With these things in mind, we will now discuss a set of conditions that involve the properties of the uniform or nearly uniform electron gas.

- **Uniform density:** When the density is uniform, $E_{\rm xc} = n\, e_{\rm xc}^{\rm unif}(n)\,\mathcal{V}$, where $e_{\rm xc}^{\rm unif}(n)$ is the xc energy density per particle of a uniform electron gas of density n, and $\mathcal{V}$ is the volume. This forms the basis of LDA.

- **Slowly varying density:** For slowly varying densities, $E_{\rm xc}$ should recover the gradient expansion approximation (GEA):

$$\begin{aligned} E_{\rm xc}[n] &= \int d^3r\, n\, e_{\rm xc}^{\rm unif}(n) + \int d^3r\, n\, \Delta e_{\rm xc}^{\rm GEA}(n,\nabla n) + \cdots \\ &= E_{\rm xc}^{\rm LDA}[n] + \Delta E_{\rm xc}^{\rm GEA}[n] + \cdots\,, \end{aligned} \tag{19}$$

where $\Delta e_{\rm xc}^{\rm GEA}(n,\nabla n)$ is the leading correction to the LDA xc energy density for a slowly varying electron gas [21]. However, the GEA was found to give poor results and violate several important sum rules for the xc hole when applied to other systems [22]. Fixing those sum-rules led to the development of ab initio GGAs. Though important in obtaining the energy for the ground-state, the xc hole rules have not been used in TDDFT and therefore will not be further discussed in this chapter.

- **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 [23], and approximations can be tested against it.

III. OVERVIEW FOR TDDFT

The time-dependent problem is more complex 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 $v_{\rm xc}[n](\boldsymbol{r},t)$ 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.

In the time-dependent problem, the energy does not play a central role. Formally, the action plays an analogous role (see Chapter 9), but in practice, we never evaluate the action in TDDFT calculations (and 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.

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 real space, such as the energy. Thus approximations that work well for ground-state energies are sometimes very poor as adiabatic approximations in TDDFT. Their failure to satisfy Eq. (17) leads to large errors in the KS energies of higher-lying orbitals (for example, consider the LDA potential for Helium in Fig. 4.3 of Chapter 4, which falls off exponentially rather than as $-1/r$), and (18) is often violated by several eV.

In place of the energy, there are a variety of physical properties that people wish to calculate. For example, quantum chemists are most often focused on the 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. At the other extreme, people who study matter in strong laser fields are often focused on ionization probabilities (see Chapter 18), and there the violation of Eq. (18) makes explicit density approximations too crude, and requires orbital-dependent approximations instead.

III.1. Definitions

In this section, we remind our readers of some of the basics from Chapter 4, the building blocks from which the exact conditions in TDDFT are proved. In contrast to the ground-state problem, the xc potential depends not only on the density but on the initial wavefunction

$\Psi(0)$ and KS Slater determinant $\Phi(0)$, written symbolically as $v_{\rm xc}[n;\Psi(0),\Phi(0)](\boldsymbol{r},t)$. This more complicated dependence comes about because two different wavefunctions, which are chosen to have the same density for all time, can come from completely different external potentials, which the xc potential accounts for. We can get rid of this initial wavefunction dependence if we start from a non-degenerate ground-state, where the wavefunction is a functional of the density alone, via the Hohenberg-Kohn theorem [24]. These things are further discussed in Chapter 8.

As the density evolves, the xc potential is determined not solely by the present density $n(\boldsymbol{r},t)$, but also by the history $n(\boldsymbol{r},t')$ for $0 \le t' < t$. However, it is useful to break the xc potential up into two pieces, an *adiabatic* piece which only deals with the present density, and a *dynamic* piece which incorporates the memory dependence:

$$v_{\rm xc}[n;\Psi(0),\Phi(0)](\boldsymbol{r}t) = v_{\rm xc}^{\rm dyn}[n;\Psi(0),\Phi(0)](\boldsymbol{r}t) + v_{\rm xc}^{\rm adia}[n](\boldsymbol{r}t). \tag{20}$$

The adiabatic piece of the potential,

$$v_{\rm xc}^{\rm adia}[n](\boldsymbol{r},t) = \left.\frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})}\right|_{n(t)}, \tag{21}$$

is the xc potential for electrons as if their instantaneous density were a ground state. In the spirit of DFT, the dynamic piece is everything else.

In the linear response regime, small enough perturbations to the density will continuously change the xc potential:

$$v_{\rm xc}[n+\delta n](\boldsymbol{r}t) - v_{\rm xc}[n](\boldsymbol{r}t) = \int dt' \int d^3r'\, f_{\rm xc}[n](\boldsymbol{r},\boldsymbol{r}';t,t')\,\delta n(\boldsymbol{r}'t'), \tag{22}$$

where $f_{\rm xc}$ is the xc kernel, which can be written formally as the functional derivative:

$$f_{\rm xc}[n_0](\boldsymbol{r}t,\boldsymbol{r}'t') = \left.\frac{\delta v_{\rm xc}[n](\boldsymbol{r},t)}{\delta n(\boldsymbol{r}',t')}\right|_{n_0}. \tag{23}$$

The evaluation at n_0 reminds us that $f_{\rm xc}$ is used for the linear response of a density variation away from a ground-state density n_0.

Like the xc potential, the kernel can also be broken down into an adiabatic piece:

$$f_{\rm xc}^{\rm adia}(\boldsymbol{r}t,\boldsymbol{r}'t') = \left.\frac{\delta^2 E_{\rm xc}[n]}{\delta n(\boldsymbol{r})\,\delta n(\boldsymbol{r}')}\right|_{n(t)} \delta(t-t'), \tag{24}$$

and a dynamic piece, which includes memory and everything else. The kernel is often Fourier-transformed from position space in the relative coordinate $(\boldsymbol{r}-\boldsymbol{r}')$ to momentum space (with wave-vector $\boldsymbol{q}$), from the relative time $(t-t')$ to frequency (ω) domain, or both. Some conditions are more naturally expressed in momentum space and/or in the frequency domain. In the frequency domain, the adiabatic piece can be written as

$$f_{\rm xc}^{\rm adia}(\boldsymbol{r},\boldsymbol{r}') = \lim_{\omega\to 0} f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}';\omega). \tag{25}$$

The kernel is discussed in more detail in Chapter 4.

III.2. Approximations

As we go through the various exact conditions, we will discuss whether the simplest approximations in present use satisfy them. We can divide all approximations into two classes based on whether or not the approximation neglects the dynamic term of Eq. (20); these classes are respectively adiabatic and non-adiabatic (i.e. memory) approximations. In the adiabatic approximation, familiar ground-state functionals (such as LDA, GGA, and hybrids) can produce xc potentials when one uses the approximate $E_{\rm xc}$ in Eq. (21). We mention two notable adiabatic approximations now.

- **ALDA:** The prototype of all TDDFT approximations is the adiabatic local density approximation, and it is the simplest pure density functional. The xc potential is as simple as can be:

$$v_{\rm xc}^{\rm ALDA}[n](\boldsymbol{r},t) = \left.\frac{d\left[n\, e_{\rm xc}^{\rm unif}(n)\right]}{dn}\right|_{n(\boldsymbol{r},t)}. \tag{26}$$

  In linear response, the ALDA kernel is

$$f_{\rm xc}^{\rm ALDA}(\boldsymbol{r}t,\boldsymbol{r}'t') = \left.\frac{d^2\left[n\, e_{\rm xc}^{\rm unif}(n)\right]}{dn^2}\right|_{n(\boldsymbol{r},t)} \delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t-t'). \tag{27}$$

  Like its ground-state inspiration, ALDA satisfies important sum rules by virtue of its simplicity, namely its locality in space and time. ALDA is commonly used in many calculations, and is described further in Chapter 4.

- **AA:** In the 'exact' adiabatic approximation, we use the exact $E_{\rm xc}$ in Eq. (21). This approximation is the best that an adiabatic approximation can do, unless there is some lucky cancellation of errors. Hessler *et al.* [25] investigated AA applied to a time-dependent Hooke's atom system and found large errors in the instantaneous correlation energy. For the double ionization of a model Helium atom, Thiele *et al.* [26] discovered that non-adiabatic effects were important only for high-frequency fields.

A key aim of today's methodological development is to build in correlation memory effects. Any attempt to build in memory goes beyond the adiabatic approximation, and thus belongs in the non-adiabatic class of approximations. The next three approximations belong to this dynamic class.

- **GK:** The Gross-Kohn approximation is simply to use the local frequency-dependent kernel of the uniform gas,

$$f_{\rm xc}^{\rm GK}(\boldsymbol{r},\boldsymbol{r}';\omega) = \delta(\boldsymbol{r}-\boldsymbol{r}')\, f_{\rm xc}^{\rm unif}(n(\boldsymbol{r});\omega), \tag{28}$$

  where

$$f_{\rm xc}^{\rm unif}(n;\omega) \equiv \lim_{q\to 0} f_{\rm xc}^{\rm unif}(n;q,\omega) \tag{29}$$

is the response of the uniform electron gas with density n. GK was the first approximation to go beyond the adiabatic approximation, but was found to violate translational invariance (see Sect. IV.6).

- **VK:** The Vignale-Kohn approximation sought to improve upon the shortcomings of GK. The VK approximation is simply the gradient expansion in the current density for a slowly-varying gas (see Chapter 24).

- **EXX:** Exact exchange, the orbital-dependent functional, is treated as an implicit density functional (see Chapter 6). When treated this way, EXX has some memory for more than two unpolarized electrons.

With the exception of EXX, non-adiabatic approximations are usually limited to the linear response regime and approximate the kernel, $f_{\rm xc}$. There is now a major push to go beyond linear response for non-adiabatic approximations. The first such attempt was a bootstrap approach of [27]. More recent attempts are described in Chapter 25 of this book and in [28].

IV. GENERAL CONDITIONS

In this section, we discuss conditions that apply no matter how strong or how weak the time-dependent potential is. They apply to anything: weak fields, strong laser pulses, and everything in between. They apply also to the linear response regime, yielding the more specific conditions discussed in Sect. V.

IV.1. Adiabatic limit

One of the simplest exact conditions 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. This is the adiabatic theorem of quantum mechanics, which can be proven 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.

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

$$v_{\rm xc}(\boldsymbol{r},t) \to v_{\rm xc}[n(t)](\boldsymbol{r})\,, \qquad (\tau\to\infty) \tag{30}$$

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

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

IV.2. Equations of motion

In this section, we discuss some elementary conditions that any reasonable TDDFT approximation should satisfy. Because these conditions are satisfied by almost all approximations, they are best applied to test the quality of propagation schemes. For a scheme that does not automatically satisfy a given condition, then a numerical check of its error provides a test of 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 equation 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 the Chapter 24 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 [29, 30]:

$$\int d^3r\, n(\boldsymbol{r},t)\, \nabla v_{\rm xc}(\boldsymbol{r},t) = 0 \tag{31a}$$

$$\int d^3r\, n(\boldsymbol{r},t)\, \boldsymbol{r}\times\nabla v_{\rm xc}(\boldsymbol{r},t) = \int d^3r\, \boldsymbol{r}\times\frac{\partial \boldsymbol{j}_{\rm xc}(\boldsymbol{r},t)}{\partial t}, \tag{31b}$$

where $\boldsymbol{j}_{\rm xc}(\boldsymbol{r},t)$ is the difference between the interacting current density and the KS current density [31]. 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), as discussed in Sect. 4.4.4 of Chapter 4. The exchange-only KLI approximation, though incredibly accurate for ground state DFT, was found to violate the zero-force condition [32]. This is because KLI is not a solution to an approximate variational problem, but instead an approximate solution to the OEP equations. This means KLI also violates the virial theorem [33], which we describe next.

xc power and virial: By applying the same methodology to the equation of motion for the Hamiltonian, we find [34]:

$$\int d^3r\, \frac{dn(\boldsymbol{r},t)}{dt}\; v_{\rm xc}(\boldsymbol{r},t) = \frac{dE_{\rm xc}}{dt}\,. \tag{32}$$

while another equation of motion yields the virial theorem, which intriguingly has the exact same form as in the ground state, Eq. (11):

$$-\int d^3r\, n(\boldsymbol{r},t)\; \boldsymbol{r}\cdot\nabla v_{\rm xc}[n](\boldsymbol{r},t) = E_{\rm xc}[n](t) + T_{\rm c}[n](t)\,. \tag{33}$$

These conditions are so basic that they are trivially satisfied by any reasonable approximation, including ALDA, AA, and EXX. Thus they are more useful as detailed checks on a propagation scheme, as mentioned earlier. The correlation contribution to Eq. (33) is very small, and makes for 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 Chapter 9), testing the propagation scheme is all they are used for so far.

IV.3. Self-interaction

For any one-electron system,

$$v_{\rm x}(\boldsymbol{r},t) = -\int d^3r'\, \frac{n(\boldsymbol{r},t)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,, \qquad v_{\rm c}(\boldsymbol{r},t) = 0 \qquad (N=1)\,, \tag{34}$$

These conditions are automatically satisfied by EXX. These conditions are instantaneous in time, so any adiabatic approximation that satisfies the ground-state conditions of Eq. (15) will also satisfy these time-dependent conditions, e.g. AA. On the other hand, LDA violates self-interaction conditions in the ground-state, so ALDA also violates these conditions in TDDFT.

IV.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 [35, 36]. This follows very naturally from the fact that the Schrödinger equation is first order in time. When applied to both interacting and non-interacting systems, we find:

$$v_{\rm xc}[n;\Psi(t'),\Phi(t')](\boldsymbol{r},t) = v_{\rm xc}[n;\Psi(0),\Phi(0)](\boldsymbol{r},t) \quad \text{for } t>t'\,, \tag{35}$$

This is discussed in much detail in Chapter 8. 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 has memory (and so initial-state dependence) as a density functional (when applied to more than two unpolarized electrons).

This condition provides very difficult tests for any functional with memory. Consider any two evolutions of an interacting system, whose wavefunctions Ψ and Ψ' become equal after some time, t_c. This condition requires that the non-interacting systems have identical xc potentials at that time and forever after, even though they had different histories before then. This is illustrated in Fig. 2. An approximate functional with memory is unlikely, in general, to produce such identical potentials.

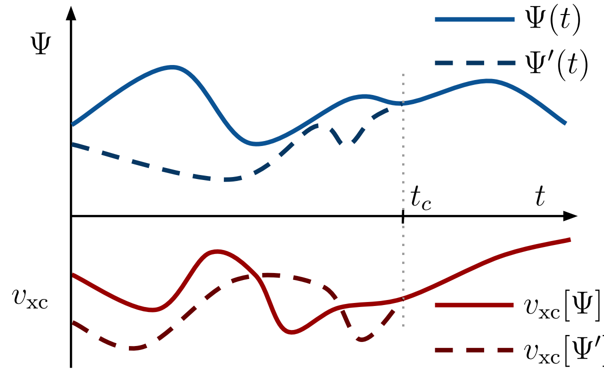

FIG. 2. An illustration of the condition based on initial state dependence. The two wavefunctions Ψ and Ψ' become equal at time t_c, and therefore the KS potentials must become equal then and forever after.

IV.5. Coupling-constant dependence

Because of the lack of a variational principle for the energy, there are no definite results for various limits, as in Eq. (14), nor is there a simple extension of the adiabatic connection formula (7), though Görling proposed an analog for time-dependent systems [37]. But there remains a simple connection between scaling and the coupling-constant for the xc potential [34]. For exchange, analogous to Eq. (12), the relation is linear:

$$v_{\rm x}[n_\gamma;\Phi_\gamma(0)](\boldsymbol{r}t) = \gamma\, v_{\rm x}[n;\Phi(0)](\gamma\boldsymbol{r},\gamma^2 t)\,, \tag{36}$$

where

$$\Phi_\gamma(0) \equiv \gamma^{3N/2}\,\Phi(\gamma\boldsymbol{r}_1,\ldots,\gamma\boldsymbol{r}_N;\, t=0) \tag{37}$$

is the normalized initial state of the Kohn-Sham system with coordinates scaled by γ, and, for time-dependent densities,

$$n_\gamma(\boldsymbol{r},t) \equiv \gamma^3\, n(\gamma\boldsymbol{r},\gamma^2 t)\,. \tag{38}$$

Though there is no simple expression for correlation scaling, we can relate it to the coupling-constant and find, analogous to Eq. (7):

$$v_{\rm C}^\lambda[n;\Psi(0),\Phi(0)](\boldsymbol{r}t) = \lambda^2 v_{\rm C}[n_{1/\lambda};\Psi_{1/\lambda}(0),\Phi_{1/\lambda}(0)](\lambda\boldsymbol{r},\lambda^2 t), \tag{39}$$

where $\Psi_{1/\lambda}(0)$ is the scaled initial state of the interacting system, defined as in Eq. (37), replacing γ with $1/\lambda$. For finite systems, it seems likely that taking the limit $\lambda\to 0$ makes the exchange term dominant (just as in the ground-state) [25], but this has yet to be proven.

IV.6. Translational invariance

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

$$v_{\mathrm{xc}}[n'](\boldsymbol{r}, t) = v_{\mathrm{xc}}[n](\boldsymbol{r} - \boldsymbol{X}(t), t) \tag{40}$$

where $n'(\boldsymbol{r}, t) = n(\boldsymbol{r} - \boldsymbol{X}(t), t)$. This condition is universally valid [29]. The GK approximation was found to violate this condition, which spurred on the development of the VK approximation. The harmonic potential theorem, a special case of translational invariance, is discussed in Chapter 24.

V. LINEAR RESPONSE

In the special case of linear response, all exchange-correlation information is contained in the kernel f_{xc}. Linear response is utilized in the great majority of TDDFT calculations, and the methods involved are thoroughly discussed in Chapter 7. As explained in [38], the chief use of linear response has been to extract electronic excitations. In this section, we shall discuss the exact conditions that pertain to f_{xc}, regardless of how it is employed.

V.1. Consequences of general conditions

Each of the conditions listed below for f_{xc} can be derived from a general condition in Sect. IV.

Adiabatic limit: For any finite system, the exact kernel satisfies:

$$\lim_{\omega \to 0} f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \frac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}')}\,, \tag{41}$$

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

Zero force and torque: The exact conditions on the potential of Sect. IV.2 also yield conditions on f_{xc}, when applied to an infinitesimal perturbation (see Chapter 24). Taking functional derivatives of Eq. (31b) yields [39]:

$$\int d^3r\, n(\boldsymbol{r})\; \nabla f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = -\nabla' v_{\mathrm{xc}}(\boldsymbol{r}') \tag{42}$$

and

$$\int d^3r\, n(\boldsymbol{r})\; \boldsymbol{r} \times \nabla f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = -\boldsymbol{r}' \times \nabla' v_{\mathrm{xc}}(\boldsymbol{r}')\,, \tag{43}$$

the latter 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 general conditions employing energies, Eqs. (32) and (33), do not yield simple conditions for the kernel, because the functional derivative of the exact time-dependent xc energy is not the xc potential.

Self-interaction error: For one electron, functional differentiation of Eq. (34) yields:

$$f_{\mathrm{x}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = -\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\,, \qquad f_{\mathrm{c}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = 0 \qquad (N = 1)\,. \tag{44}$$

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

Initial-state dependence: The initial-state condition, Eq. (35), leads to very interesting restrictions on f_{xc} for arbitrary densities. But the information is given in terms of initial-state dependence, which is very difficult to find.

Coupling-constant dependence: The exchange kernel scales linearly with coordinates, as found by differentiating Eq. (36):

$$f_{\mathrm{x}}[n_\gamma](\boldsymbol{r}, \boldsymbol{r}', \omega) = \gamma\, f_{\mathrm{x}}[n](\gamma \boldsymbol{r}, \gamma \boldsymbol{r}', \omega/\gamma^2)\,. \tag{45}$$

A functional derivative and Fourier-transform of Eq. (39) yields [40]

$$f_{\mathrm{c}}^{\lambda}[n](\boldsymbol{r}, \boldsymbol{r}', \omega) = \lambda^2 f_{\mathrm{c}}[n_{1/\lambda}](\lambda \boldsymbol{r}, \lambda \boldsymbol{r}', \omega/\lambda^2)\,. \tag{46}$$

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 Eq. (7).

A similar condition has also been derived for the coupling-constant dependence of the vector potential in TDCDFT [41].

V.2. Properties of the kernel

The kernel has many additional properties that come from its definition and other physical considerations.

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

$$f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = f_{\mathrm{xc}}(\boldsymbol{r}', \boldsymbol{r}; \omega)\,. \tag{47}$$

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.

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

$$\Delta f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega) = f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega) - f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}'; \infty)\,, \tag{48}$$

we find

$$\Re e\, \Delta f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mathcal{P}\int \frac{d\omega'}{\pi}\frac{\Im m\, f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}',\omega')}{\omega'-\omega} \quad (49a)$$

$$\Im m\, f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\mathcal{P}\int \frac{d\omega'}{\pi}\frac{\Re e\, \Delta f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}',\omega')}{\omega'-\omega}\,, \quad (49b)$$

where $\mathcal{P}$ denotes the principle value of the integral. The kernel $f_{\rm xc}(\boldsymbol{r}t,\boldsymbol{r}'t')$ is real-valued in the space and time domain, which leads to the condition in the frequency domain,

$$f_{\rm xc}(\boldsymbol{r},\boldsymbol{r}';\omega) = f^*_{\rm xc}(\boldsymbol{r},\boldsymbol{r}';-\omega)\,. \quad (50)$$

The simple lesson here is that any adiabatic kernel (no frequency dependence) is purely real, and any kernel with memory has an imaginary part in the frequency domain (or else is not sensible). Many of the failures of current TDDFT approximations, e.g. the fundamental gap of solids, are linked to the lack of an imaginary part of the kernel [39]. Because adiabatic approximations produce real kernels, we see that memory is required to produce complex kernels. Hellgren *et al.* [42] showed that EXX has a complex kernel, since it has frequency-dependence (for more than two electrons). Both GK and VK have complex kernels satisfying the Kramers-Kronig conditions.

Adiabatic connection: A beautiful condition on the exact xc kernel is given simply by the adiabatic connection formula for the ground-state correlation energy (see Chapter 22)

$$-\frac{1}{2}\int d^3r\int d^3r'\, v_{\rm ee}(\boldsymbol{r}-\boldsymbol{r}')\times$$
$$\int_0^\infty \frac{d\omega}{\pi}\int_0^1 d\lambda\, \Im m\left[\chi^\lambda(\boldsymbol{r},\boldsymbol{r}';\omega)-\chi_{\rm KS}(\boldsymbol{r},\boldsymbol{r}';\omega)\right] = E_{\rm c}\,. \quad (51)$$

Combined with the Dyson-like equation of Chapter 4 for χ^λ as a function of $\chi_{\rm KS}$ and $f_{\rm xc}$, this is being used to generate new and useful approximations to the ground-state correlation energy [43, 44]. Although computationally expensive, ways are being found to speed up the calculations [45].

Eq. (51) 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 $f_{\rm xc}$. Note that, e.g, using ALDA for the kernel implicit in (51) does *not* yield the corresponding $E_{\rm xc}^{\rm LDA}$, but rather a much more sophisticated functional [40]. Even insertion of $f_{\rm x}$ yields correlation contributions to all orders in $E_{\rm c}$. And lastly, even the exact adiabatic approximation, $f_{\rm xc}[n_0](\boldsymbol{r},\boldsymbol{r}';\omega=0)$, does not yield the exact $E_{\rm xc}[n_0]$.

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 of Chapter 4 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 will violate important underlying sum-rules, such as S_{-2} in Eq. (55).

V.3. Excited states

The following conditions have to do with the challenges of obtaining excited states in the linear response regime.

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 exact exchange, but not so clear when memory approximations are used. As mentioned in Sect. V.2, the Kramers-Kronig relations mean that memory implies imaginary xc kernels, and these can yield imaginary contributions to the transition frequencies. Such effects were seen in calculations using the VK for atomic transitions [46]. Indeed, very long lifetimes were found when VK was working well, and much shorter ones occurred when VK was failing badly.

Single-pole approximation for exchange: This is another odd condition, in which two wrongs make something right. Using Görling-Levy perturbation theory [47], one can calculate the exact exchange contributions to excited state energies [48, 49]. To recover these results using TDDFT, one does *not* simply use $f_{\rm x}$, and solve the Dyson-like equations. Like with Eq. (51), the infinite iteration yields contributions to all orders in the coupling-constant.

However, the single-pole approximation 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 the linear response equations, and *not* by a full solution [50]. This procedure can be extended to the next order [51].

Double excitations and branch cuts: Maitra et al [52, 53] argued that a strong ω-dependence in $f_{\rm xc}$ allows double excitation solutions to Casida's equations, which effectively couples double excitations to single excitations. Similarly, the second ionization of the He atom implies a branch cut in its $f_{\rm xc}$ at the frequency needed [54]. Under limited circumstances, this frequency dependence can be estimated, but a generalization [55] has been proposed. It would be interesting to check its compliance with the conditions listed in this chapter. A detailed discussion of double excitations can be found in Chapter 8.

Excitations in the adiabatic approximation: One misleading use of linear response has been to test the quality of different approximations to the ground-state $E_{\rm xc}$. For instance, Jacquemin *et al.* [56] calculated the excitation energies for approximate $E_{\rm xc}$ functionals within adiabatic TDDFT and compared them to experimental values. However, even within AA — using the adiabatic approximation with the exact $E_{\rm xc}$ — the exact excitations would not be not obtained. Thus a good ground-state $E_{\rm xc}$ used in adiabatic linear response will not necessarily give good excitation energies.

Frequency sum-rules: In the limit that the wavelength of the incident light is much greater than the scale of the system, the linear response function determines the optical spectrum by [57]

$$\sigma(\omega) = \frac{4\pi\omega}{3c}\Im m \left[\int d^3r\int d^3r'\, \boldsymbol{r}\cdot\boldsymbol{r}'\chi(\boldsymbol{r},\boldsymbol{r}',\omega)\right], \quad (52)$$

where $\sigma(\omega)$ is the photoabsorption cross-section. In physics, the spectrum is usually described by the dimensionless oscillator strength $f(\omega)$. In atomic units, $f(\omega)$ is related to $\sigma(\omega)$ by [58]

$$\sigma(\omega) = \frac{2\pi^2}{c} f(\omega)\,. \quad (53)$$

The moments of the oscillator strength spectrum, S_n, are defined by

$$S_n = \sum_{\nu\,\in\,\text{excitedstates}} (E_\nu - E_0)^n f(E_\nu - E_0)\,, \quad (54)$$

where the sum over continuum states will turn into an integral. Eqs. (52) and (53) show that S_n is related to the linear response function. Using basic quantum mechanics, S_n can be related to various general properties of the system, known as oscillator strength sum rules [59–61]; S_0 is the usual Thomas-Reich-Kuhn sum rule. In atomic units, the most used sum rules S_{-2} to S_2 are

$$S_{-2} = \alpha(\omega=0)\,, \quad S_{-1} = \frac{2}{3}\langle\Big|\textstyle\sum_j \boldsymbol{r}_j\Big|^2\rangle_0\,, \quad S_0 = N$$
$$S_1 = \frac{2}{3}\langle\Big|\textstyle\sum_j \mathbf{p}_j\Big|^2\rangle_0\,, \quad S_2 = \frac{4\pi}{3}\sum_{A\,\in\,\text{nuclei}} Z_A\, n(\boldsymbol{r}=\boldsymbol{R}_A)\,, \quad (55)$$

where $\alpha(\omega=0)$ is the static polarizability, Z_A is the charge of nucleus A and $\boldsymbol{R}_A$ its position. Sum rules for $n>2$ do not converge due to the $\omega^{-7/2}$ asymptotic decay of $f(\omega\to\infty)$ [62], and $S_{n<-2}$ are related to various other properties of the system [60]. For each sum rule, a new exact condition can be found for the kernel. Within the exact adiabatic (AA) approximation, the S_{-2} sum rule will be equal to the polarizability $\alpha(\omega=0)$ of the real system, because the AA kernel is correct for $\omega\to 0$. By definition, the sums S_0 and S_2 for the exact Kohn-Sham ground state are equal to their counterparts in the interacting system, whereas the other sums are not. Since S_n is related to the linear response function, these differences yield exact conditions on $f_{\rm xc}$, which connects the linear response functions of the Kohn-Sham system and the real system.

Scattering theory and real-time propagation: A vastly under-appreciated exact condition for TDDFT is the equivalence of time-dependent propagation and scattering theory. This can be particularly important in understanding the relation between bound and continuum states.

For example, much early work in TDDFT was performed by Yabana and Bertsch [63], propagating ALDA for atoms and molecules in weak electric fields. By Fourier transformation of the time-dependent dipole moment, one can extract the photoabsorption spectrum. The fruitfly of such calculations is benzene, with a large $\pi\to\pi^*$ transition at about 6.5 eV, accurately given by ALDA. But closer inspection shows that the LDA ionization threshold is at about 5 eV, because the LDA xc potential is not deep enough. Thus this transition is in the LDA continuum, yet its position and area are given reasonably well by ALDA. This is no coincidence: ALDA describes the time-dependent density and its propagation for moderate times very well. All that has changed is the choice of a complete set of states onto which to project the results!

By following this logic, Wasserman *et al.* [64] could capture the effect of Rydberg transitions using ALDA. However, ALDA puts many bound states in the continuum due to the exponential fall-off of the KS-LDA potential (as mentioned in Sect. III). Thus the ionization potentials for the ALDA states are wrong, but the oscillator strength in the LDA continuum accurately approximates that of the true Rydberg transitions to the exact bound states. (However, it is *not* an exact condition that the KS oscillator strengths be correct, not even at the threshold where KS captures the right energy [65].) For an illustration, see Fig. 4.4 in Chapter 4 for the optical absorption for the helium atom. Using a trick due to Fano [66], Wasserman showed [67] that the Rydberg transition frequencies, could be extracted from ALDA. In [68] it is shown the accuracy of this calculation for He, Be, and Ne, whereas [69] shows the qualitative failure of ALDA for transitions to high angular momentum eigenstates (starting at the d orbitals).

One can go further, and even consider true continuum states. In scattering theory, the continuum states of the $N+1$ particle system describe how a single electron scatters from an N particle system. Wasserman [70] and van Faassen [71] developed methods to calculate scattering amplitudes and phase shifts based on time-propagation within TDDFT. With a given approximation, one can calculate the susceptibility of an atomic anion and deduce the scattering amplitude for an incident electron [72]. Both these examples (the quantum defect and scattering) can be connected in the same framework [73], and they illustrate that TDDFT fundamentally concerns time-propagation. Present-day approxi-

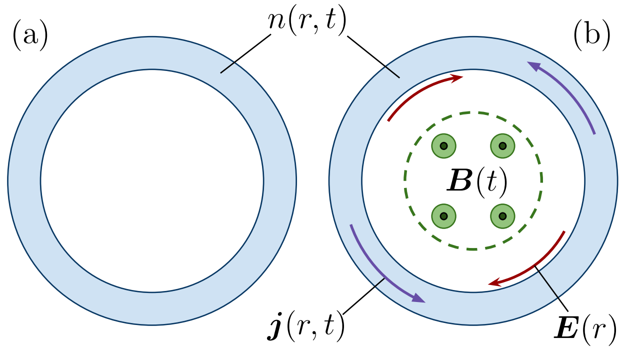

FIG. 3. Electrons on a ring. A magnetic field $\boldsymbol{B}(t)$ is turned on and steadily increases in (b); the resulting electric field $\boldsymbol{E}(r)$ is uniform on a thin ring, accelerating electrons around the ring, producing the probability current $\boldsymbol{j}(r,t)$. Note that in both (a) and (b) the densities are equal.

mations yield promising results; simple approximations like ALDA often yield accurate time-dependent densities, but their projection onto individual Kohn-Sham eigenstates may appear far more complicated.

VI. EXTENDED SYSTEMS AND CURRENTS

As mentioned in Sect. II.4, care must be taken when extending exact ground-state DFT results to extended systems. This is even more so the case for TDDFT. The first half of the Runge-Gross theorem (see Chapter 4) 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. Without this condition, it can readily be seen that two periodic systems with completely different physics can have the same density [74], as in Fig. 3. 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.

VI.1. Gradient expansion in the current

As discussed elsewhere (Chapter 24) and first pointed out by Dobson [75], the frequency-dependent LDA (GK approximation) violates the translational invariance condition of Sect. IV.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 [76], and later simplified by Vignale, Ullrich, and Conti [77], and is discussed in much detail in the Chapter 24.

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 [76].

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, which for the ground-state was found to violate sum rules, as mentioned in Sect. II.4. It is therefore likely that there exists something like a generalized gradient approximation, which is more accurate than VK.

VI.2. Polarization of solids

A decade ago, Gonze, Ghosez, and Godby [78] pointed out that the periodic density in an insulating solid in an electric field is insufficient to determine the periodic one-body potential, in apparent violation of the Hohenberg–Kohn theorem [24]. In fact, this effect appears straightforwardly in the static limit of TDCDFT, and is even estimated by calculations using the VK approximation [74, 79]. When translated back to TDDFT language, one finds a $1/q^2$ dependence in $f_{\rm xc}$, where $\boldsymbol{q}$ is the wavevector corresponding to $\boldsymbol{r}-\boldsymbol{r}'$. This requires $f_{\rm xc}$ to have the same degree of nonlocality as the Hartree kernel, and this is missed by any local or semilocal approximation, such as ALDA, but *is* built in to EXX [80] or AA. The need for a $1/q^2$ contribution in the optical response of solids led to much development [81] for a kernel that allows excitons [82, 83]. Since the RG theorem can be proven for solids in electric fields of nonzero q, one can extract the $q \to 0$ (a constant $\boldsymbol{E}$ field) result at the end of the calculation [74].

VII. SUMMARY

What lessons can we take away from this brief survey?

1. In the ground-state theory, the total xc energy is crucial for determining the energy of the system, and many conditions are proven for that functional. This is not so for TDDFT, for which only the time-dependent density matters. In the non-interacting system, the KS potential, and specifically its xc component, is what counts.

2. Approximate functionals depending explicitly on the density have poor-quality potentials, e.g. LDA and GGA. Thus successes in ground-state DFT do not translate directly into successes in TDDFT. One of the greatest challenges is that the potential is a far more sensitive functional of the density than vice versa. Though we have enumerated many conditions on the xc potential, it is important to determine which conditions significantly affect the

density, including those aspects of the density that are relevant to experimental measurements.

3. 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.

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.

---

[1] J. P. Perdew and S. Kurth, "Density functionals for nonrelativistic Coulomb systems in the new century," in *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. A. L. Marques (Springer, Berlin / Heidelberg, 2003) pp. 1–55.

[2] M. Levy, "Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem," Proceedings of the National Academy of Sciences of the United States of America, **76**, 6062 (1979).

[3] E. H. Lieb, "Density functionals for coulomb systems," International Journal of Quantum Chemistry, **24**, 243 (1983).

[4] S. Kümmel and L. Kronik, "Orbital-dependent density functionals: Theory and applications," Rev. Mod. Phys., **80**, 3 (2008).

[5] J. B. Krieger, Y. Li, and G. J. Iafrate, "Systematic approximations to the optimized effective potential: Application to orbital-density-functional theory," Phys. Rev. A, **46**, 5453 (1992).

[6] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, "Prescription for the design and selection of density functional approximations: More constraint satisfaction with fewer fits," The Journal of Chemical Physics, **123**, 062201 (2005).

[7] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, "Tests of a ladder of density functionals for bulk solids and surfaces," Phys. Rev. B, **69**, 075102 (2004), *ibid.* **78**, 239907(E) (2008).

[8] J. P. Perdew, K. Burke, and Y. Wang, "Generalized gradient approximation for the exchange-correlation hole of a many-electron system," Phys. Rev. B, **54**, 16533 (1996), *ibid.* **57**, 14999(E) (1998).

[9] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., **77**, 3865 (1996), *ibid.* **78**, 1396(E) (1997).

[10] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," Phys. Rev. A, **38**, 3098 (1988).

[11] C. Lee, W. Yang, and R. G. Parr, "Development of the colle-salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B, **37**, 785 (1988).

[12] A. D. Becke, "Density-functional thermochemistry. iii. the role of exact exchange," The Journal of Chemical Physics, **98**, 5648 (1993).

[13] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, "Orbital functionals in density functional theory: the optimized effective potential method," in *Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation*, edited by V. Anisimov (Gordon & Breach, Amsterdam, 2000) pp. 203–311.

[14] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, "Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids," Phys. Rev. Lett., **91**, 146401 (2003).

[15] D. Rappoport, N. R. M. Crawford, F. Furche, and K. Burke, in *Computational Inorganic and Bioinorganic Chemistry*, edited by E. Solomon, R. King, and R. Scott (Wiley, John & Sons, Inc., 2009).

[16] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," Phys. Rev., **140**, A1133 (1965).

[17] M. Levy and J. Perdew, "Hellmann-feynman, virial, and scaling requisites for the exact universal density functionals. shape of the correlation potential and diamagnetic susceptibility for atoms," Phys. Rev. A, **32**, 2010 (1985).

[18] M. Seidl, J. P. Perdew, and S. Kurth, "Simulation of all-order density-functional perturbation theory, using the second order and the strong-correlation limit," Phys. Rev. Lett., **84**, 5070 (2000).

[19] J. P. Perdew and A. Zunger, "Self-interaction correction to density-functional approximations for many-electron systems," Phys. Rev. B, **23**, 5048 (1981).

[20] E. H. Lieb and S. Oxford, "Improved lower bound on the indirect coulomb energy," International Journal of Quantum Chemistry, **19**, 427 (1981).

[21] D. C. Langreth and J. P. Perdew, "Theory of nonuniform electronic systems. i. analysis of the gradient approximation and a generalization that works," Phys. Rev. B, **21**, 5469 (1980).

[22] K. Burke, J. P. Perdew, and M. Ernzerhof, "Why semilocal functionals work: Accuracy of the on-top pair density and importance of system averaging," The Journal of Chemical Physics, **109**, 3760 (1998).

[23] S. Moroni, D. M. Ceperley, and G. Senatore, "Static response and local field factor of the electron gas," Phys. Rev. Lett., **75**, 689 (1995).

[24] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev., **136**, B864 (1964).

[25] P. Hessler, N. T. Maitra, and K. Burke, "Correlation in time-dependent density-functional theory," The Journal of Chemical Physics, **117**, 72 (2002).

[26] M. Thiele, E. K. U. Gross, and S. Kümmel, "Adiabatic approximation in nonperturbative time-dependent density-functional theory," Phys. Rev. Lett., **100**, 153004 (2008).

[27] J. F. Dobson, M. J. Bünner, and E. K. U. Gross, "Time-dependent density functional theory beyond linear re-

sponse: An exchange-correlation potential with memory," Phys. Rev. Lett., **79**, 1905 (1997).
[28] Y. Kurzweil and R. Baer, "Time-dependent exchange-correlation current density functionals with memory," The Journal of Chemical Physics, **121**, 8731 (2004).
[29] G. Vignale, "Center of mass and relative motion in time dependent density functional theory," Phys. Rev. Lett., **74**, 3233 (1995).
[30] G. Vignale, "Sum rule for the linear density response of a driven electronic system," Physics Letters A, **209**, 206 (1995).
[31] R. van Leeuwen, "Key concepts in time-dependent density-functional theory," International Journal of Modern Physics B, **15**, 1969 (2001).
[32] M. Mundt, S. Kümmel, R. van Leeuwen, and P.-G. Reinhard, "Violation of the zero-force theorem in the time-dependent krieger-li-iafrate approximation," Phys. Rev. A, **75**, 050501 (2007).
[33] L. Fritsche and J. Yuan, "Alternative approach to the optimized effective potential method," Phys. Rev. A, **57**, 3425 (1998).
[34] P. Hessler, J. Park, and K. Burke, "Several theorems in time-dependent density functional theory," Phys. Rev. Lett., **82**, 378 (1999), *ibid.* **83**, 5184(E) (1999).
[35] N. T. Maitra, K. Burke, and C. Woodward, "Memory in time-dependent density functional theory," Phys. Rev. Lett., **89**, 023002 (2002).
[36] N. T. Maitra, "Memory formulas for perturbations in time-dependent density functional theory," International Journal of Quantum Chemistry, **102**, 573 (2005).
[37] A. Görling, "Time-dependent Kohn-Sham formalism," Phys. Rev. A, **55**, 2630 (1997).
[38] P. Elliott, F. Furche, and K. Burke, "Excited states from time-dependent density functional theory," in *Reviews of Computational Chemistry*, edited by K. B. Lipkowitz and T. R. Cundari (Wiley, Hoboken, NJ, 2009) pp. 91–165.
[39] G. F. Giuliani and G. Vignale, eds., *Quantum Theory of the Electron Liquid* (Cambridge University Press, 2008).
[40] M. Lein, E. K. U. Gross, and J. P. Perdew, "Electron correlation energies from scaled exchange-correlation kernels: Importance of spatial versus temporal nonlocality," Phys. Rev. B, **61**, 13431 (2000).
[41] M. Dion and K. Burke, "Coordinate scaling in time-dependent current-density-functional theory," Phys. Rev. A, **72**, 020502 (2005).
[42] M. Hellgren and U. von Barth, "Exact-exchange kernel of time-dependent density functional theory: Frequency dependence and photoabsorption spectra of atoms," The Journal of Chemical Physics, **131**, 044110 (2009).
[43] M. Fuchs and X. Gonze, "Accurate density functionals: Approaches using the adiabatic-connection fluctuation-dissipation theorem," Phys. Rev. B, **65**, 235109 (2002).
[44] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, "Describing static correlation in bond dissociation by kohn–sham density functional theory," The Journal of Chemical Physics, **122**, 094116 (2005).
[45] H. Eshuis, J. Yarkony, and F. Furche, "Fast computation of molecular random phase approximation correlation energies using resolution of the identity and imaginary frequency integration," The Journal of Chemical Physics, **132**, 234114 (2010).
[46] C. A. Ullrich and K. Burke, "Excitation energies from time-dependent density-functional theory beyond the adiabatic approximation," The Journal of Chemical Physics, **121**, 28 (2004).
[47] A. Görling and M. Levy, "Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion," Phys. Rev. B, **47**, 13105 (1993).
[48] C. Filippi, C. J. Umrigar, and X. Gonze, "Excitation energies from density functional perturbation theory," The Journal of Chemical Physics, **107**, 9994 (1997).
[49] F. Zhang and K. Burke, "Adiabatic connection for near degenerate excited states," Phys. Rev. A, **69**, 052510 (2004).
[50] X. Gonze and M. Scheffler, "Exchange and correlation kernels at the resonance frequency: Implications for excitation energies in density-functional theory," Phys. Rev. Lett., **82**, 4416 (1999).
[51] H. Appel, E. K. U. Gross, and K. Burke, "Excitations in time-dependent density-functional theory," Phys. Rev. Lett., **90**, 043005 (2003).
[52] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, "Double excitations within time-dependent density functional theory linear response," The Journal of Chemical Physics, **120**, 5932 (2004).
[53] R. J. Cave, F. Zhang, N. T. Maitra, and K. Burke, "A dressed TDDFT treatment of the 2^1A_g states of butadiene and hexatriene," Chemical Physics Letters, **389**, 39 (2004).
[54] K. Burke, J. Werschnik, and E. K. U. Gross, "Time-dependent density functional theory: Past, present, and future," The Journal of Chemical Physics, **123**, 062206 (2005).
[55] M. E. Casida, "Propagator corrections to adiabatic time-dependent density-functional theory linear response theory," The Journal of Chemical Physics, **122**, 054111 (2005).
[56] D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, and D. G. Truhlar, "On the performances of the m06 family of density functionals for electronic excitation energies," Journal of Chemical Theory and Computation, **6**, 2071 (2010).
[57] G. D. Mahan and K. R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum, New York, 1990).
[58] H. Friedrich, *Theoretical Atomic Physics* (Springer-Verlag, Berlin, 2006).
[59] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).
[60] U. Fano and J. W. Cooper, "Spectral distribution of atomic oscillator strengths," Rev. Mod. Phys., **40**, 441 (1968).
[61] M. Inokuti, "Inelastic collisions of fast charged particles with atoms and molecules—the bethe theory revisited," Rev. Mod. Phys., **43**, 297 (1971).
[62] A. R. P. Rau and U. Fano, "Transition matrix elements for large momentum or energy transfer," Phys. Rev., **162**, 68 (1967).
[63] K. Yabana and G. F. Bertsch, "Time-dependent local-density approximation in real time," Phys. Rev. B, **54**, 4484 (1996).
[64] A. Wasserman, N. T. Maitra, and K. Burke, "Accurate rydberg excitations from the local density approximation," Phys. Rev. Lett., **91**, 263001 (2003).
[65] Z. Yang, M. van Faassen, and K. Burke, "Must kohn–sham oscillator strengths be accurate at threshold?" The Journal of Chemical Physics, **131**, 114308 (2009).

[66] U. Fano, "Sullo spettro di assorbimento dei gas nobili presso il limite dello spettro d'arco," Il Nuovo Cimento (1924-1942), **12**, 154 (1935), 10.1007/BF02958288.
[67] A. Wasserman and K. Burke, "Rydberg transition frequencies from the local density approximation," Phys. Rev. Lett., **95**, 163006 (2005).
[68] M. van Faassen and K. Burke, "The quantum defect: The true measure of time-dependent density-functional results for atoms," The Journal of Chemical Physics, **124**, 094102 (2006).
[69] M. van Faassen and K. Burke, "A new challenge for time-dependent density functional theory," Chemical Physics Letters, **431**, 410 (2006).
[70] A. Wasserman, *Scattering States from Time-dependent Density Functional Theory*, Ph.D. thesis, Rutgers University (2005).
[71] M. van Faassen, A. Wasserman, E. Engel, F. Zhang, and K. Burke, "Time-dependent density functional calculation of $e-h$ scattering," Phys. Rev. Lett., **99**, 043005 (2007).
[72] A. Wasserman, N. T. Maitra, and K. Burke, "Continuum states from time-dependent density functional theory," The Journal of Chemical Physics, **122**, 144103 (2005).
[73] M. van Faassen and K. Burke, "Time-dependent density functional theory of high excitations: to infinity, and beyond," Phys. Chem. Chem. Phys., **11**, 4437 (2009).
[74] N. T. Maitra, I. Souza, and K. Burke, "Current-density functional theory of the response of solids," Phys. Rev. B, **68**, 045109 (2003).
[75] J. F. Dobson, "Harmonic-potential theorem: Implications for approximate many-body theories," Phys. Rev. Lett., **73**, 2244 (1994).
[76] G. Vignale and W. Kohn, "Current-dependent exchange-correlation potential for dynamical linear response theory," Phys. Rev. Lett., **77**, 2037 (1996).
[77] G. Vignale, C. A. Ullrich, and S. Conti, "Time-dependent density functional theory beyond the adiabatic local density approximation," Phys. Rev. Lett., **79**, 4878 (1997).
[78] X. Gonze, P. Ghosez, and R. W. Godby, "Density-polarization functional theory of the response of a periodic insulating solid to an electric field," Phys. Rev. Lett., **74**, 4035 (1995).
[79] M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, "Application of time-dependent current-density-functional theory to nonlocal exchange-correlation effects in polymers," The Journal of Chemical Physics, **118**, 1044 (2003).
[80] Y.-H. Kim and A. Görling, "Excitonic optical spectrum of semiconductors obtained by time-dependent density-functional theory with the exact-exchange kernel," Phys. Rev. Lett., **89**, 096402 (2002).
[81] G. Onida, L. Reining, and A. Rubio, "Electronic excitations: density-functional versus many-body green's-function approaches," Rev. Mod. Phys., **74**, 601 (2002).
[82] L. Reining, V. Olevano, A. Rubio, and G. Onida, "Excitonic effects in solids described by time-dependent density-functional theory," Phys. Rev. Lett., **88**, 066404 (2002).
[83] F. Sottile, M. Marsili, V. Olevano, and L. Reining, "Efficient ab initio calculations of bound and continuum excitons in the absorption spectra of semiconductors and insulators," Phys. Rev. B, **76**, 161103 (2007).