

## A Guided Tour of Time-Dependent Density Functional Theory

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**Abstract.** This chapter briefly reviews progress to date in the density functional theory of time-dependent phenomena. We discuss the fundamental theorems and their relation to other approaches. Several exact conditions are treated. We review the special case of the linear response to a weak external potential and look specifically at the linear response of the uniform electron gas, which is important for local density approximations. We discuss recent suggestions for functional approximations, including both the local current density approximation and the local-with-memory density approximation. We review applications of the theory in three situations: Beyond linear response, linear response, and excitation energies, and conclude with a brief outlook.

### 1 Introduction and User's Guide

Density functional theory is the study of the one-to-one correspondence[1] between an interacting many-body system, and a fictitious non-interacting analog, the Kohn-Sham system[2], whose equations are much easier to solve numerically. This mapping is exact in principle, but must be approximated in practice. Over the last several years, there has been an explosion of interest in density functional theory, driven largely by its applications in quantum chemistry[3]. This is due to recent progress in the accuracy of available approximations[4], and because of the wealth of chemical problems that can be tackled with such a computationally inexpensive tool[5].

Much of this interest has focussed on the problem of  $N$  electrons in the ground state of an external time-independent potential. Accurate solution to this problem yields predictions of atomic energies, reaction energies in chemistry, cohesive energies in solids, vibrational energies, phonon spectra, activation barriers, rotational energies, etc. [6]. Much of the other chapters in this book are devoted to this subject.

But the basic idea of mapping an interacting problem onto a non-interacting one via the density is extremely general, and has been applied to many circumstances beyond the original ground-state problem mentioned above. In the present article, we briefly survey the progress that has been made on the time-dependent problem. For those less familiar with the time-dependent case, we emphasize the comparison between it and the static ground-state case. For those more familiar with the time-dependent case, this article should serve as an update of an earlier, more comprehensive review[7]. Throughout this article, we use atomic units, in which  $e^2 = \hbar = m = 1$ . We also use the shorthand  $x = (\mathbf{r}, t)$  for the pair  $\mathbf{r}$  and  $t$ , which makes the equations shorter and more legible. In the remainder of this introduction, we first demonstrate how far time-dependent density functional theory has come in the last few years (section 1.1), and then give an overview of each of the remaining sections in this chapter.

### 1.1 Why time-dependent density functional theory is exciting

To give some feeling for the power of time-dependent density functional theory, consider the He atom as a prototypical system. From a ground-state point of view, this system might be regarded as rather dull. Not much chemistry occurs with He.<sup>1</sup> Furthermore, most physicists are more interested in extended systems, whether or not they are metallic, superconducting, etc. What can you do with a ground-state density functional theory of the He atom? You can examine how well your favorite exchange-correlation energy approximations perform. Among them might be the local density approximation (LDA)[2], using the latest uniform gas input[12], and the Colle-Salvetti approximation[13], an orbital-dependent correlation approximation. You can construct the exact Kohn-Sham potential[14], examine how good the functional derivative of your favorite energy approximation is, and argue about the implications[15]. You might turn on a uniform electric field, and calculate the static polarizability, or hyperpolarizability[16].

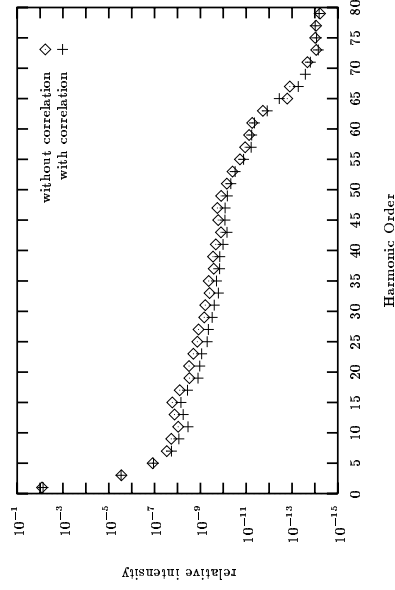


Fig. 1. Harmonic spectrum of He with and without correlation (see text). The laser parameters are  $\lambda = 616 \text{ nm}$  and  $I = 7.0 \times 10^{14} \text{ W/cm}^2$  [10].

Now consider the He atom when you have a fully time-dependent density functional theory[17, 18, 19, 20]. In the most dramatic case, you can apply a strong laser field, whose strength is comparable to the electron-nuclear electrostatic field. You can then watch the system evolve, see if any electrons are ionized, watch them oscillate back and forth, calculate the induced dipole moment, etc. You compare results with experiment, or other more computationally demanding techniques, and find the most reliable functional approximations. You can then search

<sup>1</sup> Although see the recent interest in van der Waals dimers[8, 9, 10, 11].

the vast parameter space of the problem on the computer, guiding the experimentalists in their search for greater gain, etc. As an example of interest to the density functional community, Fig. 1 displays the harmonic generation spectrum of He for a 616 nm,  $7 \times 10^{14}$  W/cm<sup>2</sup> laser pulse, with and without correlation[19]. While the overall pattern is the same in both cases, the effect of correlation reduces the peak heights by a factor of 2 or 3. There are few examples in the ground-state lexicon where correlation effects are so large.

If the complexity of this application is too much for you, you might wish to consider the more simple linear response regime, where the external time-dependent potential is weak relative to the ground-state Kohn-Sham potential. Then the formalism gives all the response functions as a function of frequency  $\omega$ , including the static limit ( $\omega \rightarrow 0$ ) as a special case. Such quantities are related to photoabsorption for our simple He atom[21], bulk and surface plasmon dispersions for metals[22, 23, 24, 25], etc.

(and other atoms[28]) have been calculated this way, testing various approximations. Fig. 2 shows the *exact* Kohn-Sham eigenvalues of the He atom[29] (left-hand side), which typically lie between the experimental spin-split levels (right-hand side). In the middle, we show the spin-split levels calculated with linear response time-dependent density functional theory, using the exact Kohn-Sham potential, and an approximation to the response kernel (defined in section 6.3). Clearly, progress is being made toward an accurate, reliable calculational scheme for the excitation energies of a system.

## 1.2 Fundamentals

In section 2 of this chapter, we review fundamental ideas. To find the ground state energy of He or any other electronic system in density functional theory, one first establishes the Hohenberg-Kohn theorem[1]. This was done thirteen years ago for the time-dependent problem by Runge and Gross[31]. Application of this theorem to a non-interacting system immediately yields the Kohn-Sham equations[2], which are simply generalized to the time-dependent case.

In the ground state, the energy satisfies a minimization principle, and the value of the energy is of great interest in most applications. The time-dependent analog of the energy is the action, which satisfies a stationarity condition. However, the action plays a much less significant role in the time-dependent problem, where its actual value is never of interest, but only its functional derivatives are, in striking contrast to the ground-state energy.

A fruitful area of progress in the ground-state case has been the relation of density functional to standard perturbation techniques. The Sham-Schlüter equation[32] relates the exchange-correlation potential of density functional theory to the exchange-correlation contribution to the self-energy of many-body theory, which was useful in understanding the difference between the Kohn-Sham gap and physical gap in bulk semiconductors and insulators. We discuss the time-dependent generalization of this equation[33].

The optimized effective potential (OEP) formalism has been developed as a method for calculating the Kohn-Sham potential of explicitly orbital-dependent functionals[34, 35]. The (highly accurate) Krieger-Li-Iafrate (KLI) approximation[36] makes this a practical scheme for calculations. We show the time-dependent equivalent of this approach. This scheme includes exact exchange by construction, since the Fock integral is an explicit functional of the orbitals. In time-dependent and excited-state problems, this can be much more important than in the ground state, given the emphasis on unoccupied orbital energies, in contrast to the total ground-state energy.

Lastly in this section, we generalize all results to include spin-dependence. This is very useful for the accurate treatment of open-shell atoms, e.g., Li.

## 1.3 Exact conditions

In section 3 of the chapter, we discuss exact conditions satisfied by the time-dependent exchange-correlation potential. An extremely useful guide to building accurate approximations to the ground-state energy has been the study of conditions satisfied by *exact* functionals. Our next section is rather short, where we discuss exact conditions which must be satisfied by the time-dependent exchange-correlation potential. These may be divided into two kinds: those

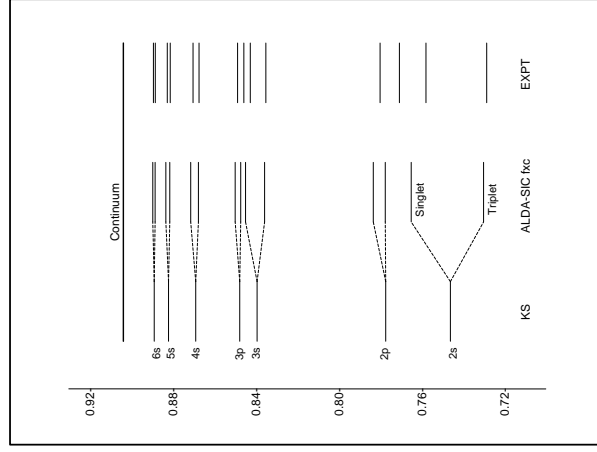


Fig. 2. Typical excitation energies from the ground-state of He, including the orbital energies of the exact Kohn-Sham potential (KS), the time-dependent OEP spin-split correction, calculated within the self-interaction corrected adiabatic local density approximation[30], and experiment [27].

To appreciate how sophisticated the frequency dependence of these response functions is, note that a single response function has poles at *all* the excitation energies of the system[26]. Thus a simple application is to extract these energies from the response function, producing a very natural excited-state density functional theory. Many of the excitation energies of He[27]

that have a ground-state analog (e.g., zero net exchange-correlation force and torque[37, 38]), and those that have not (e.g. translational invariance[39]). The brevity of this section suggests that much work is yet to be done in this area.

### 1.4 Linear response

In section 4, we develop the special case of linear response, i.e., what happens when the time-dependent external potential can be treated as a weak perturbation of the ground state. This is formally analogous to the linear response theory of the ground-state, only now there is a non-zero frequency  $\omega$  in the perturbation. This leads to a much richer variety of behavior in the response functions. We introduce the exchange-correlation kernel, which characterizes the deviations from the bare Kohn-Sham response, and discuss its exact restraints. We also show the OEP equation for this kernel. We generalize these results to the response to a time-dependent *vector* potential[40], which we later need for the development of a frequency-dependent local density (type) approximation[40]. We end this section with some results for the exchange-correlation kernel of a uniform gas[41, 42].

### 1.5 Approximate functionals

In section 5, we present a variety of approximate functionals. These fall into two broad categories: the majority are LDA-type, using uniform (or slowly-varying) gas input, and the rest are perturbative in the Coulomb repulsion, e.g., exact exchange-only. This mirrors the situation in ground-state density functional theory. The LDA-type approximations have gone through a very interesting development, in which appreciation of the essential differences between the time-development in an inhomogeneous system and that in a uniform system has been crucial to the construction of approximate functionals. Dobson[39] observed that the two distinct components of fluid flow, a compressive piece and a rigid displacement, *must* have different frequency-dependences, if certain exact constraints are to be satisfied. This has led to two of the latest approximations: the local current-density approximation (LCDA) of Vignale and Kohn for the high-frequency linear response[40], and the local-with-memory density approximation (LMDA) of Dobson, B nner, and Gross[43], which goes beyond linear response. Lastly, we discuss a simple exchange-only approximation to the KL exchange-correlation kernel, which is used in practical calculations[44].

### 1.6 Applications, including excitation energies

In section 6.3, we discuss (in more detail than in section 1.1 above) recent applications of density functional theory. The most exciting is perhaps the phenomena seen when atoms are subjected to superintense laser pulses (section 6.1), as illustrated in Fig. 1. For these problems, it appears that density functional theory is the *only* practical way to perform calculations which include electronic correlations.

A more standard application of time-dependent density functional theory has been in the photoresponse of a large variety of electronic systems[45], mostly in the linear regime. More recent has been the application of linear response theory to the problem of finding excitation

energies[26]. This can be done exactly in principle, since the poles of the interacting susceptibility are at the true excitation energies of the system. We discuss the accuracy of the various approximations needed to make this a practical scheme.

## 2 Fundamentals

### 2.1 Hohenberg-Kohn Theorem

The analog of the Hohenberg-Kohn theorem for time-dependent problems is the Runge-Gross theorem[31]. Consider  $N$  non-relativistic electrons, mutually interacting via the Coulomb repulsion, in a time-dependent external potential. The Runge-Gross theorem states that the densities  $n(x)$  and  $n'(x)$  evolving from a common initial state  $\Psi_0 = \Psi(t_0)$  under the influence of two potentials  $v(x)$  and  $v'(x)$  (both Taylor expandable about the initial time  $t_0$ ) are always different provided that the potentials differ by more than a purely time-dependent ( $\mathbf{r}$ -independent) function:

$$v(x) \neq v'(x) + c(t). \quad (1)$$

Thus there is a one-to-one mapping between densities and potentials.

We can prove this theorem by first showing that the corresponding current densities:

$$\mathbf{j}(x) = \langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \rangle, \quad (2)$$

where

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i} \sum_{j=1}^N (\nabla_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \nabla_j) \quad (3)$$

is the paramagnetic current density operator, must differ. The equation of motion for the difference of the two current densities is:

$$\begin{aligned} \frac{\partial}{\partial t} (\mathbf{j}(x) - \mathbf{j}'(x)) \Big|_{t=t_0} &= -i \langle \Psi_0 | [\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Psi_0 \rangle \\ &= -n_0(\mathbf{r}) \nabla (v(\mathbf{r}, t_0) - v'(\mathbf{r}, t_0)), \end{aligned} \quad (4)$$

with the initial density

$$n_0(\mathbf{r}) = n(\mathbf{r}, t_0), \quad (5)$$

since the Hamiltonians differ only in their external potentials. Repeated use of the equation of motion yields, after some algebra[7],

$$\left( \frac{\partial}{\partial t} \right)^{k+1} (\mathbf{j}(x) - \mathbf{j}'(x)) \Big|_{t=t_0} = -n_0(\mathbf{r}) \nabla w_k(\mathbf{r}) \quad (6)$$

with

$$w_k(\mathbf{r}) = \left( \frac{\partial}{\partial t} \right)^k (v(x) - v'(x)) \Big|_{t=t_0}. \quad (7)$$

If (1) holds, and the potentials are Taylor expandable about  $t_0$ , then there must be some finite  $k$  for which the right hand side of (4) does *not* vanish, so that

$$\mathbf{j}(x) \neq \mathbf{j}'(x). \quad (8)$$

To extend this result to the densities, we use continuity,

$$\frac{\partial}{\partial t}(n(x) - n'(x)) = -\nabla \cdot (\mathbf{j}(x) - \mathbf{j}'(x)) \quad (9)$$

and calculate the  $(k+1)$ th time derivative of (9) at  $t = t_0$ :

$$\left(\frac{\partial}{\partial t}\right)^{k+2} (n(x) - n'(x)) \Big|_{t=t_0} = \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad (10)$$

To see that the right-hand-side cannot vanish for all  $k$ , note the following identity:

$$\int d^3r \left\{ w_k(\mathbf{r}) \nabla \cdot (w_k(\mathbf{r}) n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) = \int d^3r \left\{ w_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) + n_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 \right\} \right. \quad (11)$$

The left-hand side may be transformed into a surface integral via Green's theorem, and vanishes for physically realistic potentials (i. e., potentials arising from normalizable external charge densities), because for such potentials the quantities  $w_k(\mathbf{r})$  fall off at least as  $1/r$ . Since there must exist some  $k$  for which  $\nabla w_k(\mathbf{r})$  does not vanish everywhere, the second integral on the right must be non-zero. Thus the right-hand side of (10) cannot vanish everywhere for all values of  $k$ , and the densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  will become different infinitesimally later than  $t_0$ .

Note that the difference between  $n(x)$  and  $n'(x)$  is non-vanishing already in first order of  $v(x) - v'(x)$ , ensuring the invertibility of the linear response operators of section 4.

Since the density determines the potential up to a time-dependent constant, the wavefunction is in turn determined up to a time-dependent phase, which cancels out of the expectation value of any operator.

## 2.2 Kohn-Sham Equations

The Runge-Gross theorem can also be applied to a fictitious system of non-interacting electrons having the same density as the physical system, thereby establishing the *uniqueness* of the Kohn-Sham potential (but not its existence) for an arbitrary  $n(x)$ . Assuming  $v_s[n]$  exists, the density of the interacting system is

$$n(x) = \sum_{j=1}^N |\varphi_j(x)|^2, \quad (12)$$

with orbitals  $\varphi_j(x)$  satisfying the time-dependent KS equation

$$i \frac{\partial \varphi_j(x)}{\partial t} = \left( -\frac{\nabla^2}{2} + v_s[n](x) \right) \varphi_j(x) \quad (13)$$

We may then define the exchange-correlation potential as

$$v_{xc}[n](x) = v_s[n](x) - v(x) - v_H[n](x), \quad (14)$$

where  $v(x)$  is the external time-dependent field, and  $v_H[n](x)$  is the time-dependent Hartree potential generated by  $n(x)$ :

$$v_H(x) = \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \quad (15)$$

As in the static case, the great advantage of the time-dependent KS scheme lies in its computational simplicity compared to other methods such as time-dependent Hartree-Fock or time-dependent configuration interaction [46, 47, 48, 49, 50, 51, 52, 53]. In contrast to time-dependent Hartree-Fock, the effective single-particle potential  $v_s$  is a *local* potential, i. e., a multiplicative operator in configuration space, which, in principle, contains all correlation effects.

An important difference between ground-state density functional theory and the time-dependent formalism developed above is that in the time-dependent case the 1–1 correspondence between potentials and densities can be established only for a *fixed* initial many-body state  $\Psi_0$ , so that functionals depend implicitly on  $\Psi_0$ . However, if both  $\Psi_0$  and the initial KS determinant  $\Phi_0$  are non-degenerate ground states, then they are uniquely determined by the density, and all quantities are functionals of the density alone.

## 2.3 Stationary-action principle

At this point, it is customary to define an action functional, which has a stationary point at the solution of the time-dependent Schrödinger equation, with initial condition  $\Psi(t_0) = \Psi_0$ . A standard choice has been [7]:

$$\mathcal{A} = \int_{t_0}^{t_1} dt \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle \quad (16)$$

which may be considered as a functional of  $n(x)$ . Variation of this functional with respect to  $n(x)$  yields an Euler equation whose solution should yield the physical density. In the Kohn-Sham scheme,

$$\mathcal{A}_s = \int_{t_0}^{t_1} dt \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}_s(t) | \Psi(t) \rangle, \quad (17)$$

where  $H_s$  is the non-interacting Kohn-Sham Hamiltonian. An exchange-correlation action functional can then be readily identified as

$$\mathcal{A}_{xc}[n] = \mathcal{B}_s[n] - \mathcal{B}[n] - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}, t) n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (18)$$

where

$$\mathcal{B}[n] = \mathcal{A}[n] + \int_{t_0}^{t_1} dt \int d^3r n(x) v(x) \quad (19)$$

is the universal (i. e., potential-independent) contribution to  $\mathcal{A}$ , and likewise for  $\mathcal{B}_s$ . Employing these definitions and the Euler equation, we find

$$v_{xc}(x) = \delta \mathcal{A}_{xc} / \delta n(x). \quad (20)$$

However, some difficulties with the action defined as in (16) have been noticed (see section 4.1). Here we give a simple demonstration of the inadequacy of (16). Since the stationary

point satisfies the Schrödinger equation,  $\mathcal{A} = 0$  at this point. This is likewise true in the Kohn-Sham system, so that  $\mathcal{A}_s = 0$  also. Inserting the definitions of  $\mathcal{B}$  and  $\mathcal{B}_s$  into (18), and using the definition of the exchange-correlation potential, and the fact that  $\mathcal{A} = \mathcal{A}_s = 0$  at the stationary point, we find:

$$A_{xc}[n] = \int_{t_0}^{t_1} dt \int d^3r n(x) \{v_H[n](x)/2 + v_{xc}[n](x)\} \quad (21)$$

Functional differentiation of this suspiciously simple result yields a result which is only true for the one-electron case:

$$v_H(x) = - \int_{t_0}^{t_1} dt' \int d^3r' n(x') \frac{\delta v_{xc}(x)}{\delta n(x')} \quad (22)$$

From this simple exercise, we conclude that the definition of the action of (16) is inadequate.

Note that the same reasoning may be applied to the ground state problem, but with different results. The energy is analogous to the action, but in this case, the value of the energy at the minimum differs in the physical and KS systems, thereby avoiding the conundrum.

## 2.4 Relation to many-body theory

Van Leeuwen[33] has recently shown how to connect time-dependent density functional theory to the better-known language of many-body perturbation theory. However, because of the explicit time-dependence of the external potential, we are always dealing in non-stationary states, so that one cannot use the usual technique of time-ordered products and Wick's theorem[54]. This difficulty shows up whenever there is explicit time-dependence in the many-body problem, and Keldysh[55] devised a method used to get round it, by parametrizing the physical time  $t(\tau)$  with a pseudotime  $\tau$ .

Employing this formalism, one can derive the time-dependent Sham-Schlüter equation[32]:

$$\int dy' G(y, y') G_s(y', y) v_{xc}(y') = \int d^4y' \int d^4y'' G_s(y', y'') \Sigma_{xc}(y', y'') G(y'', y) \quad (23)$$

where  $y = (\mathbf{r}, \tau)$ ,  $\int d^4y = \int_{-\infty}^{\infty} d\tau dt/d\tau \int d^3r$ , and  $G(y, y')$  is the one-particle Green's function, with  $G_s$  its Kohn-Sham analog, while  $\Sigma_{xc}$  is the exchange-correlation contribution to the self-energy[33].

Van Leeuwen has also constructed an action functional which does not suffer the causality difficulty. In the Keldysh formalism, all response functions are symmetric in pseudotime, but become causal when transformed back to real time[56].

## 2.5 Explicit orbital dependence

Since the Kohn-Sham orbitals are implicit functionals of the density, we can consider the Kohn-Sham potential as an explicit functional of the orbitals, rather than of the density alone. The theory remains formally exact, but is written in a different way. Such a procedure can be useful for approximate functional development. In particular, with explicit orbital functionals, the exchange contribution becomes exact.

When the action is written as a functional of the orbitals, the condition used to determine the potential is  $\delta A/\delta v_s(x) = 0$ . Hence the name optimized effective potential (OEP), but we

emphasize that this potential is simply the usual Kohn-Sham potential. Here we do not give a derivation of the time-dependent OEP equations, but instead we just state the results:

$$\int_{-\infty}^{t_1} dt \int d^3r \left( G^{\text{ret}}(x, x') \sum_{j=1}^N \phi_j(x) \phi_j^*(x') [v_{xc}(x') - u_{xc,j}(x')] + c.c. \right) = 0, \quad (24)$$

where

$$u_{xc,j}(x) = \frac{1}{\phi_j^*(x)} \frac{\delta A_{xc}[\Phi]}{\delta \phi_j(x)}. \quad (25)$$

Here  $\Phi$  denotes the Kohn-Sham wavefunction, and the kernel  $G^{\text{ret}}(x, x')$  is the retarded one-particle Green's function of the system:

$$\{i\partial/\partial t - (-\nabla^2/2 + v_s(x'))\} G^{\text{ret}}(x, x') = \delta(x - x') \quad (26)$$

with initial condition  $G^{\text{ret}}(x, x') = 0$  for  $t' > t$ . Explicitly,

$$iG^{\text{ret}}(x, x') = \sum_{j=1}^{\infty} \phi_j^*(x) \phi_j(x') \Theta(t - t') \quad (27)$$

Note that the functions  $u_{xc,j}$  are given as functional derivatives of the exchange-correlation action. While the definition (16) has serious difficulties for other purposes, it appears to yield the correct results in this context.

The solution of these time-dependent OEP equations (with some approximation for  $A_{xc}[\Phi]$ ) is extremely computationally demanding. The Krieger-Li-Iafrate (KLI) approximation is very useful in this regard, because the error made in this approximation is expected to be so small relative to the errors made in functional approximations[36], that we can treat its results as 'exact.' By ignoring an orbital-dependent contribution which averages to zero over each orbital, one can rewrite the integral equation (24) so that it has an *analytic* solution for the exchange-correlation potential, Equation (22) of Ref. [44], which is used for practical calculations.

## 2.6 Spin-density functional theory

The above arguments can all be easily generalized to the common case of spin-density functional theory[7], in which the external field can differ for each of the two spin components along some fixed direction. This corresponds physically to the coupling to the spin of an electron of an external magnetic field which has only one non-zero component. Then we can establish a one-to-one mapping between spin densities  $n_{\uparrow}(x)$  and  $n_{\downarrow}(x)$  and potentials  $v_{\uparrow}(x)$  and  $v_{\downarrow}(x)$ , and all quantities can be considered functionals of the two spin densities, e.g., the Kohn-Sham potential is  $v_{s,\sigma}(x)[n_{\uparrow}, n_{\downarrow}]$ , where  $\sigma = \uparrow, \downarrow$ .

In analogy to the ground-state problem, when  $B = 0$ ,  $v_{\uparrow} = v_{\downarrow} = v$ , but the spin-dependent Kohn-Sham equations do not reduce to the regular Kohn-Sham equations, unless the system is spin-unpolarized. The great practical benefit of spin-density functional theory when  $B = 0$  is the improvement in accuracy of approximations for spin-polarized systems (e.g., local spin density approximation over local density approximation).

### 3 Exact Conditions

#### 3.1 Newton's third law

Consideration of the equation of motion for the  $\hat{\mathbf{r}}$  operator leads to [38, 57, 7]

$$\langle \hat{\mathbf{r}} \rangle = \frac{d^2}{dt^2} \int d^3r \mathbf{r} n(x) = - \int d^3r n(x) \nabla v_{\text{ext}}(x), \quad (28)$$

i.e., the net external exchange-correlation force must be zero. The analogous statement is true for the Kohn-Sham system, which must reproduce the same equation of motion. Then, from the relation between the Kohn-Sham and external potentials (14), and the fact that

$$\int d^3r n(x) \nabla v_{\text{H}}(x) = 0, \quad (29)$$

we find

$$\int d^3r n(x) \nabla v_{\text{xc}}(x) = 0. \quad (30)$$

Similarly, one obtains

$$\int d^3r n(x) \mathbf{r} \times \nabla v_{\text{xc}}(x) = 0, \quad (31)$$

i.e., the net exchange-correlation torque must vanish.

#### 3.2 Translational invariance

Consider a rigid boost  $\mathbf{X}(t)$  of a static density,  $n(\mathbf{r})$ . Then the exchange-correlation potential of the boosted static density will be that of the unboosted density, evaluated at the boosted point, i.e.,

$$v_{\text{xc}}[n](\mathbf{r}, t) = v_{\text{xc}}[n](\mathbf{r} - \mathbf{X}(t)), \quad n(\mathbf{r}, t) = n(\mathbf{r} - \mathbf{X}(t)), \quad \mathbf{X}(t_0) = 0 \quad (32)$$

This condition is universally valid [37]. It was first discovered [39] in the special case of a harmonic external potential driven by driving force  $\mathbf{F}(t)$ , where  $\mathbf{X}(t)$  is the classical motion of an oscillator under this driving force. This is the harmonic potential theorem [58], which is an extension of the generalized Kohn theorem [59].

### 4 Linear Response

Consider an external potential of the form

$$v_{\text{ext}}(x) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t) \Theta(t - t_0), \quad (33)$$

where  $\Theta(t) = 1$  for  $t > 0$ , but is zero otherwise, and assume that at times  $t \leq t_0$  the system is in the *ground state* corresponding to  $v_0(\mathbf{r})$ . In this case, the initial density  $n_0(\mathbf{r})$  can be obtained from the self-consistent solution of the static ground-state Kohn-Sham equations and, via the Hohenberg-Kohn theorem, the time-dependent density is a functional of the external potential alone,  $n[v_{\text{ext}}](x)$ . We expand this functional in a Taylor series in  $v_1(\mathbf{r}, t)$ :

$$n(x) = n_0(\mathbf{r}) + n_1(x) + \dots, \quad (34)$$

where the lower indices denote the orders in  $v_1$ . The first order density response  $n_1$  is given by

$$n_1(x) = \int d^4x \chi(x, x') v_1(x') \quad (35)$$

with the density-density response function

$$\chi(x, x') [n_0] = \frac{\delta n[v_{\text{ext}}](x)}{\delta v_{\text{ext}}(x')} \Big|_{n_0}. \quad (36)$$

The same reasoning applies to the Kohn-Sham system, yielding

$$\chi_{\text{s}}(x, x') [n_0] = \frac{\delta n[v_{\text{s}}](x)}{\delta v_{\text{s}}(x')} \Big|_{n_0[n_0]}, \quad (37)$$

which can be found by inverting the dependence  $v_{\text{s}}[n]$ , and can be expressed in terms of the static unperturbed Kohn-Sham orbitals  $\phi_k$ :

$$\chi_{\text{s}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{j,k} (f_k - f_j) \frac{\phi_j(\mathbf{r}) \phi_k^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}. \quad (38)$$

Here,  $(f_k, f_j)$  are the occupation numbers (0 or 1) of the KS orbitals. The summation in (38) ranges over both occupied and unoccupied orbitals, including the continuum states.

A Dyson-like equation may be derived between  $\chi$  and  $\chi_{\text{s}}$ . Using the chain rule, we write

$$\chi(x, x') = \int d^4x'' \frac{\delta n(x)}{\delta v_{\text{s}}(x'')} \frac{\delta v_{\text{s}}(x'')}{\delta v_{\text{ext}}(x')} \Big|_{n_0}. \quad (39)$$

We can write an expression of the second functional derivative above in terms of  $v_{\text{xc}}$  using its definition, (14):

$$\frac{\delta v_{\text{s}}(x)}{\delta v_{\text{ext}}(x')} \Big|_{n_0} = \delta(x - x') + \int d^4x'' \frac{\delta v_{\text{Hxc}}(x)}{\delta n(x'')} \frac{\delta n(x'')}{\delta v_{\text{ext}}(x')}. \quad (40)$$

where  $v_{\text{Hxc}} = v_{\text{H}} + v_{\text{xc}}$  and  $\delta v_{\text{H}}(x)/\delta n(x') = \delta(t - t')/|\mathbf{r} - \mathbf{r}'|$ . Insertion of this result into (39), and using the definitions of the physical and Kohn-Sham response functions, we find

$$\chi(x, x') = \chi_{\text{s}}(x, x') + \int d^4x_3 \int d^4x_4 \chi_{\text{s}}(x, x_3) \frac{\delta v_{\text{Hxc}}(x_3)}{\delta n(x_4)} \chi(x_4, x'). \quad (41)$$

This equation has the form of the time-dependent random phase approximation (RPA), and reduces to that approximation if  $\delta v_{\text{xc}}/\delta n$  is ignored.

From (41), we can extract the *exact* linear response of the physical system, by multiplying  $\chi$  by the perturbing potential, and integrating over  $x'$ , to find the self-consistent linear response equations:

$$n_1(x) = \int d^4x' \chi_{\text{s}}(x, x') v_{\text{s},1}(x'), \quad (42)$$

where

$$v_{\text{s},1}(x) = v_1(x) + v_{\text{H}}(x) + \int d^4x' \frac{\delta v_{\text{xc}}(x)}{\delta n(x')} [n_0] n_1(x') \quad (43)$$

consists of the external perturbation  $v_1$  and the Hartree- and exchange-correlation contributions to first order in the perturbing potential  $v_1$ .

The results here have been generalized to finite temperature in thermal equilibrium [60, 61].

#### 4.1 Exchange-correlation kernel

In these derivations, the quantity

$$f_{xc}(x, x') = \frac{\delta v_{xc}(x)}{\delta n(x')} \quad (44)$$

plays a key role, and is called the exchange-correlation kernel. In the theory of classical liquids [62],  $f_{\text{HXC}} = \delta v_{\text{HXC}}/\delta n$  is the Ornstein-Zernike function. The Fourier transform with respect to time of  $f_{xc}$  is

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} f_{xc}(\mathbf{r}, t; \mathbf{r}', 0) \quad (45)$$

and the relation to the static case is[7]

$$\lim_{\omega \rightarrow 0} f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}. \quad (46)$$

An exact formal representation of  $f_{xc}$  is readily obtained by solving (35) for  $v_1$  and inserting the result in (43):

$$f_{\text{HXC}}(x, x') = \chi_s^{-1}(x, x') - \chi^{-1}(x, x') \quad (47)$$

where  $\chi_s^{-1}$  and  $\chi^{-1}$  stand for the kernels of the corresponding inverse integral operators whose existence on the set of densities specified by (33) and (35) follows from (10), as mentioned in section 2.1.

As a consequence of causality,

$$f_{xc}(x, x') = 0 \quad \text{for } t' > t. \quad (48)$$

making  $f_{xc}$  asymmetric under interchange of  $x$  and  $x'$ . This is the difficulty in treating  $f_{xc}$  as a second functional derivative of the action defined by (16) in section 2.3.

#### 4.2 Exact conditions

The kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$  is an analytic function of  $\omega$  in the upper half of the complex  $\omega$ -plane and approaches a real function  $f_{xc}(\mathbf{r}, \mathbf{r}'; \infty)$  for  $\omega \rightarrow \infty$  [63]. Therefore, the function  $(f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - f_{xc}(\mathbf{r}, \mathbf{r}'; \infty))$  satisfies Kramers-Kronig relations:

$$\Re f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - f(\mathbf{r}, \mathbf{r}', \infty) = \mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega} \quad (49)$$

$$\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Re f_{xc}(\mathbf{r}, \mathbf{r}', \omega') - f_{xc}(\mathbf{r}, \mathbf{r}'; \infty)}{\omega' - \omega}. \quad (50)$$

Also, since  $f_{xc}(x, x')$  is real-valued,

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}^*(\mathbf{r}, \mathbf{r}'; -\omega). \quad (51)$$

Besides that, the response functions  $\chi_s$  and  $\chi$  satisfy the symmetry relations [64]

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \chi(\mathbf{r}', \mathbf{r}; \omega) \quad (52)$$

provided that the unperturbed system has time-reversal symmetry. Equation (47) then implies that

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}(\mathbf{r}', \mathbf{r}; \omega). \quad (53)$$

The exact conditions on the potential of section (3) also yield conditions on  $f_{xc}$ , when applied to an infinitesimal perturbation. Taking functional derivatives of (30) and (31) yields

$$\int d^3r' n(\mathbf{r}) \nabla f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = -\nabla' v_{xc}(\mathbf{r}') \quad (54)$$

and

$$\int d^3r' n(\mathbf{r}) \mathbf{r} \times \nabla f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = -\mathbf{r}' \times \nabla' v_{xc}(\mathbf{r}'). \quad (55)$$

Taking  $\int d^3r' n(\mathbf{r}')$  of each side, and using (30) and (31) once again, yields

$$\int d^3r' \int d^3r n(\mathbf{r}) n(\mathbf{r}') \nabla f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = 0 \quad (56)$$

and

$$\int d^3r' n(\mathbf{r}) \int d^3r' n(\mathbf{r}') \mathbf{r} \times \nabla f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = 0. \quad (57)$$

These equations place strong restrictions on the frequency dependence of  $f_{xc}$ , since the right hand sides are all frequency independent[38].

#### 4.3 Explicit orbital-dependence

One can also consider the linear response regime of the OEP equations, and ask what integral equation  $f_{xc}$  satisfies[27]. This turns out to be identical to the OEP equation itself, (24), but with  $v_{xc}(x)$  replaced by  $f_{xc}(x, x')$  and  $v_{xc,j}(x)$  replaced by  $g_{xc,j}(x, x')$ , where

$$g_{xc,j}(x, x') = \left[ \frac{1}{\phi_j^*(x')} \frac{\delta v_{xc}(x)}{\delta \phi_j(x')} \right]_{\{\phi_k(\mathbf{r}) \exp(-i\epsilon_k(t-t_0))\}} \quad (58)$$

and the  $\{\phi_k(\mathbf{r})\}$  are the ground-state Kohn-Sham orbitals. Thus  $g_{xc,j}$  involves a straightforward functional derivative of  $v_{xc}$ , but evaluated on the time-evolved ground-state Kohn-Sham orbitals.

#### 4.4 Tensor exchange-correlation kernel

This scalar linear response theory may be easily generalized to the time-dependent current response  $\mathbf{j}(x)$  to a vector potential  $\mathbf{a}_1(x)$  [65, 40]. Following the reasoning above, we find

$$\mathbf{j}_1(\mathbf{r}, \omega) = \int d^3r' \chi_s(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{a}_{s,1}(\mathbf{r}', \omega), \quad (59)$$

where

$$\mathbf{a}_{s,1} = \mathbf{a}_1 + \mathbf{a}_{\text{H}} + \mathbf{a}_{xc} \quad (60)$$

is the Kohn-Sham vector potential,

$$\mathbf{a}_{\text{H}} = \frac{1}{(i\omega)^2} \int d^3r' \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla' \cdot \mathbf{j}_1(\mathbf{r}', \omega) \quad (61)$$

is the longitudinal vector Hartree potential, and

$$\mathbf{a}_{xc}(\mathbf{r}, \omega) = \int d^3r' \mathbf{f}_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{j}_1(\mathbf{r}'; \omega) \quad (62)$$

is a linear functional of  $\mathbf{j}_1$ . The boldface  $\chi$  and  $\mathbf{f}_{xc}$  indicates that these are now  $3 \times 3$  tensors. The tensor exchange-correlation kernel is

$$\mathbf{f}_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - \nabla \otimes \frac{\nabla'}{|\mathbf{r} - \mathbf{r}'|} \quad (63)$$

where  $\otimes$  denotes the outer product of two vectors, and the Kohn-Sham susceptibility tensor is

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \mathbb{1} + \sum_{j,k} (f_j \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \nabla \phi_k^*(\mathbf{r}) \otimes \nabla \phi_k(\mathbf{r}')) \frac{\omega - (\epsilon_j - \epsilon_k) + i\eta}{\omega - (\epsilon_j - \epsilon_k) + i\eta} \quad (64)$$

This generalization is necessary for the construction of a local density type approximation for time-dependent problems, as in section 5.4.

#### 4.5 Homogeneous gas

In order to investigate  $f_{xc}$  for the uniform gas, we consider (47) in the uniform case. Fourier transformation with respect to  $(\mathbf{r} - \mathbf{r}')$  and  $(t - t')$  leads to

$$f_{xc}^{\text{unif}}(n, q; \omega) = \frac{1}{\chi_s^{\text{unif}}(n, q; \omega)} - \frac{1}{\chi^{\text{unif}}(n, q; \omega)} - \frac{4\pi}{q^2} \quad (65)$$

where  $\chi_s^{\text{unif}}$  is the Lindhard function[54]. In the theory of the uniform electron gas [63, 66, 67, 68]  $f_{xc}^{\text{unif}}(q, \omega)$  is proportional to the local field correction

$$\mathcal{G}(q, \omega) = -\frac{q^2}{4\pi} f_{xc}^{\text{unif}}(q, \omega). \quad (66)$$

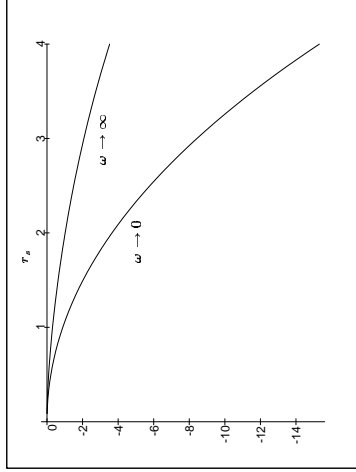


Fig. 3.  $f_{xc}^{\text{unif}}(q=0, \omega \rightarrow 0)$  and  $f_{xc}^{\text{unif}}(q=0, \omega \rightarrow \infty)$  as functions of  $r_s$ .

We focus here on the limit  $q \rightarrow 0$ , as this is used in the Gross-Kohn approximation (see section 5.2). Writing

$$f_\omega(n) = \lim_{q \rightarrow 0} f_{xc}^{\text{unif}}(q, \omega), \quad (67)$$

then  $f_0(n)$  is known from the compressibility sum-rule, while  $f_\infty(n)$  is known from the third frequency-moment sum rule[42], each in terms of the accurately-known uniform gas exchange-correlation energy[69]. We plot these functions in Fig. 3. Furthermore, the imaginary part of  $f_{xc}^{\text{unif}}$  exhibits the high-frequency behavior

$$\lim_{\omega \rightarrow \infty} \Im f_{xc}^{\text{unif}}(q, \omega) = -\frac{c}{\omega^{3/2}} \quad (68)$$

for any  $q < \infty$  [70]. A second-order perturbation expansion [70, 71] of the irreducible polarization propagator leads in the high-density limit to  $c = 23\pi/15$ , while others [72, 73] find double this value; see also Ref. [74]. Some exact features of  $\chi^{\text{unif}}$  are known, which lead to some exact properties of  $f_{xc}^{\text{unif}}$ . Many of the corresponding properties for  $q \rightarrow \infty$  are also known[7].

Taking into account the exact high- and low-frequency limits, Gross and Kohn [41] proposed the following smooth interpolation for  $f_\omega(n)$ :

$$\Im f_\omega(n) = -c \frac{\omega^{5/3}(n)}{(1 + \alpha^{A/3}(n) \omega^{2/5})^4}, \quad (69)$$

where

$$\alpha(n) = (\gamma/c)(f_\infty(n) - f_0(n)), \quad (70)$$

and  $\gamma = (r_s(1/4))^2/(4\sqrt{2}\pi)$ . The real part can then be found in terms of elliptic integrals using the Kramers-Kronig relation (49). An extension of the parametrization (69) to non-vanishing  $q$  was given by Dabrowski [75]. The spin-dependent case was treated by Liu[76]. A similar interpolation for the exchange-correlation kernel of the 2-dimensional electron gas has been derived by Holas and Singwi[70].

More recently, Böhm, Conti, and Tosi[77, 78] have calculated  $f_{xc}^T(\omega)$  within several different approximations for the uniform gas. They find that two-plasmon processes induce a strong peak in the imaginary part just above twice the plasmon frequency, leading to highly nonmonotonic behavior in the real part. The resulting frequency dependence is very different from the smooth interpolation of (69).

Lastly, we discuss the response of the uniform gas to the vector potential of section 4.4. In the limit of small wavevector  $q$ , i.e.,  $q \ll k_F$  and  $q \ll \omega/v_F$ ,

$$\mathbf{f}_{xc}^{\text{unif}}(\mathbf{q}, \omega) = \omega^{-2} [f_\omega(n) \mathbf{q} \otimes \mathbf{q} + f_\omega^T(n)(q^2 \mathbb{1} - \mathbf{q} \otimes \mathbf{q})], \quad (71)$$

where  $f_\omega^T(n)$  is the transverse exchange-correlation long wavelength response function of the uniform gas. Thus the exchange-correlation vector potential of a uniform gas in response to a slowly varying perturbation is

$$\mathbf{a}_{xc}^{\text{unif}}(\mathbf{r}, \omega) = \omega^{-2} \{ \nabla [f_\omega(n) \nabla \cdot \mathbf{j}_1(\mathbf{r}, \omega)] - \nabla \times [f_\omega^T(n) \nabla \cdot \mathbf{j}_1(\mathbf{r}, \omega)] \}. \quad (72)$$

The behavior of the transverse kernel  $f_\omega^T(n)$  is also known in the limits  $\omega \rightarrow 0$  [79] and  $\omega \rightarrow \infty$  [40]. Conti, Nifosi, and Tosi have calculated this transverse component, again finding strong structure around twice the plasmon frequency[79].



## 5 Approximate functionals

In this section, we sketch the historical evolution of functional approximations for  $v_{xc}$  and  $f_{xc}$ . This illustrates how exact conditions are used to refine and sophisticate approximate functionals. What is perhaps lacking is more calculational comparison between these various functionals. After all, the simplest approximation (ALDA) satisfies all exact conditions except, oddly enough, recovery of the frequency-dependent response of the uniform gas.

### 5.1 Adiabatic local density approximation

The simplest possible approximation of the time-dependent exchange-correlation potential is the adiabatic local density approximation (ALDA). It employs the functional form of the static LDA with a time-dependent density:

$$v_{xc}^{\text{ALDA}}[n](x) = v_{xc}^{\text{unif}}(n(x)) = \frac{d}{d\rho} (\rho \epsilon_{xc}^{\text{unif}}(\rho)) \Big|_{\rho=n(x)}. \quad (73)$$

Here  $\epsilon_{xc}^{\text{unif}}$  is the accurately known exchange-correlation energy per particle of the uniform electron gas. Naively, one might expect ALDA to be a good approximation only for nearly uniform densities, i.e., for functions  $n(x)$  that are slowly varying both spatially and temporally. However, for the ground-state energy, LDA is moderately accurate for almost all systems[80], so there is room for optimism. For the time-dependent exchange-correlation kernel of (44), (73) leads to

$$f_{xc}^{\text{ALDA}}[n_0](x, x') = \delta(x - x') \frac{d^2}{d\rho^2} (\rho \epsilon_{xc}^{\text{unif}}(\rho)) \Big|_{\rho=n_0(\mathbf{r})}. \quad (74)$$

The time Fourier-transform of the kernel has no frequency-dependence at all. This is not such a bad thing, as it means that translational invariance, (32), is satisfied, although in a rather crude fashion.

### 5.2 Frequency-dependent LDA

In order to incorporate the frequency-dependence of  $f_{xc}$  in some approximate fashion, Gross and Kohn[41] suggested using the frequency-dependent exchange-correlation kernel  $f_{xc}^{\text{unif}}$  of the uniform electron gas in a local approximation:

$$f_{xc}^{\text{LDA}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}^{\text{unif}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega). \quad (75)$$

The LDA of non-local quantities, such as response functions, always involves some ambiguity[2] as to where the inhomogeneous  $n_0(\mathbf{r})$  is to be evaluated. To avoid this, Gross and Kohn[41] treated the case where  $n_1(\mathbf{r}, \omega)$  is slowly varying on the length scale given by the range of  $f_{xc}^{\text{unif}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega)$ . The change in the exchange-correlation potential is then

$$v_{xc}(\mathbf{r}, \omega) = n_1(\mathbf{r}, \omega) \int d^3r' f_{xc}^{\text{unif}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega). \quad (76)$$

Thus the Gross-Kohn approximation may be written as

$$f_{xc}^{\text{GK}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') f_{xc}^{\text{unif}}(n_0(\mathbf{r}), q = 0; \omega), \quad (77)$$

whereas ALDA uses the zero-frequency limit of this kernel for all  $\omega$ . As we see in the next two sections, the GK approximation, by incorporating the full frequency dependence of the uniform gas exchange-correlation kernel, violates several of the exact conditions developed in section 3.

### 5.3 Following a fluid element

The difficulties with the frequency-dependent LDA of Gross and Kohn were first noted by Dobson[39]. Harmonic potential motion causes a static ground-state density to be rigidly boosted, as discussed in section 3.2, leading to a response kernel with no frequency dependence. This suggested the following general property of the time-evolution of an inhomogeneous system (in the linear response regime). Consider a fluid element at  $x = (\mathbf{r}, t)$ . It has evolved from an element at  $x'$ , where  $t' < t$ , and in general,  $\mathbf{r}' \neq \mathbf{r}$ . The position  $\mathbf{r}'$  of the fluid element at earlier  $t'$  is determined by the differential equation:

$$\dot{\mathbf{r}} = \mathbf{u}(x') = \mathbf{j}(x')/n(x') \quad (78)$$

where the dot denotes a time derivative, and  $\mathbf{u}(x)$  is the fluid velocity, with initial condition  $\mathbf{r}'_{t'=t} = \mathbf{r}$  (not to be confused with  $v_{xc,i}$ ). This uniquely determines the fluid displacement history. The linearized continuity equation (9) then yields

$$\dot{n}_1(x) = \dot{n}_1^{\text{comp}}(x) + \dot{n}_1^{\text{rigid}}(x) = -n_0(\mathbf{r}) \nabla \cdot \mathbf{u}(x) - \mathbf{u}(x) \cdot \nabla n_0(\mathbf{r}). \quad (79)$$

The first term above is the compressive component of the fluid motion, which comes from changes in the velocity distribution of the fluid. The second term originates from the rigid translation of the fluid, without any changes in the velocity distribution, such as occurs in the boost described in translational invariance. Thus the response to the compressive component should be frequency-dependent, but not that of the rigid component, i.e.,

$$v_{xc}(\mathbf{r}, \omega) = f_{\omega}(n_0(\mathbf{r})) n_1^{\text{comp}}(\mathbf{r}, \omega) + f_{\omega=0}(n_0(\mathbf{r})) n_1^{\text{rigid}}(\mathbf{r}, \omega). \quad (80)$$

Clearly, for the boosts used in translational invariance,  $n_1^{\text{comp}} = 0$ , while this ansatz is also exact for the response of the uniform gas, where  $n_1^{\text{rigid}} = 0$ .

### 5.4 Local current-density approximation – LCDA

Consider applying (54) to a slowly varying density, so that  $f_{xc}$  could be replaced by its uniform electron gas limit, which is known to be short-ranged. Then we find

$$f_{xc}^{\text{unif}}(q = 0, \omega, n(\mathbf{r})) \nabla n(\mathbf{r}) = \nabla v_{xc}(\mathbf{r}), \quad (81)$$

which is impossible, as the left-hand-side is frequency dependent, while the right is not. Thus  $f_{xc}$  for an inhomogeneous system is long-range in space and a nonlocal functional of the density[38].

Using the current density formalism, Vignale and Kohn[40] have shown how to overcome this difficulty, and produce a semilocal current-density approximation. Consider an almost uniform gas, where the deviations are both small and slowly-varying:

$$n_0(\mathbf{r}) = n [1 + 2\gamma \cos(\mathbf{q}_1 \cdot \mathbf{r})], \quad (q_1 \ll k_F, \omega/k_F; \gamma \ll 1). \quad (82)$$

VK deduce an analytic expression for  $\mathbf{f}_{\text{xc}}$  to first order in  $\gamma$ , by using (56) and (57) and the Ward identity. This contrasts with the scalar version, in which  $f_{\text{xc}}(\mathbf{q} + \mathbf{q}_1, \mathbf{q}; \omega)$  has a singularity of the form  $\mathbf{q} \cdot \mathbf{q}_1/q^2$  as  $q \rightarrow 0$  at finite  $q_1$ , which causes the long-rangedness and non-locality of the scalar case. These effects do not show up here, as the tensor  $\mathbf{f}_{\text{xc}}$  contains only differences and derivatives of  $f_\omega(n)$  values.

Next, VK consider the problem of determining  $\mathbf{a}_{\text{xc}}$  for a slowly-varying inhomogeneity, but which may have large global deviations from uniformity, and deduce the general form in terms of gradients of the density and current, up to two gradient operators. Then they equate these results to the perturbative ones mentioned above, in the same way as the gradient expansion coefficients have been found in the ground-state problem[81]. Some contributions of order  $\gamma^2$  are not fixed by this comparison, but are fixed by requiring translational invariance (32). They give an explicit formula for the exchange-correlation vector potential in terms of  $n(x)$  and  $\mathbf{j}_1(x)$  and their gradients, with coefficients determined by  $f_\omega$  and  $f_\omega^\pi$  [40].

In the case where  $|\nabla n_1/n| \ll q$ , they recover the GK result, while in the case of a parabolic well and uniform perturbing electric field, they recover (80), thereby justifying that ansatz under those conditions.

Finally, note that this analysis applies only for  $\omega \gg k_F q$ , i.e., high frequency response, for which ALDA is not justified. A complete local current density response theory for all frequencies remains to be developed.

Very recently[82], the VK result has been simplified, as

$$-i\omega \mathbf{a}_{\text{xc}} = -\nabla v_{\text{xc}}^{\text{ALDA}} + \frac{1}{n_0(\mathbf{r})} \nabla \sigma_{\text{xc}}(\mathbf{r}, \omega) \quad (83)$$

where

$$\sigma = \tilde{\eta}_{\text{xc}} \left( \nabla \otimes \mathbf{u} + \mathbf{u} \otimes \nabla^{\leftarrow} - \frac{2}{3} \nabla \cdot \mathbf{u} \mathbf{1} \right) + \tilde{\zeta}_{\text{xc}} \nabla \cdot \mathbf{u} \mathbf{1} \quad (84)$$

is a visco-elastic stress tensor with complex viscosity coefficients which are simply related to  $f_\omega(n)$  and  $f_\omega^\pi(n)$ . For sufficiently slowly varying densities, these expressions yield the nonlinear response also[82].

### 5.5 Local-with-memory density approximation – LMDA

Some recent work goes way beyond the linear response regime, while being constrained to respect all the exact conditions discussed here. The ansatz suggested is[43]

$$\mathbf{F}_{\text{xc}}(x) = -\nabla v_{\text{xc}}(x) = -\frac{1}{n(x)} \nabla \int_{-\infty}^{\infty} dt' II_{\text{xc}}(n(\mathbf{r}'_t(x')), t-t'), t-t' \quad (85)$$

where  $\mathbf{F}_{\text{xc}}$  is the exchange-correlation force, and  $II_{\text{xc}}(n, \tau)$  is a pressure-like scalar local memory function of  $n$  and  $\tau$ , where  $\mathbf{r}'_t(x)$  is the fluid displacement function. Thus locality is defined relative to the fluid element, rather than to a fixed position  $\mathbf{r}$ . This LMDA is the natural generalization of LDA from the static case.

To see explicitly that (85) satisfies translational invariance (32), note that under a rigid boost  $\mathbf{X}(t)$ , the many-body wavefunction also moves rigidly, so that  $\mathbf{j}(x) = n_0(\mathbf{r} - \mathbf{X}(t))\mathbf{X}$ ,

and  $\mathbf{u}$  is independent of  $\mathbf{r}$ . Thus  $\mathbf{r}'_t = \mathbf{r} + \mathbf{X}(t) - \mathbf{X}(t)$ , and

$$\mathbf{F}_{\text{xc}}(x) = -\frac{1}{n(x)} \nabla II_{\text{xc}}(n_0(\mathbf{r} - \mathbf{X}(t)), \omega = 0) = \mathbf{F}_{\text{xc}}[n_0](\mathbf{r} - \mathbf{X}(t)), \quad (86)$$

satisfying (32).

Interestingly, the function  $II_{\text{xc}}(n, \omega)$  is fully determined by requiring it to reproduce the scalar linear response of the uniform gas. Consider small motions at frequency  $\omega$  in a uniform gas of density  $n$ . One finds the simple condition

$$\delta II_{\text{xc}}/\delta n = n f_\omega(n) \quad (87)$$

which implies

$$II_{\text{xc}}(n, \omega) = \int_0^n dn' n' f_\omega(n'). \quad (88)$$

Thus any parametrization of  $f_{\text{xc}}^{\text{unif}}$  of section 4.5 fixes  $II_{\text{xc}}$ .

Note that (85) defines the exchange-correlation force, rather than potential. For a one-dimensional inhomogeneity, one can simply integrate this force up to a point to determine the potential. Thus this scheme recovers the exact VK result for the slowly varying one-dimensional perturbation. In the more general three-dimensional case, work is continuing.

### 5.6 Expansion in powers of $e^2$

An alternative route to useful approximations is in powers of the Coulomb repulsion. To lowest order, one gets the time-dependent exchange-only density functional theory, which is most easily expressed in the OEP formalism, since the exchange action is an explicitly orbital-dependent functional:

$$u_{x,j}(x) = -\frac{1}{\phi_j^*(x)} \sum_{i=1}^N \int d^3r' \frac{\phi_i^*(\mathbf{r}', t) \phi_i(\mathbf{r}', t) \phi_i(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \quad (89)$$

This can be derived either by inserting the exchange action into the OEP equations[44], or directly from the Sham-Schlüter equation[33], expanded to first-order. These equations are computationally similar to the time-dependent Hartree-Fock equations, but their solution has one very important practical advantage over Hartree-Fock. The unoccupied orbitals in exchange-only density functional theory suffer no self-interaction error, whereas those in HF see  $N$  remaining occupied orbitals. This feature is not so important in the ground-state problem, but is very significant in time-dependent and excited-state problems.

One can also imagine going to higher order in  $e^2$ , via the Sham-Schlüter equation (23), to get ever more accurate results. Of course, for extended systems such as metals, one must include all orders within the random-phase approximation, to avoid blatantly unphysical results, just as in the ground-state problem.

For practical calculations, one can make a simple analytic approximation to the KLI exchange-correlation potential, which we denote PGG[26]:

$$v_{\text{xc}}^{\text{PGG}}(x) = \sum_{j=1}^N \frac{|\phi_j(x)|^2}{n(x)} [u_{\text{xc},j}(x) + c.c.] \quad (90)$$

which comes about by retaining only the dominant contribution. This leads to a simple analytic form for the exchange-correlation kernel:

$$f_{xc}^{PGG}(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{\left| \sum_{j=1}^N \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \right|^2}{2 n(\mathbf{r}) |\mathbf{r} - \mathbf{r}'| n(\mathbf{r}')} \quad (91)$$

This approximate form is exact for exchange for two-electron spin-unpolarized systems. For more than two electrons, even at the exchange-only level, the exchange-correlation kernel has some frequency dependence.

## 6 Applications, Including Excitation Energies

### 6.1 Way beyond the linear response regime: Atoms in short laser pulses

Recently, experiments have been performed in which atoms are subjected to very intense, femto-second laser pulses. The external potential is then

$$v(x) = -\frac{Z}{r} + E_o f(t) z \sin(\omega_0 t), \quad (92)$$

where  $Z$  is the nuclear charge,  $E_o$  is the electric field of the laser, and  $f(t)$  is the envelope function of the pulse.

In these experiments, the strength of the perturbation is comparable to the static field of the nucleus, so that linear response theory is simply inadequate. The full time-dependent Kohn-Sham equations are solved, and two quantities extracted from the self-consistent density. The induced dipole moment

$$d(t) = \int d^3r z n(x) \quad (93)$$

whose Fourier transform,  $d(\omega)$ , when squared, is proportional to the harmonic spectrum, i.e., the intensity distribution of emitted photons as a function of their frequency. Also, decreases in the norm of the single-particle Kohn-Sham orbitals in a finite volume

$$N_j(t) = \int_V d^3r |\phi_j(x)|^2 \quad (94)$$

where  $V$  is a finite volume, can be loosely equated with the probability of ionization of an electron from a given orbital. Calculations of these quantities have been performed for Be[44] and Ne[18] subjected to single frequency laser, and for He subjected to two-color lasers[18, 20]. Most recently, the formalism has been extended to include the nuclear motion as well[20], which must be treated fully quantum mechanically when the nuclear probability densities do not stay in a tight classical distribution during the motion. It is also important to include the motion of *all* electrons in the outermost shell[20], which is not done in the single active electron (SAE) model in the traditional wavefunction approach [83].

### 6.2 Linear Response and a Little Beyond

Many applications of time-dependent density functional theory have been in the linear response regime[16]. Calculations of photoresponse have been performed on atoms[21, 84, 85, 86, 87, 88], molecules [89, 90] and clusters [91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101] metallic surfaces[22, 23, 24, 25, 102, 103, 104] and semiconductor heterostructures[105, 106, 107, 108, 109] bulk semiconductors [110] and bulk metals[111, 112, 113, 114].

For sufficiently long wavelengths, the electric field experienced by the system is spatially uniform, and the dipole approximation holds. For a finite system, the dynamic polarizability is

$$\alpha(\omega) = -\frac{2}{E} \int d^3r z n_1(\mathbf{r}, \omega) \quad (95)$$

and the photoabsorption cross section is

$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im\alpha(\omega). \quad (96)$$

Most calculations of this kind have used the ALDA in the past, with reasonably good results. A similar formula defines the Feibelman  $d$ -parameter,  $d_{\perp}(\omega)$ , which characterizes the surface response in the long-wavelength limit and determines, e.g., the initial dispersion of the surface plasmon[115].

Another off-shoot of these calculations is the question of incorporating van der Waals forces into density functional approximations. Because these forces arise from *dynamic* fluctuations at separated points in the system, there is no (transparent) way to build them into a local or semilocal (GGA) ground-state exchange-correlation energy functional (but see [9, 10]). A more natural language is that of dynamic linear response. Thus approximations for  $\alpha(\omega)$  lead to predictions for  $C_6$ , the coefficient of the  $1/R^6$  attractive potential between two widely separated neutral species[116, 8], or the  $C_3$  coefficient of the  $1/R^3$  potential between an atom and a surface[117, 118]. Furthermore, some approximation for  $f_{xc}$ , inserted in the linear response formula and then inserted in the adiabatic connection formula for the exchange-correlation energy, will produce an energy estimate which includes van der Waals forces, at both small and large separations[11].

Senatore and Subbaswamy [119] have found explicit expressions for the response up to third order, while Gonze and Vigneron [120] have calculated the static case. Recently[7], it has been shown how to go to arbitrarily higher order response functions, order-by-order. Interestingly, the  $k$ -th order density response satisfies an integral equation whose kernel is independent of  $k$ , i.e., is the same for *any* order, but whose driving term depends on all  $k - 1$  lower order solutions:

$$n_k(x) = M_k(x) + \int d^3x' \chi_s(x, x') f_{\text{fixc}}(x', x'') n_k(x''). \quad (97)$$

(This corrects Eq. (185) of Ref. [7], which contains typographical errors.) Therefore once the first-order response is found, the next can be found by the same means, once the driving term is constructed.

### 6.3 Excitation Energies

The linear response of any system can be used to determine its excitation energies. Simply apply an oscillating potential and vary its frequency, and a resonance occurs whenever the frequency equals the difference of two energy eigenvalues of the system. This familiar physical statement can be used to great effect in time-dependent density functional theory, since the exact susceptibility  $\chi$  must therefore contain poles at the exact excited state energy differences. To see this explicitly, we rewrite (42) and (43) as an integral equation for the first-order density response in terms of only the Kohn-Sham susceptibility and the exchange-correlation kernel:

$$\begin{aligned} \int d^3r' \left\{ \delta(\mathbf{r} - \mathbf{r}') - \int d^3r'' \chi_s(\mathbf{r}, \mathbf{r}''; \omega) f_{\text{HXC}}(\mathbf{r}', \mathbf{r}''; \omega) \right\} n_1(\mathbf{r}', \omega) \\ = \int d^3r' \chi_s(\mathbf{r}, \mathbf{r}'; \omega) v_1(\mathbf{r}', \omega) \end{aligned} \quad (98)$$

where the driving term contains the *external* potential. Since the true excitation energies  $\Omega$  are generally not identical to the Kohn-Sham excitation energies, the right-hand-side remains finite as  $\omega \rightarrow \Omega$ , whereas  $n_1$  has a pole at  $\Omega$ . The operator acting on  $n_1$  cannot be invertible here, so its eigenvalues must vanish, i.e., writing

$$\int d^3r' \int d^3r'' \chi_s(\mathbf{r}, \mathbf{r}'; \omega) f_{\text{HXC}}(\mathbf{r}', \mathbf{r}''; \omega) \zeta(\mathbf{r}'', \omega) = \lambda(\omega) \zeta(\mathbf{r}, \omega) \quad (99)$$

we have  $\lambda(\Omega) = 1$ . This is an exact condition for determining the excitation energies of the system.

In practice, we usually don't want the full frequency-dependence of the functions in (99), which contain a vast amount of information on the response of the system. In the case where the poles are well-separated, we make a single-pole approximation (SPA), where we expand everything about a single Kohn-Sham energy difference, assuming the difference between the true excitation frequency and the Kohn-Sham one is smaller than the difference between energy levels[26]. We then find

$$\Omega = \omega_{jk} + 2\mathcal{R}(f_k - f_j) \int d^3r \int d^3r' \phi_j^*(\mathbf{r}) \phi_k^*(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'; \omega) \phi_j(\mathbf{r}') \phi_k(\mathbf{r}') \quad (100)$$

This expression estimates the leading correction to the Kohn-Sham eigenvalues as excited state energies. It was used[30] to calculate the energies displayed in Fig. 2, starting from the exact Kohn-Sham orbitals, and using the self-interaction corrected adiabatic local density approximation for the exchange-correlation kernel.

These formulas have been applied to excited state calculations for atoms with considerable success[26], in the sense that the excitation energies are always improved, often significantly. The Kohn-Sham eigenvalues do not distinguish between the spin states of the excited states. When the excited state is degenerate at the Kohn-Sham level, the correction usually splits this degeneracy. In particular, the spin-dependent version of (100) yields the separate singlet and triplet levels, raising the singlet and lowering the triplet[28]. It is important to begin with a good approximation to  $v_{\text{XC}}(\mathbf{r})$  for the ground-state, since the orbital energies, especially of the higher lying states, are very sensitive to the decay of the potential[27]. Beyond that, the time-dependent X-only approximation to  $f_{\text{XC}}$  is usually better than  $f_{\text{XC}}^{\text{ALDA}}$ , while the correlation correction within ALDA is usually in the right direction.

Other routes to excited state energies are also being explored, such as ensemble DFT[121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131],  $\Delta$ SCF theory[132, 133, 134], and Göling-Levy perturbation theory[135, 136]. It remains to be seen which will provide the best approach to the problem. Very likely, each of the various approaches will suggest its own approximations, etc., and be useful in its own way.

## 7 Outlook

The purpose of this chapter has been to review the current state of time-dependent density functional theory, especially for those who are more familiar with the traditional ground-state formulation and applications.

We believe that this subject is about to see an exponential growth in interest, as practical approximations are currently appearing and being developed, which should lead to applications in areas of chemistry[137], such as laser-induced photochemistry[138]. We anticipate that ultimately it will reach the same level of development and application as the ground-state theory currently enjoys, in both physics and chemistry.

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