

# Chapter 8

## Memory: History, Initial-State Dependence, and Double-Excitations

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### 8.1 Introduction

In ground-state DFT, the fact that the xc potential is a functional of the density is a direct consequence of the one-to-one mapping between ground-state densities and potentials. In TDDFT, the one-to-one mapping is between densities and potentials for a given initial state. This means that the potentials, most generally, are functionals of the initial state of the system, as well as of the density; and, not just of the instantaneous density, but of its entire history. These dependences are explicitly displayed in Eq. 4.28. Of particular interest is the xc potential, as that is the quantity that must be approximated. The Hartree potential has no memory, as the classical Coulomb interaction depends on the instantaneous density only, but since both the interacting and non-interacting mappings can depend on the initial state, the xc potential must be a functional of both the initial states and the density.

We use the term memory to refer to the dependence on quantities at earlier times: initial-state dependence and history-dependence of the density.

In a sense, memory arises because of the reduced nature of the density as a basic variable: if the wave function of the system was known, there would be no memory-dependence, since the wavefunction at time  $t$  contains the complete information about the system at time  $t$ , from which we can determine any observable. The density however traces out much of the information, desirably reducing the description involving  $3N$  spatial variables plus time to a description using three variables plus time. Analogously to the theories of open systems, from this tracing out of degrees of freedom emerges memory dependence. In treating open systems bath degrees of freedom are traced out to get a reduced description in terms of system variables only (see Chaps. 10 and 11): the effect of the bath is embodied in an influence functional

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that is non-local in time. Much like in open system theory with a low-dimensional bath, the TDDFT memory of early history persists at long times: time does not wash it away (as it would if we were tracing out a bath of a continuous spectrum).

In linear response, e.g. calculating spectra, (Chaps. 4 and 7) the system starts in its ground-state, which, by virtue of the Hohenberg–Kohn theorem, is itself a functional of its own density, assuming it is non-degenerate. Initial-state dependence is not explicitly needed in the functionals, provided that the functional space is reduced to that where the initial state is a non-degenerate ground state. The exact xc kernel has history-dependence, which translates into non-trivial frequency-dependence when a time-frequency Fourier transform is done.

In an adiabatic approximation, as discussed in Chap. 4, memory-dependence is completely neglected: the instantaneous density is input as a “ground-state” density into a ground-state xc potential approximation. In fact, even before Runge and Gross (RG) formally established their theory, adiabatic calculations of optical spectra were performed, that plugged the instantaneous density into the LDA (Ando 1977a, b; Zangwill and Soven 1980a, 1981); this is the ALDA, Eq. 4.100. The xc kernel in an adiabatic approximation is proportional to a  $\delta(t-t')$  (Eq. 4.86a), which, upon Fourier transforming, yields a frequency-independent xc kernel. Since the inception of the RG theorem, there have been attempts to develop functionals with some memory dependence, with varying degrees of success and applicability. The earliest and simplest is the Gross–Kohn approximation (GK) for the xc kernel (Gross and Kohn 1985, 1990). Considering densities that are slowly varying in space, GK bootstraps the local density approximation to finite frequencies, i.e. the frequency-dependent kernel is approximated via the homogeneous electron gas response at finite frequency (Eq. 4.107), a spatially-local but time-nonlocal kernel. In the mid-nineties, it was realized, however, that a theory that depends on the density non-locally in time must also depend on it non-locally in space; otherwise, exact conditions, importantly the harmonic potential theorem, are violated (Vignale 1995a; Dobson 1994a) (see Chap. 24).

The idea that memory is locally carried by the electron “fluid”, in a Lagrangian framework, was exploited by Dobson et al. (1997), who essentially applied the GK approximation in a frame moving along with the local velocity of the electron fluid. At about the same time, Vignale and Kohn showed that a theory local in space and non-local in time is possible instead in terms of the current density (Vignale and Kohn 1996; Vignale et al. 1997). Their functional has begun to be tested on a variety of systems with mixed successes (see Chap. 24). A fully spatially- and time-nonlocal hydrodynamic formulation using Landau Fermi-liquid theory was presented in 2003 (Tokatly and Pankratov 2003—see Chap. 25). Tokatly (2005a, b, 2007) further developed this, considering many-body dynamics in the co-moving Lagrangian frame, leading to time-dependent deformation functional theory. In this frame, xc is spatially local, and all complications, including memory, are contained in Green’s deformation tensor characterizing the frame. A theory based on a Galilean-invariant “memory action functional” has also been formulated (Kurzweil and Baer 2004). Noting that functionals of the instantaneous KS orbitals incorporate infinite “KS memory” leads to another approach, e.g. time-dependent EXX displays memory

effects near intersubband resonances in semiconductor quantum wells (Wijewardane and Ullrich 2008). We note none of the functionals proposed so far incorporate initial-state dependence, although orbital-dependent functionals do have memory of the KS initial state.

Today, however, almost all applications of TDDFT utilize an adiabatic approximation, absolutely memory-less. Certainly, an adiabatic approximation will work well if the system is slowly-varying enough that the system remains in a slowly-evolving ground-state, but this is hardly the typical case in dynamics.

Most of the rest of this chapter investigates memory properties of the *exact* functional, with general real-time dynamics and strong external fields in mind (Some specific phenomena are discussed in [Chap. 18](#)). Cases where exact results are available indicate that memory-dependence can play a vital role. Understanding how the exact functional behaves should prove a useful tool in constructing accurate approximations. We discuss history-dependence in the next section, followed by a section on initial-state dependence. We then show how these two sources of memory-dependence are entangled, and discuss an exact condition relating the two in [Sect. 8.4](#). Implications of memory-dependence for quantum control type problems are then discussed. In the last section, we turn to the double-excitation problem in linear response, and discuss the frequency-dependent kernel that captures them. As in [Chap. 4](#), atomic units are used throughout this chapter.

## 8.2 History Dependence: an Example

Consider a system in its ground state, assumed to be non-degenerate. As discussed in the introduction, we may then put aside initial-state dependence, and ask how far back does the system remember its past? How far back in time do observables at the present depend on the density in the past?

A useful tool to study this question is a time-dependent problem with at least two electrons, for which both the KS system and the interacting system are exactly, or exactly numerically, solvable. Two electrons in a Mathieu oscillator provides a good case (Hessler et al. 2002); the external potential has the form:

$$v_{ext}(\mathbf{r}, \mathbf{t}) = \frac{1}{2}k(t)r^2, \quad \text{with } k(t) = \bar{k} - \epsilon \cos(\omega t), \quad (8.1)$$

with  $\bar{k}$ ,  $\epsilon$ , and  $\omega$  appropriately chosen constants. The static version is often called the Hooke's atom; a paradigm for studies of exchange and correlation in the ground state (Taut 1993; Frydel et al. 2000), largely because, for some parameters, the interacting problem can be solved analytically. For the exact interacting solution of the time-dependent problem, transforming to center-of-mass and relative coordinates renders the Hamiltonian separable. Due to the spherical symmetry, one needs only to solve numerically two uncoupled one-dimensional time-dependent Schrödinger equations. From the evolving wavefunction, beginning in the ground state, the exact evolving

density is obtained. Now, the KS wavefunction involves just one doubly-occupied spatial orbital, evolving in time. By requiring its density to yield half the density of the interacting wavefunction for all time, one can invert the KS equation to obtain the KS potential in terms of the evolving density (Hessler et al. 2002).

The exact interacting dynamics has the useful property that the evolving density breathes in and out while retaining the same (near Gaussian) profile: at each time  $t$ , it is essentially the density of a *ground state* of a certain Hooke's atom of spring constant  $k_{\text{eff}}$ . This spring constant is not equal to the actual spring constant in Eq. 8.1 at time  $t$ , except when the latter is modulated slowly enough such that the state remains an instantaneous ground state. In the general case, the state is *not* a ground state, but, at each instant in time, its *density* is that of a ground state of a Hooke's atom of spring constant  $k_{\text{eff}}(t)$ . This property allows us to compare the exact calculation with that of an exact adiabatic one in a relatively simple way.

Many interesting phenomena arise (Hessler et al. 2002); one typically finds significant differences between the adiabatic approximation and the exact KS case (except for very slow modulations). For example, the instantaneous correlation energy can become positive, which is impossible in any adiabatic approximation, since for ground states  $E_c$  is tied down below zero by the variational principle.

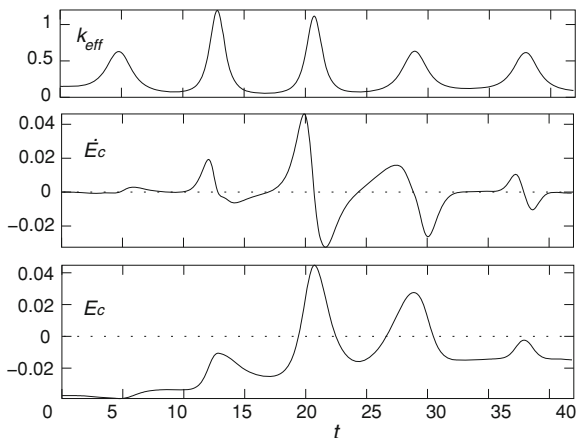
We now show that the correlation potential displays severe non-locality in time due to history dependence. It is convenient to define a type of density-weighted correlation potential via (Hessler et al. 1999)

$$\dot{E}_c(t) = \int d^3r v_c(\mathbf{r}, t) \dot{n}(\mathbf{r}, t), \quad (8.2)$$

where the dot represents a time derivative. If  $\dot{E}_c(t)$  depends not just on the density at and near time  $t$ , but also on its earlier history, then  $v_c(t)$  must too. That is, non-locality in  $\dot{E}_c$  directly implies non-locality in the correlation potential  $v_c(t)$ . The top panel of Fig. 8.1 plots the value of  $k_{\text{eff}}(t)$ , which, as discussed earlier, completely identifies the density profile. The density profiles within a time slice centered near  $t = 4.8$  and one centered near  $t = 28.9$  are almost the same, yet the values of  $\dot{E}_c(t)$  near those times are significantly different. Other pairs of time-slices having this feature may also be found. The density at times near  $t$  is not enough to specify  $v_c(t)$ : in fact the exact correlation potential  $v_c(t)$  is a highly non-local-in-time functional of the density, depending on its entire history. Any adiabatic approximation has no history dependence and fails to capture this effect.

This example, together with other studies (Ullrich 2006b; Wijewardane and Ullrich 2008) of dynamics in strong-fields (starting in a ground-state) suggest the exact functional typically has strong memory-dependence. However, not always: in strong-field double-ionization, for example, the xc potential appears not to be significantly non-local in time in a wide range of cases, although this depends on how the field is ramped on (Thiele et al. 2008). Likewise when a very high-frequency intense field is turned on very very slowly (Baer 2009).

**Fig. 8.1** Non-locality in time: the *top panel* shows  $k_{\text{eff}}(t)$ , *middle panel*  $\dot{E}_c$ , *bottom panel*  $E_c$ . The parameters in Eq. 8.1 are  $\bar{k} = 0.25$ ,  $\omega = 0.75$  and  $\epsilon = 0.1$



The instantaneous momentum-density in the Mathieu oscillator distinguishes time-slices where the instantaneous density is the same (Rajam et al. 2009). This suggests that memory-dependence is likely gentler in a theory that uses a joint position-momentum density, or density-matrix, as basic variable.

### 8.3 Initial-State Dependence

For a given time-dependent density how does the potential that yields this density depend on the choice of the initial wavefunction? Initial-state dependence has only begun to be explored (Maitra and Burke 2001, 2002b; Holas and Balawender 2002); unlike density-dependence, there is no precedent for initial-state dependence in ground-state DFT. For example, there is no analogue of the adiabatic approximation that could be used as a starting point for investigations.

One may wonder whether initial-state dependence actually exists. That is, if we constrain the density to evolve in a certain way, are the implicit constraints on the initial state enough to completely determine it? If this were the case, then there would be no initial-state dependence: knowing the history of the density would be enough to determine the functionals. We shall argue shortly that this is in fact the case for one electron, but not for more than one.

Let us first rephrase the question: consider a many-electron density  $n(\mathbf{r}, t)$  evolving in time under an external time-dependent potential  $v_{\text{ext}}(\mathbf{r}, t)$ . Can we obtain the same density evolution by propagating a different initial state in a different potential?

**One electron case.** Consider one electron, evolving with density  $n(\mathbf{r}, t)$ . Let the electron's wavefunction be  $\varphi(\mathbf{r}, t)$ , where  $n(\mathbf{r}, t) = |\varphi(\mathbf{r}, t)|^2$ . An alternate candidate wavefunction  $\tilde{\varphi}(\mathbf{r}, t)$  that evolves with identical density (in a different potential)

must then be related to  $\varphi(\mathbf{r}, t)$  by a (real) phase  $\alpha(\mathbf{r}, t)$  :

$$\tilde{\varphi}(\mathbf{r}, t) = \varphi(\mathbf{r}, t)e^{i\alpha(\mathbf{r}, t)}. \quad (8.3)$$

The wavefunction at time  $t$  determines not just the density at time  $t$  but also its first time-derivative through the continuity equation:

$$\dot{n}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \quad (8.4)$$

where the current-density  $\mathbf{j}(\mathbf{r}, t)$  is determined from:

$$\mathbf{j}(\mathbf{r}, t) = \frac{i}{2} [\varphi(\mathbf{r}, t)\nabla\varphi^*(\mathbf{r}, t) - \varphi^*(\mathbf{r}, t)\nabla\varphi(\mathbf{r}, t)]. \quad (8.5)$$

Because they evolve with the same density at all times, both  $\varphi(\mathbf{r}, t)$  and  $\tilde{\varphi}(\mathbf{r}, t)$  share the same  $\dot{n}(\mathbf{r}, t)$ . From the continuity equation it follows that they have identical longitudinal currents, so:

$$0 = \dot{n}_\varphi(\mathbf{r}, t) - \dot{n}_{\tilde{\varphi}}(\mathbf{r}, t) = \nabla \cdot [n(\mathbf{r}, t)\nabla\alpha(\mathbf{r}, t)], \quad (8.6)$$

where on the right-hand side we have inserted the difference in the currents of  $\tilde{\varphi}$  and  $\varphi$ , calculated using Eq. 8.5. Now if we multiply Eq. 8.6 by  $\alpha(\mathbf{r}, t)$  and integrate over all space, we obtain

$$0 = \int d^3r \alpha(\mathbf{r}, t) \nabla \cdot [n(\mathbf{r}, t)\nabla\alpha(\mathbf{r}, t)] = - \int d^3r n(\mathbf{r}, t) |\nabla\alpha(\mathbf{r}, t)|^2 \quad (8.7)$$

In the last step, we integrated by parts, taking the surface term  $\int_S d\sigma e_n \cdot (\alpha n \nabla\alpha)$ , evaluated on a closed surface at infinity, to be zero. This will be true for any finite system, where the density decays at infinity, while the potential remains finite (or, if the potential grows, the density decays still faster).

Because the integrand in Eq. 8.7 cannot be negative anywhere, yet it integrates to zero, the integrand must be identically zero. Thus  $\nabla\alpha(\mathbf{r}, t) = 0$  everywhere. This is true even at nodes of the wavefunction, where  $n(\mathbf{r}_0, t) = 0$ : if  $\nabla\alpha$  was zero everywhere except at the nodes, then as a distribution it is equivalent to being zero everywhere, unless it was a delta-function at the node—but in that case the potential would be highly singular, and therefore unphysical. So, for physical potentials,  $\alpha(\mathbf{r}, t)$  must be constant in space, i.e. the wavefunctions  $\varphi(\mathbf{r}, t)$  and  $\tilde{\varphi}(\mathbf{r}, t)$  differ only by an irrelevant time-dependent phase. Thus, only one initial state (and one potential) can give rise to a particular density: the evolving density is enough to completely determine the potential and the initial states.

The vanishing of the surface term in Eq. 8.7 can be compared with the requirement on the potential in the Runge–Gross theorem, as discussed in Sect.4.4.1. In Maitra and Burke (2001), an example of a pathological initial state is given,

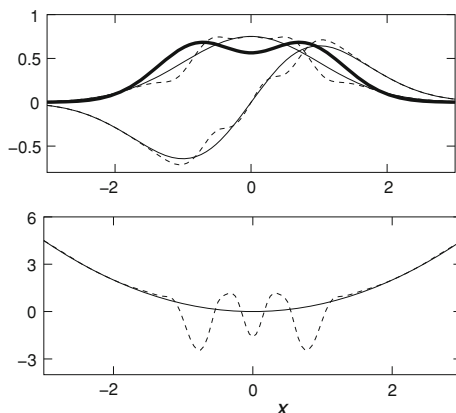
where the surface term does not vanish, even though the density decays exponentially at large distances: the potential in which it lives plummets to minus infinity at large distances, yielding wildly oscillatory behavior in the tails of the decaying wavefunction, embodying infinite kinetic energy and momentum. Such unphysical states are beyond consideration!

**Many electrons.** For many electrons, initial-state dependence is real and alive: one can find two or more different initial-states which evolve with identical density for all time in different external potentials.

A few simple examples of this are shown in Figs. 8.2 and 8.3. In Fig. 8.2, the density (thick solid line) of two non-interacting electrons in one dimension in an eigenstate (thin solid line) of the harmonic potential is considered (Maitra and Burke 2001; Holas and Balawender 2002). The two orbitals are the thin solid lines. If we keep this potential constant, the density will remain constant. We then ask, can we find another potential in which another non-interacting wavefunction evolves with this same, constant density for all time? There are in fact an infinite number of them, and one is shown here (dashed lines). The alternate potential was constructed using van Leeuwen's prescription (van Leeuwen 1999—see also Chap. 9), and is shown here at the initial time. It is not constant in time: both the alternate potential and the alternate orbitals evolve in time, in such a way as to keep the density constant at all times.

The significance of this for TDDFT comes to light when we imagine the density as the density of some *interacting* electronic system. For a KS calculation, we are free to choose any initial KS state which has this initial density: that is, both the potentials shown in the lower panel of Fig. 8.2, along with their respective orbitals, are fair game. The difference between these two KS potentials is exactly the difference in the xc potential, since the Hartree and external potentials are the same. So depending on this choice, the xc potentials are very different. Any functional without initial-state dependence would predict the same potential in both cases.

Figure 8.3 is another example of two different initial states that evolve with the same density for all time. This example, again of two non-interacting electrons, demonstrates that there is no one-to-one mapping between time-periodic densities of Floquet states and time-periodic potentials (see Maitra and Burke 2002a). Consider a periodically driven harmonic oscillator, containing two non-interacting electrons in a spin-singlet occupying two distinct quasi-energy orbitals. One can show that the density then periodically sloshes back and forth in the well. This is illustrated in the top panels of Fig. 8.3. The middle panel of Fig. 8.3 shows a doubly-occupied Floquet orbital (real and imaginary parts are the dashed lines) whose density (solid line) evolves identically to the density of the Floquet state in the top panel. This orbital sloshes back and forth in its potential, in a similar way to the orbitals of the driven oscillator. The lowest panel shows the potentials: the solid is the periodically driven harmonic potential corresponding to the Floquet state of the top panel, and the dashed is the periodically driven potential corresponding to that of the middle panel. Now, assuming there corresponds an interacting electron system whose density evolves exactly as shown, then both the Floquet state in the top panel and the middle panel



**Fig. 8.2** An example of initial-state dependence for two non-interacting electrons: two different wavefunctions may evolve with the same density in different potentials. In the *top plot*, the *solid lines* are the two occupied orbitals of one wavefunction, which happens to be a stationary state of the harmonic oscillator potential, shown in the lower plot as a *solid line*. The density is shown as the *thick solid line* in the *top figure*. The *dashed lines* are the two orbitals of an alternative initial wavefunction, that evolves with the same density in the potential which, at the initial time, is shown as the *dashed line* in the lower figure

are possible KS wavefunctions, and both the solid and dashed potentials in the lower panels are possible KS potentials; again, their difference (the sloshing “bump” in the figure) is the difference in the xc potential.

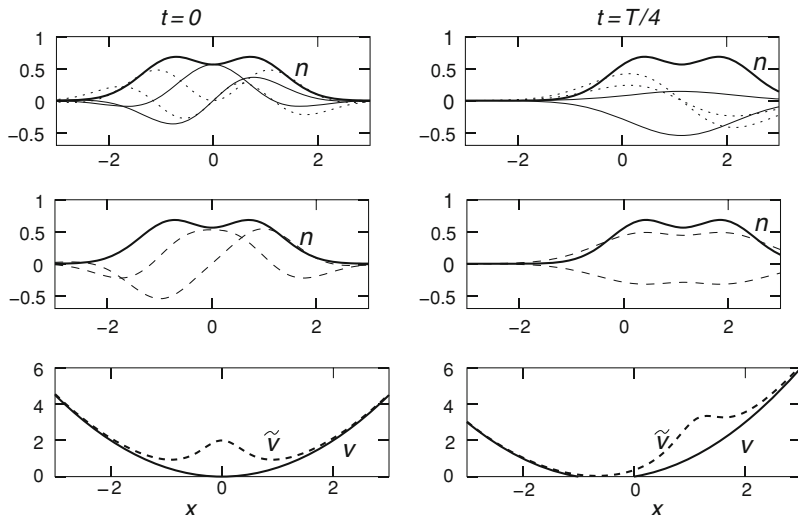
Not only any adiabatic approximation, but any density-functional approximation that lacks initial-state dependence—even with history-dependence—would incorrectly predict the same potential for all choices of KS initial states that propagate with the same density. In the next section, we discuss how, in many cases, one can eliminate the need for initial-state dependence altogether, by transforming it into a history-dependence.

## 8.4 Memory: an Exact Condition

Part of what makes the memory dependence complex, is the intricate entanglement of initial state and history effects. This has consequences even for initial ground states. On the other hand, it allows the possibility for memory-dependence to be reduced to history-dependence alone.

Consider an interacting system, beginning with wavefunction  $\Psi(0)$  at time 0, and evolving in time, with density  $n(\mathbf{r}, t)$ . The xc potential at time  $t$  is determined by the density at all previous times, the initial interacting wavefunction, and the choice of the initial KS wavefunction  $\Phi(0)$  for the KS calculation. Now say we can calculate the interacting wavefunction at a later time  $t'$ , where  $0 < t' < t$ . Then, we may think of  $t'$ , as the “initial” time for the inputs into the functional arguments of  $v_{xc}$ : that is,





**Fig. 8.3** *Top left panel:* the real and imaginary parts of the driven harmonic oscillator Floquet orbitals  $\varphi^{(0)}(x, 0)$  (solid) and  $\varphi^{(1)}(x, 0)$  (dotted) at time = 0, together with their density (thick line). *Middle left panel:* the real and imaginary parts of the alternative doubly-occupied Floquet orbital  $\tilde{\varphi}(x, 0)$  (dashed), which has the same density shown (thick line). *Bottom left panel:* the two potentials,  $v$  is the solid, and  $\tilde{v}$  is dashed. The right hand side shows the same quantities at  $t = T/4$

$$v_{\text{xc}} [n_{t'}, \Psi(t'), \Phi(t')] (\mathbf{r}, t) = v_{\text{xc}} [n, \Psi(0), \Phi(0)] (\mathbf{r}, t) \quad \text{for } t > t'. \quad (8.8)$$

Here,  $\Psi(t') = \hat{U}(t')\Psi(0)$ , where  $\hat{U}(t)$  is the unitary evolution operator, and  $\Phi(t') = \hat{U}_{\text{KS}}(t')\Phi(0)$  where  $\hat{U}_{\text{KS}}(t')$  is the KS evolution operator. The subscript on the density means that the density is undefined for times earlier than the subscript, and it equals the evolving density  $n(\mathbf{r}, t)$  for times  $t$  greater than the subscript.

Equation 8.8 displays the relation between the memory effects: any dependence of the xc potential on the density at prior times may be transformed into an initial-state dependence and vice versa.

Like other exact conditions (discussed in Chap. 5), Eq. 8.8 may be used as a test for approximate functionals, but it is a very difficult condition to satisfy. For example, any of the recent attempts to include history-dependence, while ignoring initial-state dependence, must fail. If we restrict their application to systems beginning in the ground state, then Eq. 8.8 still produces a strict test of such functionals: imagine an exact time-dependent calculation beginning in the ground state of some system. Later, when  $\Psi(t')$  is no longer a ground state, we evolve *backwards* in time in a different external potential, that leads us back to a different ground state at a different initial time. The history during the time before  $t'$  is different from the original history, but

the xc potential for all times greater than  $t'$  should be the same for both the original evolution and the evolution along the alternative path. The extent to which these two differ is a measure of the error in a given history-dependent approximation, even applied only to initial ground states. Note that any adiabatic approximation ignoring initial-state dependence (such as those in the introduction) produces no difference. By ignoring both history dependence *and* initial-state dependence, the ALDA trivially satisfies Eq. 8.8.

A technical note: although the RG theorem was proven only for time-analytic potentials, i.e. those that equal their Taylor series expansions in  $t$  about the initial time for a finite time interval (Runge and Gross 1984), it holds also for piecewise analytic potentials, i.e. potentials analytic in each of a finite number of intervals (Maitra and Burke 2002b). This means that alternative allowed “pseudo-prehistories” can connect to the same wavefunction at some later time.

This raises the possibility of eliminating the initial-state dependence altogether: if we can evolve an initial interacting wavefunction that is not a ground state, backwards in time to a non-degenerate ground state, then the initial-state dependence may be completely absorbed into a history-dependence along this pseudo-prehistory.

As discussed in Chap. 4, one may choose any initial KS state that reproduces the density and divergence of the current of the interacting initial state (van Leeuwen 1999). In the procedure above, this choice is translated into the choice of which ground state the interacting wavefunction  $\Psi(0)$  evolves back to, together with the pseudo-prehistory of the density thus generated. One can imagine that for a given wavefunction  $\Psi(0)$  there may be many paths which evolve back to some ground state, each path generating a different pseudo-prehistory. Only for those which result in the same KS wavefunction  $\Phi(0)$  [and of course interacting wavefunction  $\Psi(0)$ ] will the xc potentials be identical after time 0.

In the linear response regime, the memory formula Eq. 8.8 yields an exact condition relating the xc kernel to initial-state variations (Maitra 2005a). We consider applying Eq. 8.8 in the perturbative regime, with the initial states at time 0 (on the right-hand-side) being ground-states. The initial states on the left-hand-side (i.e. the states at  $t'$ ) are not ground-states. We wish to express deviations from the ground-state values through functional derivatives with respect to the density and with respect to the initial states. Because the initial state determines the initial density and its first time-derivative, and puts constraints on higher-order time-derivatives of the density, the definition of a partial derivative with respect to the initial state is not trivial: what should be held fixed in the variation? The partial derivative with respect to the density, holding the initial state fixed, is simpler; for example, for the external potential this is a generalized inverse susceptibility, generalized to initial states which are not ground-states. Variations of the density at times greater than zero are included. In order to define an initial-state derivative, one considers an extension of the functionals to a higher space in which the initial-state variable and density variable are independent: one drops and Eqs. 4.6 and 4.20. Then one can show that

$$\begin{aligned}
& \sum_{\alpha} \int d^3 r_1 \frac{\delta v_{\text{KS}}[n_{t'}, \Phi_{t'}](\mathbf{r}, t)}{\delta \varphi_{t', \alpha}(\mathbf{r}_1)} \Big|_{(n_{\text{GS}}, \Phi_{\text{GS}}[n_{\text{GS}}])} \delta \varphi_{t', \alpha}(\mathbf{r}_1) \\
& - \int d^4 x_1 \cdots \int d^4 x_N \frac{\delta v_{\text{ext}}[n_{t'}, \Psi_{t'}](\mathbf{r}, t)}{\delta \Psi_{t'}(\mathbf{x}_1, \dots, \mathbf{x}_N)} \Big|_{(n_{\text{GS}}, \Psi_{\text{GS}}[n_{\text{GS}}])} \delta \Psi_{t'}(\mathbf{x}_1, \dots, \mathbf{x}_N) + \text{c.c.} \\
& = \int d^3 r_1 \int_0^{t'} dt_1 f_{\text{xc}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}_1, t - t_1) \delta n(\mathbf{r}_1, t_1), \quad 0 < t' < t, \quad (8.9)
\end{aligned}$$

where the variables  $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$  represent spatial and spin coordinates,  $\delta \varphi_{t', \alpha} = \delta \varphi_{\alpha}(t') = \varphi_{\alpha}(t') - \varphi_{\alpha, \text{GS}}[n_{\text{GS}}]$  represent the deviations at time  $t$  of the spin orbitals of the KS Slater determinant away from the ground-state values and  $\delta \Psi$  is similarly the deviation of the interacting state away from its ground-state. This equation demonstrates the entanglement of initial-state dependence and history-dependence in the linear response regime: the expression for the xc kernel on the right is entirely expressed in terms of initial-state dependence on the left.

## 8.5 Memory in Quantum Control Phenomena

In recent years there have been huge advances in the control of chemical reactions, where nuclei are manipulated. The development of attosecond laser pulses opens the door to the possibility of manipulating electronic processes as well. [Chapter 13](#) derives the equations for quantum optimal control theory within the KS framework. Here, instead, we present a couple of “gedanken” experiments to explore how the exact KS picture of the controlled dynamics looks compared to the exact true dynamics.

Let us say we are interested in driving a molecule from its ground state  $\Psi_{\text{GS}}$  in potential  $v_{\text{ext}, \text{GS}}$  to its  $m$ th excited state  $\Psi_m$ . Let us say we are lucky enough to know the external time-dependent field that achieves this after a time  $\tilde{t}$ . The field is then turned off at time  $\tilde{t}$  so that the molecule remains in the excited eigenstate. We now ask how this process is described in the corresponding KS system, i.e. what is the KS potential? Initially, this is the ground-state potential  $v_{\text{KS}, 0}$  whose ground-state  $\Phi_{\text{KS}}$  has density  $n_{\text{GS}}$ , the density of the interacting ground state of the molecule. The first observation is that the KS potential after time  $\tilde{t}$  does *not* typically return to the initial KS potential, in contrast to the case of the interacting system. This is because, by definition, the density of the KS state equals the interacting density at all times; in particular, after time  $\tilde{t}$  it is the density of the interacting excited state of potential  $v_{\text{ext}, 0}$ , but this is *not* guaranteed to be the density of the KS excited state of potential  $v_{\text{KS}, 0}$ . Only the ground-state density of an interacting system is shared by its KS counterpart, not the higher excited states; the final KS state of the molecule will not typically be an eigenstate of  $v_{\text{KS}, 0}$ .

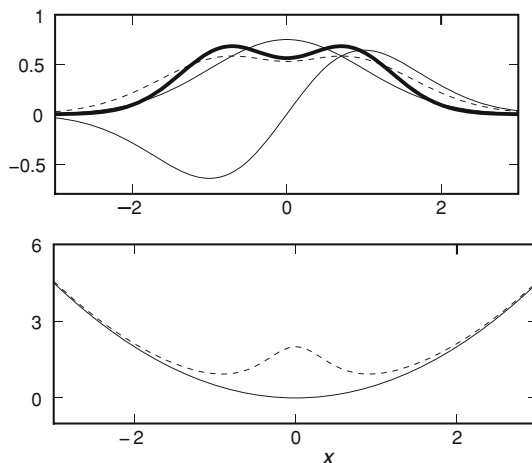
There are two possibilities for the KS potential after time  $\tilde{t}$ . The first is that it becomes static, and the static final density, call it  $\tilde{n}$ , is that of an eigenstate of it.

From the above argument, the KS potential is however different from the initial, and does not equal the ground-state KS counterpart of the interacting case. For example, if we are exciting from the ground state of the helium atom to an excited state, the external potential of the interacting system is both initially and finally  $-2/r$ . The initial KS potential is the ground-state KS potential of helium, but the final is not; the final KS eigenstate has the same density as the excited state of interest in helium. Now we will argue that any adiabatic approximation, or indeed any potential that is not ultranlocal in time, is unlikely to do well. Consider a time  $t$  beyond  $\tilde{t}$ . The density for times near  $t$  is constant, so any semi-local approximation for the potential will be any one of the potentials for which the density  $\tilde{n}$  is the density of some eigenstate of it. In particular, for an adiabatic approximation, the potential is that for which the excited state density  $\tilde{n}$  is the density of its *ground state*. There is no way for an approximate semi-local KS system to know that it should be the potential corresponding to the interacting system that has an  $m$ th excited state density of  $\tilde{n}$ . This information is encoded in the early history of the density, from times  $0 < t < \tilde{t}$ : the exact KS potential must be ultranlocal in time, since, as time gets very large, it never forgets the early history. Alternatively, taking the “initial” time to be  $\tilde{t}$  in the memory formula Eq. 8.8, this effect is an initial-state effect where the initial interacting (and non-interacting state) is not a ground-state.

The other possibility is that the KS (and xc) potential never becomes constant: it continues to change in time, with KS orbitals and orbital-densities changing in time in such a way that the total KS density remains static and equal to  $\tilde{n}$ . It is clear that any semi-local approximation will fail here, because for times beyond  $\tilde{t}$ , it will predict a constant potential since the density is constant. The exact xc (and KS) potential will be ultranlocal in time; as time gets very large, one has to go way back in time, to times less than  $\tilde{t}$ , in order to capture any time dependence in the density.

This extreme non-locality is very difficult for a density functional approximation to capture: it may be that orbital functionals, which are implicit density functionals, provide a promising approach. Even so, there are cases where TDDFT faces a formidable challenge. Consider two electrons, beginning in a spin-singlet ground state (e.g. the ground state of helium). Imagine now finding an optimal control field that evolves the interacting state to a singlet singly-excited state (e.g.  $1s2p$  of helium). Now, the KS ground state is a single Slater determinant with a doubly-occupied spatial orbital. This evolves under a one-body evolution operator, the KS Hamiltonian, so must remain a single Slater determinant. But a single excitation is a *double* Slater determinant, so can never be attained even with an orbital-dependent functional. This is a time-dependent analogue of static correlation, where a single Slater determinant is inadequate to describe a fundamentally multi-determinantal state (Maitra et al. 2002b). The KS description of the state is so far from the true description, that the exact xc potential and observable functionals consequently develop complicated structure difficult to capture in approximations. The KS state is not an eigenstate of the angular momentum operator, unlike that of the true state. If the overlap between the initial and final states is targetted, the maximum that can be achieved is 0.5 (Burke

**Fig. 8.4** In the *top panel* is the density (*thick solid line*) of the two electron singlet excited state (*solid lines*) of the harmonic oscillator (*solid line in the lower panel*). The *dashed line* is the doubly-occupied orbital resulting from evolving the singlet ground-state to a state of the same density as the excited state. The potential in which this is an eigenstate—the ground-state—is shown as the *dashed line in the lower panel*



et al. 2005a), while close to 0.98 is achieved for the true interacting problem (but see also the last paragraph of this section).

A simplified model of this is shown in Fig. 8.4. Here the density of the first excited state of two electrons in a harmonic oscillator, considered to be the final KS potential, is shown. Attempting to evolve to this density from the ground state of the harmonic oscillator, which is a doubly-occupied orbital, the best KS can do is reach another doubly-occupied orbital (dashed), whose potential is shown in the lower panel (dashed).

We note that such problems do not arise in linear response regime, where we do not need to drive the system entirely into a single excited state: only perturbations of the ground-state are needed which have a small, non-zero projection on to the various excited states of the system.

It is very important to note that in the above examples the density is the target variable; the time-dependent density is the observable which the KS system is constructed to get exactly correct. However when quantum optimal control is performed directly with the TDKS system, then it is of course possible, and in most cases, more natural, instead to define the target variable directly related to the KS wavefunction. For example, one might instead consider targeting the density of a KS excited state, or an overlap with a KS excited state. The question is then whether the optimal field found for the KS system also achieves a good outcome for the true system. In most cases studied so far by A. Castro and E.K.U. Gross (personal communication), it fortunately does. Even in the case where the maximum overlap with the target KS state is as low as 0.5, it is quite possible that, with a clever choice of target functional, the optimal field found from the KS evolution applied to the interacting system yields a target overlap in the interacting system much closer to one.

## 8.6 Memory Effects in Excitation Spectra

The vast majority of applications of TDDFT today are in the linear response regime. Adiabatic approximations are used in the many successes here, but they are also the reason behind many of its notorious failures. This section discusses one of these: states of double-excitation character, for which frequency-dependence is essential to capture.

First, we clarify what is meant by a double- or multiple-excitation. The term is defined with respect to some single-particle picture, characterized by a set of single-particle orbitals that are solutions to a one-body Hamiltonian,  $N$  of which are occupied in the ground-state of this Hamiltonian. In TDDFT, this picture is naturally the KS system. A single-excitation swaps one of these occupied orbitals for an unoccupied orbital. A double-excitation instead swaps two occupied orbitals for two unoccupied orbitals, so represents an excited state where two electrons are excited with respect to the ground configuration. On the other hand, the true interacting eigenstates are linear combinations of this ground-state and all excitations, including double, triple, and higher (thinking of the determinants composed of the single-particle orbitals as a complete set of  $N$ -electron states). When we speak of a double-excitation in the true system, we mean it as a short-hand for a “state of double-excitation character”, i.e. a state that has a significant fraction of a double-excitation with respect to a non-interacting single-particle picture. Clearly, in different theories that have different references (e.g. Hartree–Fock rather than KS), these fractions will differ.

Chapter 4 mentioned that often the KS excitations are themselves good zeroth-order approximations to the true excitations, with the xc kernel contributing a small enough correction that even the simplest adiabatic approximation does quite well. But this argument cannot apply to double-excitations, since in linear response of the KS system no double-excitations appear: to excite two electrons of a non-interacting system two photons would be required, beyond linear response. Only single-excitations of the KS system are available for an adiabatic kernel to mix. Indeed, if we consider the linear response function (Eq. 4.50) applied to the KS system, the numerator  $\langle \Phi_{\text{GS}} | \hat{n}(\mathbf{r}) | \Phi_I \rangle$  vanishes if  $\Phi_I$  and  $\Phi_{\text{GS}}$  differ by more than one orbital since the one-body operator  $\hat{n}(\mathbf{r})$  cannot connect states that differ by more than one orbital. The true response function, on the other hand, retains poles at the true excitations which are mixtures of single, double, and higher-electron-number excitations, as the numerator  $\langle \Psi_{\text{GS}} | \hat{n}(\mathbf{r}) | \Psi_I \rangle$  remains finite due to the mixed nature of both  $\Psi_{\text{GS}}$  and  $\Psi_I$ . Within the adiabatic approximation,  $\chi$  therefore contains more poles than  $\chi_{\text{KS}}$ .

How does the exact kernel of TDDFT generate more poles, and capture states of multiple-excitations? One must go beyond the adiabatic approximation (Tozer and Handy 2000). In 2004, the exact frequency-dependence that is required when a double excitation mixes with a single excitation was demonstrated, and an approximate kernel based on this was derived (Maitra et al. 2004). We now discuss this.

**A frequency-dependent kernel for double-excitations.** Consider the simplest model: a two-by-two excitation subspace consisting of one KS single excitation

$\varphi_i \rightarrow \varphi_u$ , of frequency  $\omega_q = \epsilon_u - \epsilon_i$ , and one double excitation ( $\Phi_D$ ) energetically close. We assume all other excitations lie far from these two levels, so that for frequencies close to  $\omega_q$  :

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = \frac{A(\mathbf{r}, \mathbf{r}', \omega)}{\omega - \omega_q} \quad (8.10)$$

where the numerator only weakly depends on the frequency:  $A(\mathbf{r}, \mathbf{r}', \omega) = \varphi_i^*(\mathbf{r})\varphi_u(\mathbf{r})\varphi_i(\mathbf{r}')\varphi_u^*(\mathbf{r}') + O(\omega - \omega_q)$ . The KS double-excitation does not contribute to  $\chi_{\text{KS}}$  from the argument above. Electron interaction mixes the KS single- and double-excitations, such that the true states have the form:

$$\Psi_a = m\Phi_D + \sqrt{1 - m^2}\Phi_q \text{ and } \Psi_b = \sqrt{1 - m^2}\Phi_D - m\Phi_q \quad (8.11)$$

where  $0 < m < 1$  is a parameter to represent the fraction of double- and single-excitation character in the true interacting states. Inserting these into the expression for the true response function, Eq. 4.50, we obtain

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = A(\mathbf{r}, \mathbf{r}', \omega) \left( \frac{1 - m^2}{\omega - \omega_a} + \frac{m^2}{\omega - \omega_b} \right), \quad (8.12)$$

where  $\omega_a, \omega_b$  are the true interacting excitation frequencies. Notice that the two interacting states share the oscillator strength of the KS single-excitation, in a ratio determined by the fraction of how much single-excitation each carries. Within this subspace, we then define a *dressed* (i.e. frequency-dependent) single-pole approximation (DSPA),

$$\omega = \omega_q + 2[q|f_{\text{Hxc}}(\omega)|q] \quad (8.13)$$

where the kernel on the right is derived from Eqs. 8.10 and 8.12, using

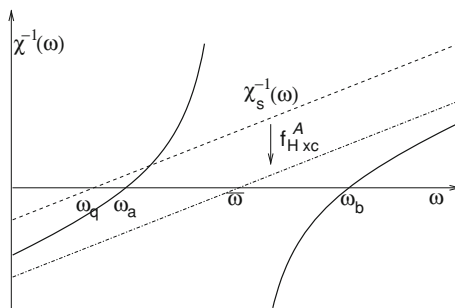
$$f_{\text{Hxc}}(\omega) = \chi_{\text{KS}}^{-1}(\omega) - \chi^{-1}(\omega). \quad (8.14)$$

(c.f. the SPA in Eq. 4.63; the square bracket notation in Eq. 8.13 indicates the doubleintegral of Eq. 4.63 but with the kernel evaluated at frequency  $\omega$ , instead of at  $\omega_q$ .)

Requiring that the DSPA recovers the exact frequencies  $\omega_a, \omega_b$  pins down the matrix element of  $A^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ , and we find

$$2[q|f_{\text{Hxc}}(\omega)|q] = (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')}, \quad (8.15)$$

where  $\bar{\omega}' = m^2\omega_a + (1 - m^2)\omega_b$  and  $\bar{\omega} = (1 - m^2)\omega_a + m^2\omega_b$ . Equation 8.15 gives the *exact* xc kernel matrix element for frequencies near the single and double of interest; we illustrate how it generates two poles in  $\chi$  from the one in  $\chi_{\text{KS}}$  in Fig. 8.5.



**Fig. 8.5** Frequency-dependence near a double excitation (see text): near a single excitation,  $\chi_{\text{KS}}^{-1}(\omega)$  (upper dashed line) has one zero at the KS transition  $\omega_q$ , which an adiabatic kernel  $f_{\text{Hxc}}^A$  shifts to  $\bar{\omega}$ . Frequency-dependence of Eq. 8.15 renders two zeroes in the exact  $\chi^{-1}(\omega)$  (solid line) at the transition frequencies  $\omega_a, \omega_b$  of the true mixed single and double states

The first term is adiabatic, while the second is strongly non-adiabatic (Maitra et al. 2004).

Equation 8.15 motivated the following practical approximation for the dressed kernel, when a single and double excitation lie near each other, in the limit of weak interaction (direct coupling to the rest of the KS excitations is neglected). Essentially one considers diagonalizing the many-body Hamiltonian in this two-by-two KS subspace, and requires that the kernel reduces to the adiabatic one ( $f_{\text{xc}}^A$ ) in the limit that the single and double only weakly interact (see Maitra et al. 2004 for details). One obtains:

$$2[q|f_{\text{xc}}(\omega)|q] = 2\left[q|f_{\text{xc}}^A(\omega_q)|q\right] + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{00})} \quad (8.16)$$

where the Hamiltonian matrix elements in the dynamical correction (second term) are those of the true interacting Hamiltonian, taken between the single ( $q$ ) and double ( $D$ ) KS Slater determinants of interest, as indicated, and  $H_{00}$  is the expectation value of the true Hamiltonian in the KS ground-state. The kernel is to be applied as an *a posteriori* correction to a usual adiabatic calculation: first, one scans over the KS orbital energies to see if the sum of two of their frequencies lies near a single excitation frequency, and then applies this kernel just to that pair. If a double-excitation mixes strongly with several single excitations, one performs the dressing Eq. 8.16 in a matrix spanned by those singles (see Cave et al. 2004; Mazur and Włodarczyk 2009, where this was done for polyenes).

Several alternate and more formal approaches have led essentially to Eq. 8.16. Casida (2005) derived Eq. 8.16 from a superoperator formalism, as a polarization propagator correction to adiabatic TDDFT. The Bethe–Salpeter equation (BSE) with a dynamically screened Coulomb interaction was used to derive a frequency-dependent kernel (Romaniello et al. 2009): here the frequency-dependence has two origins, one from folding the four-point BSE into the two-point TDDFT equation [as in the work on the optical response of solids, (e.g. Reining 2002; Gatti et al 2007a)],



and the other (essential for double-excitations) from the frequency-dependence of the BSE kernel. The resulting kernel however yielded additional unphysical poles, attributed to the self-screening of GW. There are connections between this and the superoperator formalism (see Huix-Rotllant 2011), where explicit expressions for the kernel derived from algebraic diagrammatic construction with second-order polarization-propagator applied to KS are given. The spatial-dependence of the kernel was uncovered in an approach following more closely the original derivation but using the common energy denominator approximation to account for the effect of entire spectrum on the coupled single- and double-states (Gritsenko and Baerends 2009).

**Where states of double-excitation character arise.** In some systems, they lie even amongst the lowest-energy states, but we will also argue that they underlie several other failures of adiabatic TDDFT.

- (i) In many conjugated molecules (e.g. polyenes), double-excitations infiltrate the low-lying excitations, which are as a result notoriously difficult to calculate (see Cave et al. 2004 for many references). For example, in butadiene, the  $\text{HOMO} \rightarrow (\text{LUMO} + 1)$  and  $(\text{HOMO} - 1) \rightarrow \text{LUMO}$  excitations are near-degenerate with a double-excitation of the HOMO to LUMO. If one runs an adiabatic calculation and simply assigns the energies according to an expected ordering, it may appear that one obtains a reasonable value for an expected state of double-excitation character (Hsu et al. 2001), however upon examining the make-up of the state, one will find it is instead a single-excitation (misplaced, for example due to basis-set issues). Cave et al (2004) applied dressed TDDFT to the dark  $2^1A_g$  state of butadiene and hexatriene, generalizing Eq. 8.16 to the case of two single excitations mixing with a double, obtaining results close to CASPT2. Linear polyenes were later studied in more detail (Mazur and Włodarczyk 2009; Mazur et al. 2011), analyzing more fully aspects such as self-consistent treatment of the kernel, and use of KS versus Hartree-Fock orbitals in the dressing, and successfully computing excited-state geometries with this dressed TDDFT. Dressed TDDFT was applied to low-lying excited states of 28 organic molecules (Huix-Rotllant et al. 2011b).
- (ii) It is well known that charge-transfer excitations between fragments at large separations are severely underestimated with the usual approximations of TDDFT (see Sect. 4.8.2). If we are interested in charge-transfer between two distant open-shell species (e.g. LiH), the HOMO and LUMO are delocalized over the whole molecule. This is the case for the exact ground-state KS potential, for which a step appears in the bonding region that has exactly the size to re-align the two atomic HOMOs, as well as for local or semi-local approximations (Tempel et al. 2009). The HOMO-LUMO energy difference goes as the tunnel splitting, vanishing as the molecule is pulled apart; therefore *every* excitation out of the KS HOMO is near-degenerate with a double-excitation where a second electron goes from HOMO to LUMO (at almost zero KS cost). This yields a strong frequency-dependence of the kernel near *all* excitations, charge-transfer and local, for heteroatomic molecules composed of open-shell fragments at large separation (Maitra 2005b; Maitra and Tempel 2006a).

- (iii) Double-excitations dog accurate calculations of coupled electron-nuclear dynamics (Levine et al. 2006): even when the vertical excitation does not contain much double-excitation character, the propensity for curve-crossing requires an accurate double-excitation description for accurate global potential energy surfaces. That same paper highlighted the difficulties approximate TDDFT has with obtaining conical intersections: in one example, the TDDFT dramatically exaggerated the shape of the intersection, while in another, its dimensionality was wrong, producing a seam rather than a point. Although the ground-state surface is not described well here with the approximate functionals, double-excitations are certainly relevant in the vicinity of conical intersections due to the near-degeneracy (see also [Chap. 14](#)).
- (iv) In the He atom, the lowest double-excitation ( $1s^2 \rightarrow 2s^2$ ) lies in the continuum, appearing as a resonance in the continuous spectrum. Autoionizing resonances that arise from bound core-valence single excitations are well-captured by the adiabatic kernels of TDDFT (see e.g. Stener et al. 2007; Hellgren and von Barth 2009) but those arising from double-excitations require a frequency-dependent kernel. An approximate kernel based on Fano's degenerate perturbation theory approach (Fano 1961) applied to the KS system can be derived (Krueger and Maitra 2009).

## 8.7 Outlook

Memory profoundly affects the structure of exact functionals in TDDFT. Here we have given some exact properties regarding initial-state dependence and history-dependence, and explored some memory effects on exactly solvable systems. Strong field dynamics is especially the regime where TDDFT may be the only feasible approach, as wavefunction methods for more than a few interacting electrons become prohibitively expensive. Yet it is in this regime that memory effects appear to be significant. Memory also influences the accuracy of linear response calculations, and we showed how a frequency-dependent kernel, derived from first principles, captures states of double-excitation character, missing in the usual memory-less adiabatic approximations. For TDDFT to be used for fully time-dependent phenomena as confidently as DFT is used for ground-state problems, and to build on its reliability for electronic spectra, further understanding and modeling of memory effects is required, along with further developments of memory-dependent approximations.