4 Initial-State Dependence and Memory

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4.1 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 (1.33) of Chap. 1. Of particular interest is the xc potential, as that is the quantity that must be approximated. This is the difference between the KS potential and the sum of the external and Hartree potentials. 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 density.

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

In a sense, memory arises in TDDFT because of the reduced nature of the density as a basic variable: If the wavefunction 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 in terms of $3N$ spatial variables plus time to a description in terms of 3 variables plus time. Analogously to the theories of open systems, out of this tracing out of degrees of freedom emerges memory dependence. In the treatment of open systems one traces out the bath degrees of freedom in order to get a reduced description in terms of system variables only: the effect of the bath is embodied in an influence functional 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).

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Even before Runge and Gross (RG) formally established their theory [Runge 1984], there were calculations of optical spectra that plugged the instantaneous density into the LDA [Ando 1977a, Ando 1977b, Zangwill 1980a, Zangwill 1981]. This is an adiabatic approximation, as discussed in Sect. 1.6, and neglects any memory dependence. 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 was the Gross-Kohn approximation (GK) for the xc kernel [Gross 1985, Gross 1985, Gross 1990]. Non-local dependence in the time domain translates into non-constant frequency dependence when a time-frequency Fourier transform is done. 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 as the homogeneous electron gas response at finite frequency. 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 are violated [Vignale 1995a, Dobson 1994a]. In particular, the GK approximation violates the harmonic potential theorem (see also Chap. 5). Vignale and Kohn, in 1996, showed that a theory local in space and non-local in time, is possible in terms of the current density [Vignale 1996, Vignale 1997]. Their functional, discussed in Chap. 5, has begun to be tested on a variety of systems; some of these are discussed in Part IV of this book. Most of these applications involve response properties, but the extension to the non-linear regime by Vignale, Ullrich and Conti [Vignale 1997], has recently been studied in quantum wells [Wijewardane 2005]. The idea that memory is locally carried by the electron "fluid", in a Lagrangian framework, was also exploited by Dobson, Bünner, and Gross [Dobson 1997]. In 2003, Tokatly and Pankratov [Tokatly 2003] extended the hydrodynamic formulation to the fully spatially- and time-nonlocal regime, using Landau Fermi-liquid theory (see Chap. 8). Most recently, Tokatly [Tokatly 2005a, Tokatly 2005b] further developed this, formulating TDDFT based on exact quantum many-body dynamics in the co-moving Lagrangian frame (see also Chap. 8). Also, Kurzweil and Baer [Kurzweil 2004] have formulated a theory based on a "memory action functional".

Today, almost all applications of TDDFT utilize an adiabatic approximation, where the instantaneous density is used as input for the "ground-state" density. For example, in the ubiquitous ALDA, $v_{\rm xc}^{\rm ALDA}(\boldsymbol{r},t) = v_{\rm xc}^{\rm unif}[n(\boldsymbol{r},t)]$. 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.

Yet, excitation energies are generally well approximated (to tenths of an eV) when an adiabatic approximation is used in the linear response formalism. An exception are states of double-excitation character, where indeed it is the lack of memory dependence that dooms adiabatic TDDFT. Part of the

reason for the success of adiabatic TDDFT in many excitations is that the KS eigenvalues are themselves reasonably close to the true excitations. Species in intense fields are a different story (see Part V), where memory dependence can play a vital role.

The remainder of this chapter will be investigating memory properties of the *exact* functional. Understanding how the exact functional behaves should prove a useful tool in constructing accurate approximations.

4.2 History Dependence: An Example

Consider beginning a system in its ground state, which we will assume to be non-degenerate. By virtue of the Hohenberg-Kohn theorem, a non-degenerate ground-state is a functional of its own density: initial-state dependence need not be explicitly included in the functional, provided that the functional space is reduced to that where the initial state is a non-degenerate ground state.

So, putting aside initial-state dependence, we may ask how far back does the system remember its past? How far back in time do observables at the present time 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 Kohn-Sham system and the interacting system are exactly, or exactly numerically, solvable. Two electrons in a Mathieu oscillator provides a good case [Hessler 2002]; the external potential has the form:

$$v(\boldsymbol{r}) = k(t)r^2/2, \text{ with } k(t) = \bar{k} - \epsilon\cos(\omega t) \ . \tag{4.1}$$

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 2000], largely because, for some parameters, the interacting problem can be solved analytically. For the exact interacting solution of the time-dependent problem, (4.1), we transform to center-of-mass and relative coordinates as this 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, which begins in the ground state, the exact evolving density is obtained. 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, one can invert the KS equation to obtain the KS potential in terms of the evolving density [Hessler 2002].

One may then compare the exact calculation with that of an adiabatic (albeit not self-consistent) one, where one inputs the instantaneous density into a ground-state functional. The exact interacting dynamics in the Mathieu oscillator has the useful property that the evolving density retains a Gaussian-like profile, such that at each time t, it is very close to the density of a

ground state of a certain Hooke's atom of spring constant k_{eff}. This spring constant is not equal to the actual spring constant in (4.1) 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 its *density* is that of a ground state of some Hooke's atom.

Many interesting phenomena arise [Hessler 2002]; one typically finds the differences between the adiabatic approximation and the exact KS case to be very large (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.

Of particular interest for this chapter is that the correlation potential displays severe non-locality in time due to history dependence. Before demonstrating this, we first note a simple way to track down the behavior in time of the correlation potential. The first time-derivative of the correlation energy, $\dot{E}_{\text{c}}(t)$, is intimately related to the correlation potential, $v_{\text{c}}(t)$, via [Hessler 1999]

$$\dot{E}_{\text{c}}(t) = \int \mathrm{d}^3 r \, v_{\text{c}}(\boldsymbol{r}, t) \dot{n}(\boldsymbol{r}, t) \; . \tag{4.2}$$

This shows that if $\dot{E}_{\text{c}}(t)$ depends not just on the density at and near time t, but also on its earlier history, then $v_{\text{c}}(t)$ must too. That is, non-locality in $\dot{E}_{\text{c}}$ directly implies non-locality in the correlation potential $v_{\text{c}}(t)$. We turn now to Fig. 4.1. In the top panel is a plot of the value of $k_{\text{eff}}(t)$, which, as discussed earlier, completely identifies the density profile. The density profiles for a time range centered near $t = 4.8$ and centered near $t = 28.9$ are almost the same, yet the values of $\dot{E}_{\text{c}}(t)$ near those times are significantly different. The density at times near t is not enough to specify $\dot{E}_{\text{c}}$: it depends on the entire history and this is what we mean by non-locality in time. Likewise, the exact correlation potential $v_{\text{c}}(t)$ is a highly non-local functional of the density. Any adiabatic approximation has no history dependence and will fail to capture this effect.

4.3 Initial-State Dependence

For a given time-dependent density $n(\boldsymbol{r}, t)$, how does the potential that yields that density depend on the choice of the initial wave-function? Initial-state dependence has only begun to be explored [Maitra 2001, Maitra 2002a, Holas 2002]; unlike the dependence on the density, 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 exploration.

One may wonder whether initial-state dependence actually exists. That is, if we are constraining the density to evolve in a certain way, are the implicit

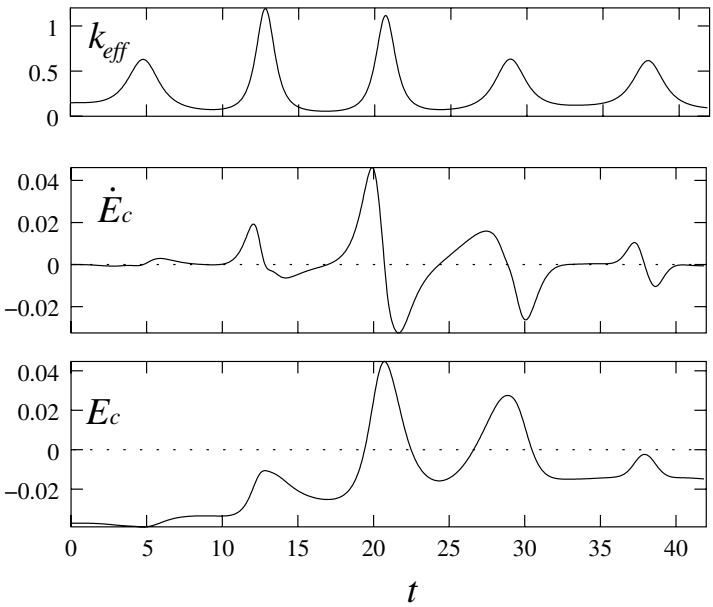

Fig. 4.1. Non-locality in time: the *top panel* shows $k_{\rm eff}(t)$, *middle panel* $\dot{E}_{\rm c}$, *bottom panel* $E_{\rm c}$. The parameters in (4.1) are $\bar{k} = 0.25$, $\omega = 0.75$ and $\epsilon = 0.1$. Atomic units are used here, and throughout this chapter: energies are measured in Hartrees, distances in Bohr radii, and times are in units of 2.419×10^{-17}s

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 $n(\boldsymbol{r}, t)$ evolving in time under an external time-dependent potential $v_{\rm ext}(\boldsymbol{r}, t)$. 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 $n(\boldsymbol{r}, t)$. Let the electron's wavefunction be $\varphi(\boldsymbol{r}, t)$, where $n(\boldsymbol{r}, t) = |\varphi(\boldsymbol{r}t)|^2$. An alternate candidate wavefunction $\tilde{\varphi}(\boldsymbol{r}, t)$ that evolves with identical density (in a different potential) must then be related to $\varphi(\boldsymbol{r}, t)$, by a (real) phase $\alpha(\boldsymbol{r}, t)$:

$$\tilde{\varphi}(\boldsymbol{r}, t) = \varphi(\boldsymbol{r}, t) \mathrm{e}^{\mathrm{i}\alpha(\boldsymbol{r}, t)} \ . \tag{4.3}$$

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

$$\dot{n}(\boldsymbol{r},t) = -\nabla \cdot \boldsymbol{j}(\boldsymbol{r},t) \ , \tag{4.4}$$

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

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\mathrm{i}}{2}[\varphi(\boldsymbol{r},t)\nabla\varphi^*(\boldsymbol{r},t) - \varphi^*(\boldsymbol{r},t)\nabla\varphi(\boldsymbol{r},t)] \ . \tag{4.5}$$

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

$$0 = \dot{n}_{\varphi}(\boldsymbol{r},t) - \dot{n}_{\tilde{\varphi}}(\boldsymbol{r},t) = \nabla \cdot [n(\boldsymbol{r},t)\nabla\alpha(\boldsymbol{r},t)] \ , \tag{4.6}$$

where on the right-hand side we have inserted the difference in the currents of $\tilde{\varphi}$ and φ, calculated using (4.5). Now if we multiply (4.6) by $\alpha(\boldsymbol{r},t)$ and integrate over all space, we obtain

$$0 = \int \mathrm{d}^3r\, \alpha(\boldsymbol{r},t)\nabla \cdot [n(\boldsymbol{r},t)\nabla\alpha(\boldsymbol{r},t)] = -\int \mathrm{d}^3r\, n(\boldsymbol{r},t)|\nabla\alpha(\boldsymbol{r},t)|^2 \tag{4.7}$$

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

Because the integrand in (4.7) cannot be negative, yet it integrates to zero, the integrand must be identically zero. Thus $\nabla\alpha(\boldsymbol{r},t) = 0$ everywhere. This is true even at nodes of the wavefunction, where $n(\boldsymbol{r}_0,t) = 0$: 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, $\alpha(\boldsymbol{r},t)$ must be constant in space, i.e., the wavefunctions $\varphi(\boldsymbol{r},t)$ and $\tilde{\varphi}(\boldsymbol{r},t)$ 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.

A note about the vanishing of the surface term in (4.7): This can be compared with the requirement on the potential in the Runge-Gross theorem, as discussed after (1.14). In [Maitra 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!

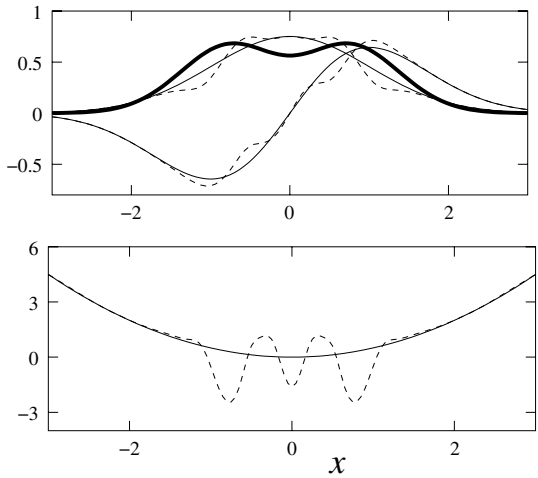

Fig. 4.2. An example of initial-state dependence for two non-interacting electrons: two different wavefunctions may evolve with the same density in different potentials. In the top plot, the *solid lines* are the two occupied orbitals of one wavefunction, which happens to be a stationary state of the 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

Many Electrons

For many electrons, initial-state dependence is real and alive: one can find two or more 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. 4.2 and 4.3. In Fig. 4.2, 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 2001, Holas 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], 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

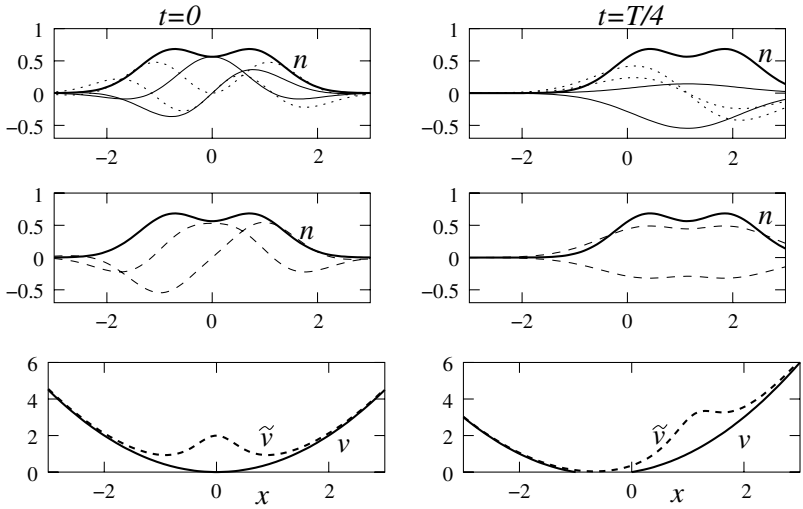

Fig. 4.3. *Top left panel*: the real and imaginary parts of the driven harmonic oscillator Floquet orbitals $\varphi_0(x,0)$ (*solid*) and $\varphi_1(x,0)$ (*dotted*) at time $= 0$, together with their density (*thick line*). *Middle left panel*: The real and imaginary parts of the alternative doubly-occupied 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 $t = T/4$

density: that is, both the potentials shown in the lower panel of Fig. 4.2, 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 [see (1.33)]. 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.

A note about the construction of the potential: In [van Leeuwen 1999], van Leeuwen answered the question of non-interacting v-representability in TDDFT. That is, given a density evolution of an interacting system, does a non-interacting system exist that can reproduce this? Given some restrictions on the initial state, the answer is in the affirmative, and it is also shown there how to construct such a potential for an appropriate choice of the initial state.

Figure 4.3 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 [Maitra 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. 4.3. The middle panel of Fig. 4.3 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 are possible Kohn-Sham wavefunctions, and both the solid and dashed potentials in the lower panels are possible Kohn-Sham 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.

4.4 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 when the initial state is a ground state. On the other hand, we shall see that due to the entanglement, memory dependence can often be reduced to history dependence alone.

Consider an interacting system, beginning with wavefunction $\Psi(0)$ at time 0, and evolving in time, with density $n(\boldsymbol{r},t)$. 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 $v_{\rm xc}$: that is,

$$v_{\rm xc}[n_{t'},\Psi(t'),\Phi(t')](\boldsymbol{r},t) = v_{\rm xc}[n,\Psi(0),\Phi(0)](\boldsymbol{r},t) \quad \text{for} \quad t > t' \,, \tag{4.8}$$

Here, $\Psi(t') = \hat{U}(t')\Psi(0)$, where $\hat{U}(t)$ is the unitary evolution operator, and $\Phi(t') = \hat{U}_{\rm KS}(t')\Phi(0)$ where $\hat{U}_{\rm KS}(t')$ 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 $n(\boldsymbol{r},t)$ for times t greater than the subscript.

Equation (4.8) displays the entanglement of 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. 11), (4.8) 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 (4.8) 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 backward 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 produces no difference. By ignoring both history dependence *and* initial-state dependence, the ALDA trivially satisfies (4.8).

A technical note: Although the RG theorem was proven only for analytic potentials (i.e., those that equal their Taylor series expansions at t in a neighbourhood of t in $[0, \infty)$ for all $t \geq 0$) [Runge 1984], it holds also for piecewise analytic potentials, i.e., potentials that are analytic in each of a finite number of intervals [Maitra 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.

In the usual formulation of TDDFT, one may choose any initial KS state which reproduces the density and divergence of the current of the interacting initial state [van Leeuwen 1999]. Here, 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 (4.8) yields an exact condition relating the xc kernel to initial-state variations [Maitra 2005a]. We consider applying (4.8) 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 [cf. 1.21]. 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 (1.5) and (1.9). Then one can show that

$$\begin{aligned}
&\sum_\alpha \int \mathrm{d}^3 r_1 \left.\frac{\delta v_{\mathrm{KS}}[n_{t'}, \Phi_{t'}](\boldsymbol{r}, t)}{\delta \varphi_{t',\alpha}(\boldsymbol{r}_1)}\right|_{(n_{\mathrm{GS}}, \Phi_{\mathrm{GS}}[n_{\mathrm{GS}}])} \delta\varphi_{t',\alpha}(\boldsymbol{r}_1) \\
&- \int \mathrm{d}x_1 \ldots \int \mathrm{d}x_N \left.\frac{\delta v_{\mathrm{ext}}[n_{t'}, \Psi_{t'}](\boldsymbol{r}, t)}{\delta \Psi_{t'}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)}\right|_{(n_{\mathrm{GS}}, \Psi_{\mathrm{GS}}[n_{\mathrm{GS}}])} \delta\Psi_{t'}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) + \text{c.c.} \\
&\qquad = \int \mathrm{d}^3 r_1 \int_0^{t'} \mathrm{d}t_1 \; f_{\mathrm{xc}}[n_{\mathrm{GS}}](\boldsymbol{r}, \boldsymbol{r}_1, t - t_1) \delta n(\boldsymbol{r}_1, t_1)\,, \quad 0 < t' < t\,, \qquad (4.9)
\end{aligned}$$

where the variables $\boldsymbol{x}_i = (\boldsymbol{r}_i, \sigma_i)$ represent spatial and spin coordinates, $\delta\varphi_{t',\alpha} = \delta\varphi_\alpha(t') = \varphi_\alpha(t') - \varphi_{\alpha,\mathrm{GS}}[n_{\mathrm{GS}}]$ 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.

4.5 Role of Memory in Quantum Control Phenomena

The challenges memory dependence presents to TDDFT emerge immediately when we attempt to describe 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.

Let us say we are interested in driving a molecule from its ground state Ψ_0 in potential $v_{\mathrm{ext},0}$ to its mth excited state Ψ_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 $v_{\mathrm{KS},\,0}$ whose ground-state Φ_{KS}, has density n_{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 $v_{\mathrm{ext},\,0}$, but this is *not* guaranteed to be the density of the KS excited state of potential $v_{\mathrm{KS},\,0}$. 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 $v_{\mathrm{KS},\,0}$.

There are two possibilities for the KS potential after time $\tilde{t}$. The first is that it does 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 ultranonlocal 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 mth 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 ultranonlocal 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 (4.8), 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 ultranonlocal 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

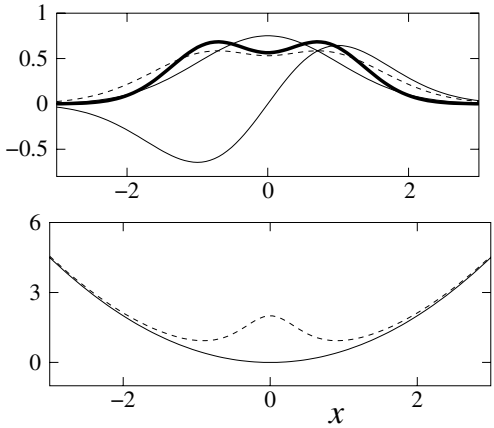

Fig. 4.4. In the *top panel* is the density (*thick solid line*) of the two electron singlet excited state (*solid lines*) of the harmonic oscillator (*solid line* in the *lower panel*). The *dashed line* is the doubly-occupied orbital resulting from evolving the singlet ground-state to a state of the 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*

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 evolving 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 case of severe static correlation, where a single Slater determinant is inadequate to describe a truly multi-determinantal state. A simplified model of this is shown in Fig. 4.4. 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 we 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.

4.6 Outlook

Memory plays a very interesting role in the behaviour of 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. For TDDFT to be used for time-dependent phenomena as confidently as DFT is used for ground-state problems, more understanding and modeling of memory effects is required, along with developments of memory-dependent approximations such as those mentioned in the introduction Sect. 4.1. In linear response, why the adiabatic approximation works so well for many typical excitations is not well understood. Strong field dynamics is especially the regime that TDDFT may be the only feasible approach, as wavefunction methods for more than a few interacting electrons becomes prohibitively expensive. Yet it is in this regime that memory effects appear to be significant, and fundamentally so for quantum control problems.