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CHAPTER 1

TEN TOPICAL QUESTIONS IN TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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1. Introduction

This book chapter is an eccentric view of the present state of time-dependent density functional theory (TDDFT). It is not intended as a comprehensive overview of the field, but merely raises some issues that face the field at the present time, and we hope it makes enjoyable reading. The opening question of Sec. 2.1 is particularly eccentric, mirroring the style of our old friend, Bob Parr.

A time-dependent N-electron system satisfies the time-dependent Schröd-inger equation :

$$\hat{H}\Psi(\mathbf{r}_1 \dots \mathbf{r}_N t) = i\dot{\Psi}(\mathbf{r}_1 \dots \mathbf{r}_N t), \tag{1}$$

where we have (for simplicity) ignored spin indices, and used atomic units ($e^2 = \hbar = m = 1$), and introduced a dot for time-derivatives. Here the Hamiltonian consists of three contributions

$$\hat{H} = \hat{T} + \hat{V}_{\rm ee} + \hat{V}_{\rm ext}, \tag{2}$$

the kinetic energy, the Coulomb repulsion, and the external potential, due to the nuclei and any external fields. Note Eq. (1) is first-order in time, and solutions depend on the initial wavefunction, $\Psi(0)$.

Rigorous modern TDDFT begins with the Runge-Gross (RG) theorem[1], although the first modern TDDFT calculations were done by Ando [2,3] for semiconductor surfaces and by Zangwill and Soven [4,5] for atoms. The RG theorem generalizes the Hohenberg-Kohn theorem [6] to time-dependent external potentials, and states that, for a given initial state, there is a unique mapping between the evolving density and the time-dependent potential. We can then consider a system of non-interacting electrons in a Slater determinant of orbitals, satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm s}(\mathbf{r}t)\right\}\phi_i(\mathbf{r}t) = i\dot{\phi}_i(\mathbf{r}t), \tag{3}$$

and beginning in Slater determinant $\Phi(0)$. Their time-dependent density is

$$n(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2. \tag{4}$$

We can require this density to match that of an interacting electronic system, by the RG theorem, and define the time-dependent exchange-correlation potential:

$$v_{\rm xc}[n;\Psi(0),\Phi(0)](\mathbf{r}t) = v_{\rm s}[n;\Phi(0)](\mathbf{r}t) - v_{\rm ext}[n;\Psi(0)](\mathbf{r}t) - v_{\rm H}[n](\mathbf{r}t), \tag{5}$$

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where the Hartree potential is

$$v_{\rm H}[n](\mathbf{r}t) = \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|}. \tag{6}$$

Note that the exchange-correlation potential is a functional of the initial states of both the interacting system and the Kohn-Sham reference system. It would be very nice to derive Eq. (3) as a stationary point of an action, but this is more subtle than first appears, and is the subject of Sec. 2.2. As in the ground-state case, for many electrons, Eq. (3) is much faster to solve than Eq. (1). It explicitly yields the time-dependent density $n(\mathbf{r}t)$, and, in principle, yields everything else we might want to know about the interacting problem. However, only the density itself is guaranteed to be the same in both systems, and even the current, whose gradient is determined by the time-derivative of the density via continuity, could differ in the two systems, as discussed in Sec. 2.3. Another example is the probability of double ionization of an atom in an intense laser field, where the KS expectation value differs greatly from the exact value, as shown in Sec. 2.6. Moreover, in general, properties of the interacting system are functionals of both the density and the initial state, as discussed in Sec. 2.8.

In practice, we must make approximations for the exchange-correlation potential. The most popular in use today is the adiabatic local density approximation (ALDA), which employs the potential for a uniform gas of electrons of density $n(\mathbf{r}t)$:

$$v_{\rm xc}^{\rm ALDA}(\mathbf{r}t) = v_{\rm xc}^{\rm unif}(n(\mathbf{r}t)), \tag{7}$$

as was used in the historic calculation of Ando [2,3]. This approximation should work well for a system beginning in its ground state which varies slowly in time and space, but most of the systems that it is used for do not fit this description. The time-dependent Kohn-Sham equations, Eq. (3), with the exchange-correlation potential approximated by ALDA, Eq. (7), have become increasingly popular for calculations of atoms and molecules in strong laser fields, some of which are discussed in Sec. 2.6. How accurate such ALDA calculations are has rarely been investigated, but is studied in Sec. 2.7. Note that this approximation is utterly forgetful. The ALDA exchange-correlation potential cares nothing for the past history of the density or the initial state, and is completely determined by the density at a given instant in time. The consequences of this are discussed in Sec. 2.9.

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Most of the applications of TDDFT at present are for the special case of an infinitely weak perturbing field applied to a system in its ground state. Analysis of this case leads to predictions for electronic transition frequencies, oscillator strengths, polarizabilities *etc.*, *i.e.*, the full optical response. We define the susceptibility $\chi[n_0](\mathbf{r}\mathbf{r}'\omega)$ as the response of the ground state of the interacting system to a small change in the external potential:

$$\delta n(\mathbf{r}\omega) = \int d^3r' \chi[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v_{\rm ext}(\mathbf{r}'\omega) \tag{8}$$

$$= \int d^3r' \chi_s[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v_{\rm s}(\mathbf{r}'\omega). \tag{9}$$

The second line follows since the density change is the same for the interacting system and the non-interacting system; $\chi_s[n_0](\mathbf{r}\mathbf{r}'\omega)$ is the Kohn-Sham susceptibility. Applying Eq. (5) to a slightly perturbed system, we find

$$\delta v_{\rm s}(\mathbf{r}\omega) = \delta v_{\rm ext}(\mathbf{r}\omega) + \int d^3r' \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\rm xc}[n_0](\mathbf{r}\mathbf{r}'\omega)\right)\delta n(\mathbf{r}'\omega) \tag{10}$$

where $f_{\rm xc}[n_0](\mathbf{r}\mathbf{r}'\omega)$ is known as the exchange-correlation kernel. In the time-domain,

$$f_{\rm xc}[n_0](\mathbf{r}\mathbf{r}', t-t') = \delta v_{\rm xc}[n_0](\mathbf{r}t)/\delta n(\mathbf{r}'t'). \tag{11}$$

These equations lead to the Dyson-type response equation [7]

$$\chi(\mathbf{r}\mathbf{r}'\omega) = \chi_{\rm s}(\mathbf{r}\mathbf{r}'\omega) + \int d^3r_1 \int d^3r_2\ \chi_{\rm s}(\mathbf{r}\mathbf{r}_1\omega) f_{\rm HXC}(\mathbf{r}_1\mathbf{r}_2\omega)\chi(\mathbf{r}_2\mathbf{r}'\omega), \tag{12}$$

where $f_{\rm HXC} = 1/|\mathbf{r}-\mathbf{r}'| + f_{\rm xc}$, and all objects are functionals of the ground-state density.

Poles of the susceptibility occur at transition frequencies, while oscillator strengths are related to pole strengths. Thus solution of Eq. (12) yields all optical response information. Casida [8] showed how to solve these equations in a finite basis, analogously to the solution of time-dependent Hartree equations. Note that explicit calculation requires two separate approximations. The first is for the ground-state Kohn Sham system, which yields the ground-state potential, from which is constructed the Kohn-Sham susceptibility, $\chi_{\rm s}$. The second is an approximation for the exchange-correlation kernel, which in principle is frequency-dependent. Sometimes, for $v_{\rm xc}$ a standard ground-state functional, such as a generalized gradient

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approximation or a hybrid with exact exchange, is employed, and $f_{\rm xc}$ is approximated by the ALDA, *i.e.*, by inserting Eq. (7) in Eq. (11). Other times, both are approximated by the same ground-state functional employing, e.g., the LDA for $v_{\rm xc}$ and the ALDA for $f_{\rm xc}$. In this way, the condition

$$\lim_{\omega\to 0} f_{\rm xc}(\mathbf{r},\mathbf{r}',\omega)|_{n_0} = \frac{\delta^2 E_{\rm xc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}|_{n_0} \tag{13}$$

is satisfied.

Applications and development of TDDFT is a rapidly expanding field, and we next review recent developments. We refer the reader to an earlier review[9] and references therein for earlier applications of TDDFT.

In quantum chemistry, the largest use of TDDFT has been to extract the excitation energies and optical response of molecules, using the linear response formalism outlined above. Section 2.4 discusses some of the errors inherent in such calculations, due to limitations of our present functionals. On the other hand, Sec. 2.5 explains how TDDFT can be quite successful despite these limitations.

Most quantum chemical codes, such as Gaussian[10] and ADF[11,12] perform TDDFT response calculations, allowing experimentalists to immediately compare with theory[13,14]. Surveys of mean polarizabilities of organic molecules have been performed[15]. Many molecular calculations, such as excitations in small organic molecules[16], in tertiophene[17], in transition metal molecules[18] and complexes[19,20,21,22], using non-empirical hybrid functionals[23], have been tested. Closed-shell polycyclic aromatic hydrocarbon cations[24] have been studied, as have been open-shell molecules[25], linear polyene oligimers[26], radical cations with N-N bonds[27], and s-tetrazine in both gas-phase and solvated[28]. The optical response of organic dyes[29] has been calculated, and explanations given of the color of 1,2-dithiins[30], and of the spectra of sulfines[31], cromone[32], and pyrazine[33]. Even aromatic radical cations[34] have been studied; also conjugated molecules[35] and of course fullerenes[36]. Weakly hydrogen-bonded species have also been studied[37]. Tests of various functionals for excitation energies on training sets of molecules are ongoing[38], just as in the ground state. One considerable benefit is to combine spectral information with structural and thermochemical data as a more thorough test of DFT calculations, as in the case of trans-stilbene[39].

Higher order response has also been calculated. TDDFT is now used for hyperpolarizabilities[40], such as in chiral molecules[41]. Both linear and magnetic circular dichroism have

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been calculated[42,43,44]. The Rydberg states of propyne have also been calculated in conjunction with resonant-energy multiphoton ionization experiments[45]. Recently TDDFT calculations showed that a candidate for strong non-linear optical response was less promising than experiment suggested[46]. Raman intensities have also been calculated[47]. Not yet understood is the ability of TDDFT to perform well, even for some states with significant double-excitation character[48].

Calculations are appearing with real biological significance, such as on chlorophyll A[49] and free-base porphrin[50,51]. A very important recent development is the attempt to study charge transfer in biological molecules[52,53]. Fluorescence of 2-aminopurine has been calculated[54]. Algorithmic developments are also occurring. Under many circumstances, the Tamm-Dancoff approximation is sufficient[55] for excitation energies. Fast algorithms for solving TDHF equations can be immediately applied to adiabatic TDDFT calculations[56,57]. Geometric derivatives for excited-states have been coded[58].

Much of the earliest work on TDDFT response was performed on metallic clusters[59]. Clusters of ZnS have also been studied[60].

In atomic and molecular physics, TDDFT is being applied to problems of (mostly) atoms in intense laser fields, including stabilization phenomena[61], and nonsequential multiple ionization[62,63]. Even the more demanding time-dependent optimized effective potential (TDOEP)[64] has been coded and applied to high harmonic generation[65,66]. Some of these calculations apply the basic formalism within Floquet theory[67,68]. Also, the original photoionization problem has been recently been revisited using more accurate ground-state potentials[69], while calculations for molecules have also been done[70]. Clusters can now also be handled[71]. Energetic collisions between atoms and ions are also being tackled[72,73,74].

For extremely large calculations, involving thousands of electrons, even the TDKS equations are too expensive to solve, and time-dependent Thomas-Fermi approaches are used[75,76].

In mesoscopic physics, TDDFT has been used for quite a while to study the optical response of quantum dots[77].

The applications mentioned above have all been to finite systems. The extension to extended systems will be a major effort of itself, for the simple reason that our present day functionals, such as LDA and GGA, do *not* provide useful approximations to the exchange-correlation kernel $f_{\rm xc}$ in this case. To see this, simply

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consider the Fourier transform of $f_{\rm HXC}$. The direct Coulomb interaction behaves as $4\pi/q^2$, where q is the wavevector corresponding to $\mathbf{r}-\mathbf{r}'$. The optical response is the long-wavelength limit, dominated by $q \to 0$. The LDA kernel is local in space, so its Fourier transform is a constant, becoming negligible as $q \to 0$. Similar reasoning applies to GGAs. The ultra non-locality in space of the exchange-correlation kernel in extended systems has recently been emphasized[78].

There have been a few attempts to perform calculations on extended systems, such as in polymers[79,80,81], and the optical response of solids[82,83,84], but these difficulties have not been fully understood or overcome.

On the other hand, other interesting properties of solids have been calculated. For many years TDDFT has been used to calculate the dielectric response of metals[85], in attempts to disentangle band-structure effects from correlation, especially in the dispersion of the bulk plasmon[86]. Recently, spin-response of magnetic metals[87,88] has been calculated using TDDFT. Also electronic damping at surfaces has recently been calculated using TDDFT[89,90].

At a conceptual level, the links between TDDFT and traditional many-body approaches for extended systems, such as GW, are only now being explored[91], as are extensions of ground-state theorems[92], and the description of potentials in terms of wavefunction quantities[93] as opposed to functional derivatives.

2. Nine questions and some answers

2.1. Parr question: Do the density and potential determine the energy?

As this volume is dedicated to Bob Parr on his eightieth birthday, we open with a question he originally raised for ground-state density functional theory. The question is: if someone gives you both the external potential for a system *and* it's exact density, can you recover the *exact* ground-state energy, without solving a many-body problem? Note that this differs from the usual practical question of DFT, in which you are given only the potential, and must find the corresponding density and energy.

For two (spin-unpolarized) electrons, the answer is yes. For example, one could deduce the ionization energy I from the tail of the density and also solve the one-electron problem for the external potential, yielding E_1. Then the two-electron ground-state energy is just $E_1 - I$.

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More generally, using a technique invented by Bob and others [94,95], one can, for any given density, construct the corresponding Kohn-Sham potential, $v_{\rm s}(\mathbf{r})$, *i.e.*, find that single-particle potential for which that density is a ground-state density (if it exists). Then one can deduce the exchange-correlation potential $v_{\rm xc}(\mathbf{r})$ by inverting its definition in Eq. (5). But note that this is not yet enough to determine the exchange-correlation energy, just the potential.

To extract the ground-state energy, we write

$$E = T_{\rm s} + U + \int d^3r\ n(\mathbf{r})\ v_{\rm ext}(\mathbf{r}) + E_{\rm xc}, \tag{14}$$

where $T_{\rm s}$ is the Kohn-Sham kinetic energy, U is the Hartree energy, and $E_{\rm xc}$ is the exchange-correlation energy. All these pieces can be extracted from what we now have, except the last. To go a step further, one can use the virial theorem applied to the exchange-correlation potential to find

$$E_{\rm xc} + T_{\rm c} = \int d^3r\ n(\mathbf{r})\ \mathbf{r}\cdot v_{\rm xc}(\mathbf{r}), \tag{15}$$

where $T_{\rm c}$ is the kinetic contribution to the correlation energy. Thus the virial of the exchange-correlation potential yields the sum of energies above, but not $E_{\rm xc}$ alone, which would finish our problem.

Several years ago, one of the authors and Bob (with collaborators) [96,97] published back-to-back articles in Phys. Rev. A on this point, noting that the remaining piece of correlation energy, *e.g.*, $E_{\rm xc} - T_{\rm c}$, is more amenable to approximation by standard density functional methods, so that use of the virial above on the exact density reduces errors significantly.

But, returning to the logical question, note that for high-density systems, correlation becomes negligible relative to exchange, so that the answer is once again yes. Interestingly, for low-density systems, in which correlation is dominated by potential contributions, so that $T_{\rm c} << |E_{\rm c}|$, one can use the virial once again to extract $E_{\rm xc}$, and get the ground-state energy.

What has this to do with TDDFT? Suppose a system begins in its ground-state, and then is disturbed by a time-dependent external potential. The Heisenberg equation of motion for the Hamiltonian is very simple[92]

$$\dot{E} = \langle \partial H/\partial t \rangle = \int d^3r\ n(\mathbf{r}t)\dot{v}_{\rm ext}(\mathbf{r}t) \tag{16}$$

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i.e., the time-evolution of the energy is given entirely by the time-evolution of the one-body perturbation. Integrating with respect to time shows that knowledge of $v_{\rm ext}(\mathbf{r}t)$ and $n(\mathbf{r}t)$ is sufficient to determine the entire evolution of the energy, *once the initial value is known, i.e.*,

$$E(t) = E(0) + \int_0^t dt'\ \dot{E}(t). \tag{17}$$

So, rather amusingly, the Parr question is trivially answered yes in TDDFT, except for the initial ground-state value.

So, the Parr question has a positive answer for the ground state of two electrons, in the high-density limit, in the low-density limit, and (up to a constant) for all time-dependent problems. Is it true in general?

2.2. What is the simplest definition of the action?

Time-independent quantum mechanics is armed with a variational principle which is very useful for ground-state DFT. By approximating the exchange-correlation energy functional, we obtain approximations for its functional derivative, the exchange-correlation potential $v_{\rm xc}[n](\mathbf{r})$ to be used in Kohn-Sham calculations.

What is the analog in the time-dependent case? In time-dependent quantum mechanics, the role of the energy is taken by the quantum mechanical action:

$$\mathcal{A}[\Psi] = \int_{t_0}^{t_1} dt \langle \Psi(t)|i\partial_t - \hat{H}(t)|\Psi(t)\rangle. \tag{18}$$

Stationary points of $\mathcal{A}$, with initial wavefunction $\Psi(t_0)$, yield solutions to the time-dependent Schrödinger equation. Translating this into TDDFT is however much more subtle than in the ground-state case. The simplest, and perhaps most natural step would be to define

$$\mathcal{A}[n;\Psi_0] = \int_{t_0}^{t_1} dt \langle \Psi[n;\Psi_0](t)|i\partial_t - \hat{H}_{v_0}(t)|\Psi[n;\Psi_0](t)\rangle, \tag{19}$$

where $\Psi[n;\Psi_0]$ is a functional of the density and the initial state Ψ_0 [1]. The potential v_0 in the Hamiltonian H_{v_0} is given and fixed. The Euler equation $\delta\mathcal{A}/\delta n(\mathbf{r}t) = 0$ would then supposedly yield the correct density. One can extract out a universal part of the action[98,9], and a part that explicitly depends on the external potential. One can define a similar object for the Kohn-Sham action [98,9] and, comparing the two, extract an exchange-correlation action $\mathcal{A}_{\rm xc}[n;\Psi_0,\Phi_0]$.

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There are, however, a number of problems with this definition of the action. First of all the density n and the initial state determine $|\Psi[n;\Psi_0](t)\rangle$ only up to an arbitrary phase factor. This means that the wavefunction $|\bar{\Psi}(t)\rangle = \exp(i\alpha(t))|\Psi[n;\Psi_0](t)\rangle$ with $\alpha(t_0) = 0$ but otherwise arbitrary, also gives the density n and the initial state $|\bar{\Psi}(t_0)\rangle = |\Psi_0\rangle$. This makes the action ill-defined since

$$\langle \Psi[n;\Psi_0](t)|i\partial_t - \hat{H}(t)|\Psi[n;\Psi_0](t)\rangle = \langle \bar{\Psi}(t)|i\partial_t - \hat{H}(t)|\bar{\Psi}(t)\rangle + \partial_t\alpha(t). \tag{20}$$

It is easily seen that the effect of $\alpha(t)$ is to add a purely time-dependent shift $\partial_t\alpha(t)$ to the potential that $|\bar{\Psi}(t)\rangle$ evolves in. To make the action well-defined we have to specify $\alpha(t)$, which means that we have to fix a gauge for the potential. One choice would be that we choose as an argument of the action functional the wavefunction $|\Psi[n;\Psi_0](t)\rangle$ that evolves in a potential $v(\mathbf{r}t)$ that vanishes at infinity. This defines the potential uniquely in terms of the density and the initial state. If we make this choice then we can express the action explicitly in terms of the density n, the potential $v[n;\Psi_0](\mathbf{r}t)$ and the potential $v_0(\mathbf{r}t)$ of the Hamiltonian that defines the action:

$$\begin{aligned}\mathcal{A}[n;\Psi_0] &= \int_{t_0}^{t_1} dt \langle \Psi[n;\Psi_0](t)|i\partial_t - \hat{H}_{v_0}(t)|\Psi[n;\Psi_0](t)\rangle \\ &= \int_{t_0}^{t_1} dt \langle \Psi[n;\Psi_0](t)|i\partial_t - \hat{H}_v(t) + \hat{V}[n;\Psi_0](t) - \hat{V}_0(t)|\Psi[n;\Psi_0](t)\rangle \\ &= \int d^3r \int_{t_0}^{t_1} dt n(\mathbf{r}t)(v[n;\Psi_0](\mathbf{r}t) - v_0(\mathbf{r}t)),\end{aligned} \tag{21}$$

where we used that $|\Psi[n;\Psi_0](t)\rangle$ satisfies the time-dependent Schrödinger equation (TDSE) with potential $v[n,\Psi_0](\mathbf{r}t)$. If we calculate the functional derivative of this action with respect to n we obtain

$$\frac{\delta\mathcal{A}}{\delta n(\mathbf{r}t)} = v[n,\Psi_0](\mathbf{r}t) - v_0(\mathbf{r}t) + \int d^3r' \int_{t_0}^{t_1} dt' n(\mathbf{r}'t') \frac{\delta v(\mathbf{r}'t')}{\delta n(\mathbf{r}t)}. \tag{22}$$

This is however not what one at first sight would have expected. One might have expected that

$$\frac{\delta\mathcal{A}}{\delta n(\mathbf{r}t)} = v[n,\Psi_0](\mathbf{r}t) - v_0(\mathbf{r}t) \tag{23}$$

which makes the action stationary for $v[n,\Psi_0](\mathbf{r}t) = v_0(\mathbf{r}t)$; then the wavefunction $|\Psi[n;\Psi_0](t)\rangle$ which makes the action stationary is the one that satisfies the TDSE

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with Hamiltonian H_{v_0}. This is, however, not the case. So what has happened? To understand this point we must go back to the original action Eq.(18) as a functional of the wavefunction, rather than the density, and see under which conditions we can derive the TDSE from the action. In fact, only under certain types of variations do the stationary points of the action yield the TDSE $(i\partial_t - \hat{H})|\Psi\rangle = 0$. We refer the reader to the recent review [99] for details, and here just state the results. Suppose the action $\mathcal{A}$ is stationary for variations $\delta\Psi$ around a certain Ψ. Then Ψ satisfies the TDSE if the variations $\delta\Psi$ are such that

(1) $\delta\Psi(t_0) = \delta\Psi(t_1) = 0$ and the real and imaginary part can be varied independently,
(2) or, alternatively, both $\delta\Psi_1 = \delta\Phi$ and $\delta\Psi_2 = i\delta\Phi$ are allowed variations for any $\delta\Phi$ [100].

Let us now go back to our TDDFT action of Eq.(19). This action is obviously defined on a restricted set of wavefunctions, namely all wavefunctions that can be parameterized by densities on the basis of the Runge-Gross theorem together with the gauge condition $v \to 0$ for $|\mathbf{r}| \to \infty$ on the corresponding potential. We will call this set of wavefunctions $\mathcal{V}$. To see if we can derive the TDSE from the restricted TDDFT action we must check that within the restricted set of wavefunctions $\mathcal{V}$ we can make the variations mentioned in points (1) and (2) above. We will see that this is not possible which is then consistent with Eq.(22). The variations $\delta\Psi$ within the set $\mathcal{V}$ must always be generated by potential variations, *i.e.* if some Ψ in this set satisfies a TDSE with Hamiltonian $\hat{H}$ then $\Psi + \delta\Psi$ satisfies

$$(i\partial_t - \hat{H}_v - \delta\hat{V})|\Psi + \delta\Psi\rangle = 0 \tag{24}$$

for some potential variation $\delta\hat{V}$. If we collect the first order terms we see that $\delta\Psi$ must satisfy

$$(i\partial_t - \hat{H}_v)|\delta\Psi\rangle = \delta\hat{V}|\Psi\rangle \tag{25}$$

with the boundary condition $\delta\Psi(t_0) = 0$ since we evolve all wavefunctions in the set $\mathcal{V}$ from a fixed initial state Ψ_0. Now it is clear that the real and imaginary part of $\delta\Psi$ are not independent, they are both determined by the potential $\delta\hat{V}$. Moreover, we see that Eq.(25) is first order in time and therefore $\delta\Psi(t)$ is completely determined by the initial condition $\delta\Psi(t_0) = 0$. We are therefore not allowed to put a second constraint $\delta\Psi(t_1) = 0$ on the variation $\delta\Psi$. Therefore we can not do the variations

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mentioned in point (1) above and are therefore not able to derive the TDSE from the TDDFT action in this way. What about the variations mentioned in point (2)? We see immediately that if $\delta\Psi_1 = \delta\Phi$ is a variation that satisfies Eq.(25) then the variation $\delta\Psi_2 = i\delta\Phi$ is produced by the potential $i\delta\hat{V}$, which is imaginary and therefore not allowed as a potential. We can therefore not make the variations mentioned in point (2) and we see that we can not derive the TDSE from the TDDFT action in this way either. We thus conclude that the action can not be used as a basis of time-dependent density functional theory.
The obvious question is then, can we define some other action functional as the basis of a time-dependent density functional theory? For instance, can we find some action $\mathcal{A}$ that satisfies Eq.(23)? If we can find such an action then we can construct the Legendre transform

$$\bar{\mathcal{A}}[v] = -\mathcal{A}[n] + \int d^3r dt n(\mathbf{r}t)(v(\mathbf{r}t) - v_0(\mathbf{r}t)), \tag{26}$$

where the density n on the right hand side must now be regarded as a functional of the potential v. The functional $\bar{\mathcal{A}}[v]$ satisfies

$$\frac{\delta\bar{\mathcal{A}}}{\delta v} = -\int \frac{\delta\mathcal{A}}{\delta n}\frac{\delta n}{\delta v} + \int (v - v_0)\frac{\delta n}{\delta v} + n = n, \tag{27}$$

where for convenience we used a shortened notation and left out the arguments. We see that if we can find a functional $\bar{\mathcal{A}}[v]$ of the external potential such that

$$\frac{\delta\bar{\mathcal{A}}}{\delta v(\mathbf{r}t)} = n(\mathbf{r}t) \tag{28}$$

then the functional $\mathcal{A}[n]$ with property Eq.(23) can be constructed from the inverse Legendre transform:

$$\mathcal{A}[n] = -\bar{\mathcal{A}}[v] + \int d^3r dt n(\mathbf{r}t)(v(\mathbf{r}t) - v_0(\mathbf{r}t)), \tag{29}$$

where v must now be regarded as a functional of n. The question therefore is: Is there a functional $\bar{\mathcal{A}}$ such that Eq.(28) is satisfied? We therefore ask the question whether or not the fundamental variable of TDDFT, namely the time-dependent density n, can be obtained as the functional derivative of some functional $\bar{\mathcal{A}}$ of the

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external potential. The answer is no if $\bar{\mathcal{A}}$ is twice differentiable because then we could differentiate Eq.(28) again and obtain

$$\frac{\delta\bar{\mathcal{A}}}{\delta v(\mathbf{r}t)\delta v(\mathbf{r}'t')} = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}. \tag{30}$$

The left hand side of this equation is symmetric in the space-time arguments since we assumed that $\bar{\mathcal{A}}$ was twice differentiable, whereas the right hand side of this equation is the density response function which has a causal structure, *i.e.* it is zero for $t > t'$. Therefore the causality and symmetry requirements contradict each other. We conclude that there is no differentiable functional of the external field with the property Eq.(28). Consequently there is no functional of the density with the property Eq.(23). We therefore conclude that the external potential $v[n, \Psi_0]$ of a many-body system with initial state Ψ_0 and density n can not be obtained as the derivative of a density functional. The same is of course true for a noninteracting system and in particular the Kohn-Sham system. We must conclude that the time-dependent Kohn-Sham potential is not a density derivative. To be more precise, there is no functional of the v-representable density $n(\mathbf{r}t)$ that has the Kohn-Sham potential as its derivative.
Is there some action functional defined on a larger class of densities that is capable of providing a derivation of the time-dependent Kohn-Sham equations? The answer to this question is yes. It turns out that that one can define a functional on a set of so-called time contour densities from which we can derive the Kohn-Sham equations. The corresponding action functional is called the Keldysh action. For further details on this functional we refer to the literature [101,99]. Let us finally answer the topical question asked in the title of this section. What is the simplest definition of the action? At the moment this is certainly the Keldysh action, as this is currently the only action functional that leads to a derivation of the Kohn-Sham equations that is free of paradoxes.

2.3. Is the Kohn-Sham current equal to the true current?

In TDDFT a noninteracting Kohn-Sham system is introduced with the same density as the true interacting system. Since the density and the current are closely related by the continuity equation we may wonder what the relation is between the Kohn-Sham current and the true current. In order to avoid confusion we stress

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that we will always be dealing with systems in time-dependent external fields that can always be transformed to a pure scalar potential by a gauge transformation. We therefore exclude magnetic fields. We start by describing some properties of the current. The current is defined as

$$\mathbf{j}(\mathbf{r}t) = \frac{1}{2i}(\nabla - \nabla')\gamma(\mathbf{r}, \mathbf{r}', t)|_{\mathbf{r}=\mathbf{r}'} \tag{31}$$

where γ is the one-particle density matrix of the system. The expectation value of the momentum $\mathbf{P}$ can be directly calculated from the current as follows

$$\mathbf{P}(t) = \int d^3r\mathbf{j}(\mathbf{r}t). \tag{32}$$

Finally, if we calculate the commutator of the density operator with the Hamiltonian we obtain the continuity equation

$$\partial_t n(\mathbf{r}t) = -\nabla \cdot \mathbf{j}(\mathbf{r}t). \tag{33}$$

Let us now turn to the Kohn-Sham system which has a current

$$\mathbf{j}_s(\mathbf{r}t) = \frac{1}{2i}\sum_{k=1}^{N}(\varphi_k^*(\mathbf{r}t)\nabla\varphi_k(\mathbf{r}t) - (\nabla\varphi_k^*(\mathbf{r}t))\varphi_k(\mathbf{r}t)) \tag{34}$$

and where φ_k are the Kohn-Sham orbitals. The Kohn-Sham current is not necessarily equal to the true current. We therefore define the exchange-correlation part $\mathbf{j}_{xc}$ of the current by

$$\mathbf{j}(\mathbf{r}t) = \mathbf{j}_s(\mathbf{r}t) + \mathbf{j}_{xc}(\mathbf{r}t). \tag{35}$$

Let us now investigate what the equations we defined at the beginning of this section can tell us about $\mathbf{j}_{xc}$. We start by considering the continuity equation Eq.(33). Since the true system and the Kohn-Sham system by definition have the same density we obtain

$$\nabla \cdot \mathbf{j}_{xc}(\mathbf{r}t) = \nabla \cdot \mathbf{j}(\mathbf{r}t) - \nabla \cdot \mathbf{j}_s(\mathbf{r}t) = 0. \tag{36}$$

We see that $\mathbf{j}_{xc}$ is a divergenceless or tranverse vector field which can therefore be written in the form $\mathbf{j}_{xc} = \nabla\times\mathbf{C}$ for some vector field $\mathbf{C}$. The continuity equation has another consequence. If we consider finite system for which densities and currents vanish at infinity then using Eq.(33) we can write the expectation value of the momentum as

$$\mathbf{P}(t) = \int d^3r\mathbf{j}(\mathbf{r}t) = \int d^3r\mathbf{r}\partial_t n(\mathbf{r}t). \tag{37}$$

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From this equation we see that the Kohn-Sham system and the true system have the same momentum and so

$$\int d^3r \mathbf{j}_{xc}(\mathbf{r}t) = 0. \tag{38}$$

The continuity equation has therefore told us that $\mathbf{j}_{xc}$ is a transverse vector field whose spatial average is zero. So far we have discussed some general relations which must be satisfied by $\mathbf{j}_{xc}$. We now turn to some more specific cases. For one-dimensional systems in which there are no transverse vector fields $\mathbf{j}_{xc}$ vanishes. For such systems the current is uniquely determined by the density from

$$j(xt) = -\int_{-\infty}^{x} dy \partial_t n(yt) \tag{39}$$

if the current vanishes at infinity. This equation immediately implies that for one-dimensional systems $j = j_s$ and $j_{xc} = 0$. It was conjectured [98] that this holds true in general. The argument was based on the fact that systems with two different time-dependent scalar potentials $v \neq v' + C(t)$ differing by more than a purely time-dependent function, yield two different currents $\mathbf{j} \neq \mathbf{j}'$. This follows immediately from the proof of the Runge-Gross theorem. Therefore the external potential is a well-defined functional $v[\mathbf{j}]$ on the set of v-representable currents. However, it was implicitly assumed that every current $\mathbf{j}$ produced by a scalar potential v in an interacting system can also be produced by a scalar potential v_s in a noninteracting system, *i.e.* the proof was based on an unproven noninteracting v-representability assumption. One may object that such an assumption is also made for the density in constructing the Kohn-Sham system in the first place. However, the density n and the scalar potential v are conjugate variables in the sense that the contribution of the external potential to the total energy is of the form of an integral over n times v. It is exactly this property that is used in the proof of the Hohenberg-Kohn theorem. The conjugate variable of the current, on the other hand, is the vector potential. On the basis of this one would expect that to reproduce an interacting current in an noninteracting system one needs an exchange-correlation vector potential $\mathbf{A}_{xc}$. Such a vector potential is indeed introduced in time-dependent current-density functional theory. On the basis of these arguments it seems unlikely that the noninteracting v-representability assumption for the current can be justified.

Another argument which suggests that $\mathbf{j}_{xc}$ is nonzero in general is provided by the following example. Consider a Kohn-Sham system with two particles in a singlet

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state, doubly occupying one spatial orbital:

$$i\partial_t \varphi(\mathbf{r}t) = \left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}t)\right)\varphi(\mathbf{r}t)$$
$$n(\mathbf{r}t) = 2|\varphi(\mathbf{r}t)|^2.$$

The Kohn-Sham orbital can then always be written in the form

$$\varphi(\mathbf{r}t) = \sqrt{\frac{n(\mathbf{r}t)}{2}} e^{i\theta(\mathbf{r}t)}. \tag{40}$$

With this expression we obtain the following equation for the Kohn-Sham current

$$\mathbf{j}_s(\mathbf{r}t) = n(\mathbf{r}t)\nabla\theta(\mathbf{r}t) \tag{41}$$

and we see that

$$\nabla \times \frac{\mathbf{j}_s(\mathbf{r}t)}{n(\mathbf{r}t)} = 0. \tag{42}$$

If we assume that $\mathbf{j} = \mathbf{j}_s$ then this implies that for any interacting two-electron system

$$\nabla \times \frac{\mathbf{j}(\mathbf{r}t)}{n(\mathbf{r}t)} = 0. \tag{43}$$

This seems an unlikely property for an arbitrary two-electron system with rotating currents, such as an Helium atom in an intense laser pulse of circularly polarized light. If the property Eq.(43) would be a general feature of two-electron systems then it must follow from some special property of the two-particle Hamiltonian. The question would of course be settled with one counterexample for which the vorticity of Eq.(43) does not vanish. However, it is not easy to give a simple example. The solvable model systems are separable and have the special feature that they decouple relative from the center-of-mass motion which leads to currents for which Eq.(43) seems to be true. For instance the separable harmonic atom has a rigid mode with current $\mathbf{j}(\mathbf{r}t) = n(\mathbf{r}t)d\mathbf{R}/dt$ where $\mathbf{R}(t)$ is the expectation value of the center-of-mass of the two-electron wavefunction. We therefore have to wait for numerical counterexamples of nonseparable systems, which must at least be two-dimensional. If such an example of nonvanishing vorticity can be found it would imply that, generally, the true current density of an interacting two-electron

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system cannot be reproduced by the current density of a *spin restricted* Kohn-Sham system. However, if we relaxed the restriction that the Kohn-Sham system is in a doubly-occupied spatial orbital, and instead considered singlet states with two distinct orbitals, then Eq. (42) does not necessarily hold. We may ask, for a given time-dependent density and current, can we find a Kohn-Sham system which reproduces both the interacting density and interacting current? If so, is this Kohn-Sham system unique? In one-dimension, the answer to the latter question is, in many cases, no, but what about in more than one dimension?

2.4. What errors does my TDDFT calculation of electronic transitions make?

As mentioned in the introduction, there are two approximations in any practical TDDFT calculation of transitions: the approximation for the ground-state potential and that for the XC kernel.

To study the first source of error, we begin with atoms, and then move on to molecules and solids. Interestingly, most of our presently used ground-state XC energy functionals have potentials that do not resemble the exact XC potential very closely, especially for the He atom. In Fig. 1, we plot the XC potential for LDA, the PW91 GGA, and the exact potential. In the asymptotic region, the exact exchange potential decays as $-1/r$, whereas the LDA and GGA decay exponentially. (How such functionals still yield good ground-state energies is an interesting question in itself[102]). This is not a difficulty for the ground-state theory, as the potential in the region where bound orbitals (in this case, just one) live is well-approximated. But excited states, especially Rydberg states, are badly described. In fact, most of them are unbound.

How can we avoid this problem? The least expensive approach is to fix up the potential by hand, by adding the known $-1/r$ tail in the asymptotic region. Several prescriptions for doing this have been suggested in the literature[103,104,105]. A statistical average of orbitals also produces an excellent potential in this regard[106,107]. Alternatively, the technology for including exact exchange in DFT calculations has been greatly developed over the last decade due to the advent of the KLI approximation, so that it has become possible for molecules. The exact exchange potential cannot be distinguished from the exchange-correlation potential in Fig. 1 and the differences in unoccupied orbital energies and matrix elements over these

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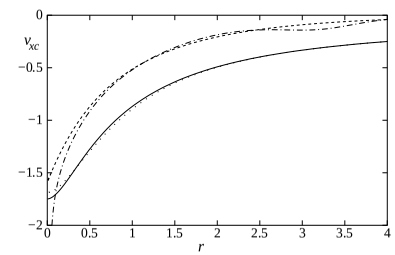

Fig. 1. The exchange-correlation potential for helium: exact (solid), exact exchange-only approximation(dotted), local density approximation (dashed) and the PW91 generalized gradient approximation (dashed-dotted).

orbitals are tiny[108,109,110]. These problems have recently been reviewed by Tozer and Handy[111]. There is a noticeable error still in the occupied orbital energy, since the correlation potential is more significant near the nucleus. Hybrid functionals, which mix in only a fraction of exact exchange with GGA, only partially cure the problem[112].

These problems are most dramatic in the long-range decay of the potential, which dominates all unoccupied states for the He atom. As we consider larger systems, the problem gets less. Even for the Be atom, the first transition from 2s to 2p is reasonable in LDA or GGA, but higher levels are bad. For many molecules and reactions of photochemical interest, it is only excitations to the first few low-lying states that are important, and so these asymptotic difficulties are irrelevant. In the limit of bulk solids, these difficulties do not exist.

Of course, if the underlying ground-state problem is not weakly correlated, then errors in the ground-state approximation become large, and difficulties arise for excitations. The H_2 molecule, stretched beyond the Coulson-Fisher point, so that an LDA or GGA ground-state calculation spontaneously breaks symmetry, is a very demanding case for TDDFT, being based on the KS determinant, and has

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been recently studied from several different angles[113,114,115].

Assuming the ground-state potential is accurate, how about approximations to $f_{\rm xc}$? In almost all applications at present, $f_{\rm xc}$ is approximated adiabatically, by the second derivative of a ground-state XC energy functional. In recent work [116], some of us investigated the effect of different approximations. Using the single-pole approximation (discussed in the next section), we analyzed the results, finding that they could be understood on the basis of trends already known for ground-state functionals. We found that the mean of the singlet and triplet levels of the He atom differed from the exact KS transition by only an expectation value of the parallel-spin correlation contribution in $f_{\rm xc}$, typically a very small part of $E_{\rm xc}$. This gives a functional explanation of why KS values are often good zero-order approximations (see the next section for more detail). We also found that the splitting depended on a cancellation between exact exchange and antiparallel correlation. Thus a hybrid of exact exchange for the mean and ALDA for splitting led to very good agreement with experiment for the spectrum of the He atom. This hybrid was designed simply to illustrate how insight into functionals could be used to improve accuracy in TDDFT calculations. Its construction depended on the system being weakly correlated and having few electrons. It worked for Be, but less well, and has been shown to yield no improvement for stretched HHe^+, or for the dispersion of the plasmon in the uniform electron gas.

Very little exact information is known about the kernel. Even for exact exchange, relatively little practical is known[117], beyond the two-electron unpolarized case. The frequency-dependence of $f_{\rm xc}$ for the uniform gas has been under constant study[118,119,120,121,122,123].

As for the question of which approximation - the one for $v_{\rm xc}$ or the one for $f_{\rm xc}$ - has a stronger influence on the calculated spectra, generally the effect of $v_{\rm xc}$ is much stronger for higher-lying excitations. A typical picture is shown in Fig. 2, where we compare the errors of the singlet excitation energies of the Be atom resulting from various approximations for $v_{\rm xc}$ and $f_{\rm xc}$. For low-lying excitations, and especially for larger systems, often it is $f_{\rm xc}$ which has the larger effect, as is seen in the 2s2p transition in the figure. These lower lying excitations are often the ones of photo-chemical interest.

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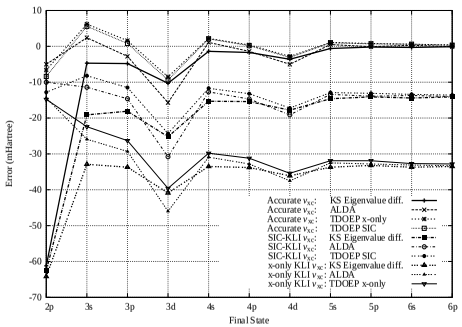

Fig. 2. Errors of singlet excitation energies from the ground state of Be, calculated using the exact exchange-correlation potential obtained from an accurate wavefunction calculation, the OEP-SIC approximation and the X-only KLI approximation and with different approximations for the exchange-correlation kernel. The errors are given in mHartrees. To guide the eye, the errors of the discrete excitation energies were connected with lines. Taken from Ref.[116]

2.5. When are Kohn-Sham transitions good approximations?

Early on, Casida[8] showed how to recast Eq. (12) into common quantum chemical notation

$$K\,\mathbf{F} = \Omega^2\,\mathbf{F}. \tag{44}$$

The eigenvalues are the squares of the physical excitation energies Ω, and the eigenvectors $\mathbf{F}$ determine the true oscillator strength of the corresponding transitions [8]. Alternatively, these equations may be written[108]:

$$\sum_{q'} (M_{q\,q'}(\Omega) + \omega_q \delta_{q\,q'})\,\beta_{q'} = \Omega\,\beta_q. \tag{45}$$

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Here the matrix elements $M_{qq'}(\omega) = \int d^3r \int d^3r' \Phi_q^*(\mathbf{r}) f_{\mathrm{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \Phi_{q'}(\mathbf{r}')$ are expressed in terms of Kohn-Sham orbitals $\Phi_q(\mathbf{r}) = \phi_a(\mathbf{r})\phi_i(\mathbf{r})$. The ω_q denote Kohn-Sham transitions $q \equiv i, a$ from an occupied KS orbital i to an unoccupied KS orbital a.

To gain more insight into the structure of the solutions to Eqs. (45) and (44), we first notice that, if f_{xc} is zero, the matrix is diagonal, and both eigenvalues and eigenvectors will equal their KS counterparts. For weakly correlated systems, we expect f_{xc} to be, in some sense, small, so that the KS values should be good approximations. But, small compared to what, *i.e.*, when will the corrections to KS values be accurate?

To analyze these corrections, we assume for simplicity that f_{xc} is frequen-cy-independent, as is the case in most currently used approximations. We then use the method of continued fractions (CF) [124], where solutions of linear equations are given in the form of a continued fraction expansion. Truncating the continued fraction at a given order corresponds to performing perturbation theory in the *distance* from the diagonal of the matrix. This is very different from the traditional Görling-Levy (GL) perturbation theory [125,126], which is an expansion in powers of the adiabatic coupling constant λ. The CF expansion does *not* assume f_{xc} is small, and can be valid even when there are large corrections to KS results. Starting from a continued fraction expression the conventional perturbation expansion may be recovered by a consistent Taylor expansion in the coupling parameter up to the desired order. Using such a low order truncated CF expansion we find for the excitation energies in our eigenvalue problem

$$\Omega = \omega_q + M_{qq} + \sum_r{}^* \frac{M_{qr}M_{rq}}{(\omega_q + M_{qq}) - (\omega_r + M_{rr})} + \sum_{rs}{}^* \frac{M_{qr}M_{rs}M_{sq}}{(\omega_q - \omega_r)(\omega_q - \omega_s)} + \cdots . \tag{46}$$

The asterisk on the sums indicates that the summation is only performed over terms having distinct indices. (At this point we should note that our result (46) remains valid even for frequency dependent matrix elements. In this case a truncated version of (46) becomes a nonlinear equation in Ω.) Looking at the result, we see that the CF method produces a power series in a (hopefully) small parameter, which is a matrix element divided by a transition frequency difference. Thus, truncation of this series is accurate when this ratio is small, i.e, when the shift away from KS

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transition frequencies is small relative to the separation. It is an approximation of weakly coupled transitions, rather than of weakly correlated systems.

The zeroth order result was dubbed the single-pole approximation (SPA) [7], and was used in early calculations of transition frequencies. It has also been used to relate TDDFT results to GL perturbation theory results for excitations[91]. But the expression in Eq. (46) tells us more. Clearly, the SPA will be a good approximation to the full excitation energies only if higher order terms like the sums in (Eq. 46) contribute little. We can expect the SPA to be valid if the SPA shift of a transition is small relative to the separation between that transition and its neighbors. By expanding f_{xc} to second-order in λ, it also yields an exact expression for the transition frequency to second-order in GL perturbation theory.

Let us now take a look at the eigenvectors. For this purpose we use the second version of the eigenvalue problem Eq. (44). Applying the CF method to Casida's formalism, we find the oscillator strength expansion to be

$$f = \frac{2}{3}\omega_q \mu_q^2 + \frac{2}{3} \sum_{q' \neq q} \frac{4M_{qq'}\omega_q \omega_{q'} \mu_q \mu_{q'}}{\omega_q^2 - \omega_{q'}^2} + \cdots . \tag{47}$$

Here ω_q and μ_q denote KS excitation energies and dipole matrix elements respectively. The leading term is the SPA result, and is simply the KS oscillator strength. Thus, contrary to the transition frequency, there is *no* correction to oscillator strengths in SPA. This can be easily seen from Eq. (46). If only diagonal matrix elements are retained, the eigenvectors remain unit vectors and don't change. But once again, with correction terms, we understand much more. Corrections to KS oscillator strengths remain small if transitions are well-separated, even for strongly correlated systems. Also, Eq. (47) is the exact GL expansion for oscillator strengths, if f_{x} is used for the matrix elements.

We end this section by studying the effect of approximate ground-state potentials on oscillator strengths. As in orbital energies, the potential must have a long-range decay to bind Rydberg states. Once that is so, the KS oscillator strengths depend on both transition frequencies and dipole matrix elements. In numerical studies on the He atom, we find that the dipole matrix elements in exact X or LDA-SIC potentials are extremely close to the values in the exact XC potential[127], and that the main source of error in such approximate calculations is then in the orbital energies, as discussed in the previous section.

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2.6. What happens to atoms in strong laser fields?

TDDFT really takes off (as do the dynamics) when atoms and molecules are subjected to strong laser fields. Many new phenomena such as multiphoton ionization (MPI),[128,129,130,131] above-threshold ionization (ATI) [132,133,134] or high-harmonic generation (HHG) [135,136] are observed when the electric field amplitude of the laser is comparable to or even exceeds the static nuclear Coulomb field experienced by the electrons. TDDFT is perhaps the only feasible method to calculate the time-dynamics of interacting many-body systems in this regime. In spite of the fact that the electron-electron interaction is much weaker than the strong external driving field, electron correlation effects can be important [137,138,139,140]. For any time-dependent calculation within TDDFT there is, however, one important point to note: it is not sufficient to know a good approximation for the exchange-correlation potential (and thus a good approximation for the time evolution of the density). It is in addition necessary to know density-functionals for the observables. Usually the quantities of interest in a time-dependent calculation are some *generalized cross sections* like $\mathcal{S}$ or $\mathcal{T}$ matrices in scattering processes, ionization yields, branching ratios for chemical reactions or dissociation probabilities, to mention just a few. By virtue of the Runge-Gross theorem all of these observables are functionals of the time-dependent density and the initial-state. Consequently, a calculation within TDDFT involves two steps

(i) The TDKS equations are solved using some approximate form for the exchange-correlation potential. The density is calculated from the time-dependent orbitals.
(ii) The (approximate) time-dependent density from step (i) is then inserted in the functionals for the physical observables of interest.

In some cases we know the exact functional dependence of such *generalized cross sections* on the time-dependent density, but in most cases we do not. One prominent example where the exact form of the functional is known is the case of harmonic spectra for atoms or molecules. Neglecting propagation effects in the medium, as well as the fact that the focal volume has an intensity profile exposing different atoms to different intensities, these spectra are given by $|d(\omega)|^2$. Here $d(\omega)$ is the Fourier transform of the induced time-dependent dipole moment of the

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system

$$d(t) = \int d^3r\, z\, n(\mathbf{r}t). \tag{48}$$

Ionization yields and photoelectron spectra are much harder to express as functionals of the density. For the ionization yields of the Helium atom some approximate functionals are known[141]. The construction of functionals yielding probabilities P^{+1} and P^{+2} for singly and doubly ionized Helium rests on a geometrical concept. Consider the spatial partitioning of the norm of the true time-dependent two-particle wavefunction in the following form

$$\begin{aligned} 1 = &\int_A d^3r_1 \int_A d^3r_2\, |\Psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2 + 2\int_A d^3r_1 \int_B d^3r_2\, |\Psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2 \\ &+ \int_B d^3r_1 \int_B d^3r_2\, |\Psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2. \end{aligned} \tag{49}$$

Here the analyzing volume A describes an appropriately chosen region which encloses the nucleus and B is its complement $B = \mathbb{R}^3 \setminus A$. The factor of two in front of the second integral appears because of the antisymmetry of the wavefunction. Due to the probability interpretation of the wavefunction the second integral (AB) in Eq. (49) is equal to the probability of finding one electron inside the volume A and simultaneously finding a second electron outside the volume A. This can be viewed as single-ionization P^{+1}. Similarly the integral (BB) corresponds to the probability of double-ionization P^{+2}. Introducing the pair-correlation function

$$g(\mathbf{r}_1,\mathbf{r}_2,t) = \frac{\Gamma(\mathbf{r}_1,\mathbf{r}_2,t)}{n(\mathbf{r}_1,t)\, n(\mathbf{r}_2,t)}, \tag{50}$$

where $\Gamma(\mathbf{r}_1,\mathbf{r}_2,t)$ is the time-dependent two particle density matrix (in the case of Helium simply $\Gamma(\mathbf{r}_1,\mathbf{r}_2,t) = 2|\Psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2$) the expressions for single- and double-ionization of Helium can be written as

$$\begin{aligned} P^{+1}(t) &= \int_A d^3r\, n(\mathbf{r},t) - \int_A d^3r_1 \int_A d^3r_2\, n(\mathbf{r}_1,t)\, n(\mathbf{r}_2,t)\, g[n](\mathbf{r}_1,\mathbf{r}_2,t) \\ P^{+2}(t) &= 1 - \int_A d^3r\, n(\mathbf{r},t) + \frac{1}{2}\int_A d^3r_1 \int_A d^3r_2\, n(\mathbf{r}_1,t)\, n(\mathbf{r}_2,t)\, g[n](\mathbf{r}_1,\mathbf{r}_2,t). \end{aligned} \tag{51}$$

Note, since the time propagations are started in the ground state, both ionization yields P^{+1},P^{+2} are functionals of the density only. For Helium, the simplest

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approximation for the pair-correlation function is the exchange-only expression

$$g_x[n](\mathbf{r}_1, \mathbf{r}_2, t) = \frac{1}{2}. \tag{52}$$

In this case the ionization probabilities P^{+1},P^{+2} reduce to

$$\begin{aligned} P^{+1}(t) &= 2p(t)\,(1-p(t)) \\ P^{+2}(t) &= (1-p(t))^2, \end{aligned} \tag{53}$$

where $p(t) = \frac{1}{2}\int_A d^3r\, n(\mathbf{r}, t)$. Note, that exactly the same result (53) is recovered when a product wavefunction is inserted in Eqs. (51).

To assess the quality of the approximation (52) involved in the functionals P^{+1},P^{+2} Lappas and van Leeuwen[144] have performed numerically exact time propagations for a 1D soft-core model of Helium in a laser field[145]. In the length gauge the Hamiltonian for their model system reads

$$\begin{aligned} H = &-\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{1}{2}\frac{d^2}{dx_2^2} - 2\,V(x_1) - 2\,V(x_2) + V(x_1 - x_2) \\ &+(x_1 + x_2)\,E_0\,f(t)\sin(\omega t). \end{aligned} \tag{54}$$

Here $f(t)$ describes the envelope of the laser pulse and $V(x) = 1/\sqrt{x^2+1}$ is the soft-core model potential. From the time-evolution of the two-electron wavefunction, using the split-operator method [146], numerically exact reference data for the ionization yields were obtained from expressions (51). This was then compared to ionization yields from Eq. (53) using the exact density calculated from the correlated wavefunction. In this way approximations in the first step (i) of the computational procedure were circumvented and the accuracy of the functionals for the cross sections can be tested directly.

The results of Lappas and van Leeuwen are shown in Fig. 3 where the ion yield for single (triangles) and double (squares) ionization is plotted as function of the laser intensity. Although the double-ionization evaluated from the approximate functional (53) still does not agree with the exact yield, the famous knee structure[147,148] is reproduced. This is in contrast to TD x-only calculations where the knee structure cannot be recovered at all. In our context this situation would amount to the evaluation of (53) with the approximate TD x-only density.

In summary we conclude that the two step procedure (i),(ii) is necessary for any time-dependent calculation in TDDFT. Both an approximation for the exchange-

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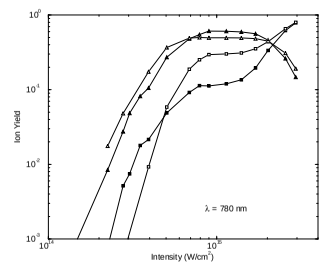

Fig. 3. Single- and double-ionization yields of He from the fully correlated exact model (full triangles and squares), and the yields based on Eqs. (53) in the text evaluated with the 'exact' electron densities (open triangles and squares). Taken from Ref. [144]

correlation potential and a functional approximation for the *generalized cross section* of interest, have to be known. The relative importance of these different types of approximations has to be investigated for any particular case of interest.

In the special case of Helium double-ionization it turned out that the functional approximation for the ion yields (53) recovers the well known knee structure only when the functionals were evaluated with the exact densities. Evaluation with approximate TD x-only densities did not reproduce the essential physics[141,142]. Thus more accurate exchange-correlation potentials, possibly including memory effects[143], have to be utilized in this case to obtain better approximations to the true time-evolving density.

2.7. When does ALDA work beyond the linear response regime?

Most of the TDDFT calculations use the simple ALDA approximation which treats the instantaneous density as if it was a ground-state density and applies the local density approximation for the exchange correlation potential Eq.(7). LDA is ubiquitous and reliable for most ground-state systems, but the time-evolving sys-

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tem is certainly not typically a ground-state, and memory effects are neglected (see Sec. 2.9). How well does such an approximation work? In the ground-state case, conditions that exact functionals satisfy are an important guide to understanding why various approximations work (or fail) as well as they do, and indeed, to their construction [149]. Exact conditions that the time-dependent functionals satisfy include Newton's Third Law [150,151,152], the harmonic potential theorem[153], behavior under uniform scaling [92], a virial theorem [92], and the memory formula [154]. For example, the violation of the harmonic potential theorem by the Gross-Kohn approximation [123] for the exchange correlation kernel provided much of the motivation for a search for other approximations which do satisfy this theorem [155].

These exact conditions provide only a small number of tools, albeit important ones, to take in the knapsack when exploring the vast expanse of possible dynamical behavior. Much has yet to be learnt about properties of time-dependent functionals in order to obtain accurate approximations.

A large part of the problem is that until two years ago, there were no exact time-dependent Kohn-Sham calculations done; that is, exact calculations of an interacting system and of the corresponding Kohn-Sham wavefunction. For this purpose, time-dependent Hooke's atom, two interacting electrons in a harmonic well of time-dependent force constant has been exploited in three recent works [156,92,157]: these are the first numerically exact time-dependent Kohn-Sham calculations of any system.

The two electrons in time-dependent Hooke's atom live in the Hamiltonian

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{2}k(t)\left(r_1^2 + r_2^2\right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{55}$$

where the time-dependent force constant is

$$k(t) = \bar{k} - \epsilon\cos(\omega t). \tag{56}$$

The one-electron version of this is the Mathieu oscillator [158]. The dynamics is largely classical, because of the quadratic nature of the potential, and classically evolving a bunch of trajectories with the same initial phase-space distribution as the initial ground-state, describes the full quantum dynamics well. For ϵ not too large, time-dependent perturbation theory tells us what frequencies appear in the dynamics. In Fig. 4, we plot the root-mean-square variance of the distribution as a function of time for one electron, calculated quantum mechanically, quasiclassically and in perturbation theory. The rough trends in the two-electron density

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are similar to those of the one-electron density, and this is also shown here. The difference is due to interaction.

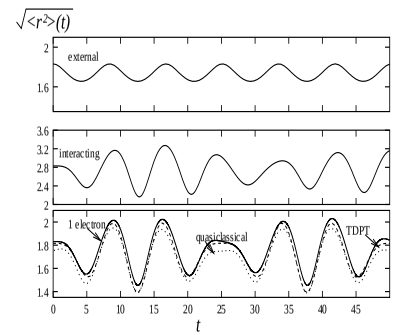

Fig. 4. Rms variance: one electron in the Mathieu oscillator, calculated quantum mechanically (solid line in bottom panel); time-dependent perturbation theory (dashed line in bottom panel); quasiclassically (dotted line); two electrons of time-dependent Hooke's atom (middle panel); the ground-state corresponding to the external force constant (top panel). The parameters in Eq.56 are $\bar{k} = 0.25, \omega = 0.75$ and $\epsilon = 0.05$.

The two electron case may be solved exactly numerically. Transforming to center-of-mass and relative coordinates renders the Hamiltonian separable, and thanks to spherical symmetry, one needs only to solve two uncoupled one-dimensional time-dependent Schrödinger equations numerically. The calculation begins in the ground-state. Thus the exact evolving wavefunction and density are obtained.

Since there is just one (complex) occupied orbital in the Kohn-Sham calculation, a simple inversion of the Kohn-Sham equation yields the Kohn-Sham

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potential in terms of the evolving density. Once $v_{\rm s}(\mathbf{r},t)$ is known, the energy components $T_{\rm s}(t), U(t), E_{\rm xc}(t)$ may then be extracted with the help of the equations of motion[92]. These energies contain global information about the potentials $v_{\rm s}(\mathbf{r}t), v_{\rm xc}(\mathbf{r}t)$. We shall describe a manifestation of this shortly.

The exact calculation may be compared with that of an exact adiabatic calculation [157]. To this end, we define the ground-state components of the various energy components as the value of the exact ground-state functional evaluated on the instantaneous density. The difference between this and the exact energy is termed the "dynamical component", *e.g.* $E_{\rm c}^{dyn}(t) = E_{\rm c}(t) - E_{\rm c}^{gs}[n(\mathbf{r}t)]$. The exact ground-state value is obtained by observing that, for our choice of time-dependent potential, the static potential which has the ground-state density matching the instantaneous density at time t is very close to that of a static Hooke's atom of a certain force constant $k_{eff}(t)$.

Dynamical effects were found to be very large: except when the force constant is varied slowly enough that the system remains in the instantaneous ground-state, the functionals behave qualitatively differently than the adiabatic approximation. We refer the reader to the paper [157] for many interesting results from a variety of runs and here just present a few.

In Fig. 5 we plot the correlation energy and its first time-derivative for a typical run. A feature which would put a ground-stater out the door is that $E_{\rm c}(t)$ can become positive. No adiabatic approximation can capture this. In the time-dependent case there is of course no variational principle holding E_c down below zero and we found positivity in all of our runs. One can prove [157] that $E_c^{dyn}(t) \geq -T_{\rm s}^{dyn}(t)$, a negative number. In all the runs we considered we found $E_c^{dyn} \geq 0$, always pulling up the negative ground-state value, but whether this is generally true, remains to be proven.

This graph also demonstrates the importance of memory effects (and now our poor ground-stater is really running). In the top panel is a plot of the value of $k_{eff}(t)$ described earlier. This parameter completely identifies the density profile. The figure suggests that the correlation potential $v_c(t)$ is a highly non-local functional of the density, meaning that $v_c(t)$ depends not just on the density at and around time t, but rather on its entire history. 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 $\dot{E}_{\rm c}(t)$ near those times are hugely different. The density at times near t is not

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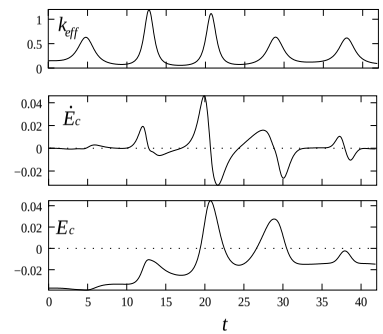

Fig. 5. Non-locality in time: the top panel shows $k_{eff}(t)$, middle panel $\dot{E}_c$, bottom panel E_c. The parameters in Eq.56 are $\bar{k} = 0.25, \omega = 0.75$ and $\epsilon = 0.1$.

enough to specify $\dot{E}_c$: it depends on the entire history and this is what we mean by non-locality in time. Now $\dot{E}_{\rm c}(t)$ is intimately related to the correlation potential [92]:

$$\dot{E}_{\rm c}(t) = \int d^3r v_{\rm c}(\mathbf{r}t)\dot{n}(\mathbf{r}t) \tag{57}$$

so that non-locality in $\dot{E}_c$ directly implies non-locality in the correlation potential $v_{\rm c}(t)$. Clearly, $E_{\rm c}(t)$ will also be a highly non-local functional of the density and this is also shown in the figure. Any adiabatic approximation has no memory and will fail to capture this effect. On the other hand, it may approximate the exchange potential well since, even for more than two electrons, this is probably not a strongly non-local in time functional of the density [157].

We end this section by looking back to the linear response theory of the previous section. One can prove that although $E_{\rm c}^{dyn}$ vanishes in linear response, $v_{\rm c}^{dyn}, T_{\rm c}^{dyn}$ and $U_{\rm c}^{dyn}$ do not [157].

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2.8. Can we always find a Kohn–Sham potential for an appropriate initial state?

The Runge-Gross theorem [1] proves that there is a 1-1 mapping between potentials and densities, much like in the ground-state case, but with one major difference: in the time-dependent case, the mapping is unique only for a specified initial state. There may be several different initial wavefunctions that evolve with the same time-dependent density in different time-dependent potentials; the exchange-correlation potential for each of them will be different. All functionals in use today completely ignore this initial-state dependence, partly because very little is known about it.

To tackle the problem of how functionals depend on the initial state we might begin by considering the simplest possible case: one electron. We ask, can we find two different initial states which evolve with the same density for all time in two different potentials? In fact, we cannot [159]! There is no initial-state dependence for one electron. The proof is very simple: the two candidate wavefunctions must be related to each other by a phase, $\bar{\phi}(\mathbf{r}t) = e^{i\alpha(\mathbf{r}t)}\phi(\mathbf{r}t)$ in order to have the same density. Imposing equal $\dot{n}(\mathbf{r}t) = -\nabla\cdot\mathbf{j}(\mathbf{r}t)$, gives $\nabla\cdot[n\nabla\alpha] = 0$. This can only be satisfied if α is a physically irrelevant constant. So in the one electron case, there is at most one wavefunction which can evolve with a given density: the evolving density uniquely specifies the potential.

The situation is however quite different for two or more electrons. Given two initial wavefunctions that have the same density and first-time derivative of the density [160], and which are well-behaved in that their expectation values of the momentum-stress tensor are finite[159], there exist two different potentials in which they each evolve with the same density for all time [160]. This holds also in the case of two different inter-particle interactions and so is a statement about non-interacting v-representability. It was also shown [160] how to construct the difference in the potentials that keeps the two wavefunctions evolving with the same density. Essentially the proof follows from requiring the second derivative of the density to be the same for each wavefunction, using the continuity equation to write this in terms of the current and then considering the Heisenberg equation of motion for the current [160]. This gives the first term in a Taylor series in time of the potential. The higher order terms may be obtained by considering higher order time-derivatives of the density; one ends up having to evaluate nested commutators of the momentum-stress tensor with the Hamiltonian.

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A simple example of initial-state dependence [159] occurs for two non-interacting electrons in one dimension. In Fig. 6 we give another example. The reference wavefunction is the lowest triplet state of the harmonic oscillator, with orbitals shown in the figure. The orbitals of the other wavefunction are also shown in the top panel; these are chosen so that the two wavefunctions have the same initial density and current. The reference wavefunction evolves with constant density in the harmonic oscillator potential shown below. The initial potential in which the second wavefunction evolves so that its density also remains constant is also shown. This alternative potential will change in the next instant of time in order to keep the alternate orbitals evolving with the same constant density as the reference ones. If we consider the density in the top panel to be that of an interacting two-electron system in some external potential, then the difference between the two potentials in the lower panel is the difference in the exchange-correlation potential when the two different initial Kohn-Sham states of the top panel are chosen.

2.9. What is memory?

One of the first things a budding quantum mechanic learns is that knowledge of the many-electron wavefunction at any instant of time is enough to completely determine all properties of the system at that time. The Runge-Gross theorem [1] says that this is overkill: knowing just the time-evolving density and just the initial wavefunction is enough to know everything about the system. Like in the ground-state case, by trading in the $6N$-variabled wavefunction for the 3-variabled density as its main player, and having to solve N uncoupled 3-variabled Schrödinger's equations instead of the daunting coupled Schrödinger equation in $6N$ variables, TDDFT provides a more feasible framework for the dynamics. The subtleties of the electron-electron interplay are hidden in the functionals, which are in practice approximated.

A feature of the time-dependent functionals is memory dependence, about which much has yet to be understood. Functionals in TDDFT are haunted by the past: in general they depend on the density along its entire history, on the initial state of the interacting system and also on the choice of Kohn-Sham initial state. Examples of the history dependence and of the initial-state dependence have been given earlier in this chapter (Secs. 2.7 and 2.8).

How does this memory arise? In any wavefunction theory, no memory is needed:

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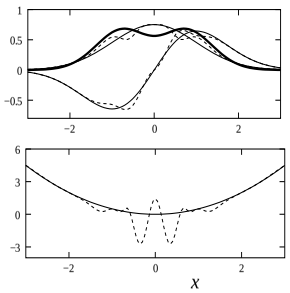

Fig. 6. Initial-state dependence: the solid lines in the top panel are the two orbitals of one wavefunction, which happens to be stationary state of the harmonic oscillator shown below as a solid line. The dashed lines are the orbitals of an alternative initial wavefunction which evolve with the same density (thick solid line in top figure) in the potential which at time 0 is shown as the dashed line in the bottom figure.

as our budding quantum mechanic would tell us, the wavefunction at time t contains all the information. The memory in TDDFT is a price we have to pay for the trading in of the complicated wavefunction for the much simpler density. In a sense, what we mean by memory is a consequence of the underlying (banished) wavefunction at time t not being a ground-state wavefunction.

Recently it has been shown that the two sources of memory in TDDFT, history dependence and initial-state dependence, are inextricably intertwined [154]. In fact, initial-state dependence can often be completely absorbed into a history-dependence. Imagine an interacting time-dependent calculation, run from $t = 0$, generating a density $n(\mathbf{r}t)$. The exchange-correlation potential at time t is determined by the density at all previous times as well as the initial interacting and Kohn-Sham states, Ψ_0 and Φ_0 respectively. Now, if we knew what these wave-

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functions evolved to at time $t' < t$, we may equally well think of t' as the initial time, and the inputs to $v_{\rm xc}$ would be the density at times between t' and t and the states $\Psi_{t'}, \Phi_{t'}$ at time t'. This gives us an exact condition on the functionals:

$$v_{\rm xc}[n_{t'}; \Psi_{t'}, \Phi_{t'}](\mathbf{r}t) = v_{\rm xc}[n; \Psi_0, \Phi_0](\mathbf{r}t) \text{ for } t \geq t', \tag{58}$$

where

$$n_{t'}(\mathbf{r}t) = n(\mathbf{r}t) \text{ for } t \geq t' \tag{59}$$

and $n_{t'}(\mathbf{r}t)$ is undefined for $t < t'$. Eq. (58) is a very difficult condition for approximate functionals to satisfy. Like other exact conditions, for example, the harmonic potential theorem [153] and the virial theorem [92], it may be used as a feasibility test for approximate functionals. Any functional with history-dependence, and *without* initial-state dependence, very likely violates this condition. On the other hand, this condition is trivially satisfied by any adiabatic approximation, which ignores *both* the dependence on the initial-state and on the history.

An important consequence of Eq. (58) is that the initial-state dependence can often be completely expressed as a history effect along a "pseudo-prehistory": once a system can be propagated backwards in time to some non-degenerate ground state, generating a density $\bar{n}(\mathbf{r}t)$, then

$$v_{\rm xc}[n; \Psi_0, \Phi_0](\mathbf{r}t) = v_{\rm xc}[\bar{n}](\mathbf{r}t) \text{ for } t \geq 0. \tag{60}$$

Here, the density $\bar{n}(\mathbf{r}t) = n(\mathbf{r}t)$ for $t \geq 0$ and is defined to be the density along a pseudo-prehistory which begins in some ground-state Ψ_{gs} (Φ_{gs} for the Kohn-Sham system) at some negative time $t = t_{gs} < 0$ and evolves under some many-electron Hamiltonian that carries us to the true initial states Ψ_0 (Φ_0) at $t = 0$. Initial-state dependence has vanished on the right-hand side of Eq. (60) since the systems "start" in the non-degenerate ground-states Ψ_{gs} and Φ_{gs} which, by the Hohenberg-Kohn theorem, are functionals of the ground-state density. Instead it has been absorbed into a pseudo-prehistory.

When can we find a pseudo-prehistory and thus eliminate initial-state dependence? It can be shown that an arbitrary initial state cannot be evolved back to some ground-state under a many-electron Hamiltonian [154]; but there are plenty of initial states that can be.

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3. Conclusions: Dante's Inferno?

When we begin applying TDDFT to quantum mechanical systems, the linear-response method looks very appealing, especially employing ALDA for $f_{\rm xc}$. We are like Dante at the edge of the woods. But once we study things a little more closely, we begin our descent through the various circles of Hell. So long as we stay within linear response, we are always looking at variations away from a ground state, and so we can consider ourselves in the outer circle. But once we begin to study fully time-dependent problems, then the initial-state dependence rears its ugly head (similar to that of Bertrand de Born) and we know we are in the inner circle.

But, there is more than just the Inferno to Dante's classic. There follows the purgatorio and finally paradiso. It is necessary to first pass through Hell, to achieve the wisdom needed to reach the paradiso. For TDDFT, we are on our way.

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