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. 1.1 is particularly eccentric, mimicking the style of our old friend, Bob Par.

A time-dependent exchange system satisfies the time-dependent Schrödinger equation:

\[ \hat{H}\psi(t) = i\hbar \frac{\partial \psi(t)}{\partial t} \]

(1)

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

\[ \hat{H} = \hat{T} + \hat{V}_e + \hat{V}_{ext} \]

(2)

de 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 Range-Ground (RG) theorem, a theorem which the first for TDDFT calculations were done by Anis et al. for semiconductors and the HARPA algorithm for a bomb. The RG theorem, generalizes the Hohenberg-Kohn theorem 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

\[ \left\{ -\frac{1}{2} \nabla^2 + V_0(r) \right\} \phi_i(r) = \phi_i(r) \]

(3)

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

\[ \rho(t) = \sum_{i=1}^{N} |\phi_i(t)|^2 \]

(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

\[ \rho_{xc}(t) \equiv \rho_{xc}(0) = \rho(t) - \rho_{xc}(0) = \rho(t) - \sum_{i=1}^{N} \phi_i^2(t) \]

(5)
The exchange-correlation potential is a functional of the initial states of both the interacting system and the Kohn-Sham reference system. It is given by

$$\mathcal{E}_{xc}(\rho_{0}) = \int d\mathbf{r} \, V_{xc}(\rho_{0}(\mathbf{r})),$$

where the Hartree potential is

$$\mathcal{E}_{H}(\rho_{0}) = \int d\mathbf{r} \, n_{0}(\mathbf{r}),$$

Note that the exchange-correlation potential is not given by a functional of the density of the initial state of the interacting system and the Kohn-Sham reference system, which is the subject of Sec. 2.2. As in the ground-state case, for many electrons, Eq. (3) is much better to solve than Eq. (1). It explicitly yields the time-dependent density $\rho_{t}(\mathbf{r})$, 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-evolution 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 functions of both the density and the initial state, as discussed in Sec. 2.6.

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

$$\mathcal{E}_{xc}^{ALDA}(\rho_{t}) = \mathcal{E}_{xc}^{ALDA}(\rho_{0}(\mathbf{r})),$$

as was used in the historic calculation of Anderson. 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 are 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 in dense electronic systems, such as alkali halides, 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 forbidden to mechanism of the density of 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.
approximation on a hybrid with exact exchange is employed, and \( f_{xc} \) is a
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 \( v_{xc} \) and
and the ALDA for \( f_{xc} \). In this way, the condition
\[
\sum_{\sigma} \int f_{xc}(\mathbf{r}, \mathbf{r}'; \mathbf{v}_{xc}) \, d\mathbf{r}' = \int f_{xc}(\mathbf{r}, \mathbf{r}; \mathbf{v}_{xc}) \, d\mathbf{r}
\]
(13)
is satisfied.

Applications and development of TD-DFT is a rapidly expanding field, and we
next review recent developments. We refer the reader to an earlier review3 and
references therein for earlier applications of TD-DFT.

In quantum chemistry, the largest use of TD-DFT 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. 7.5 explains how TD-DFT can be quite successful despite these limitations.

Most quantum chemical codes, such as Gaussian3 andADF22-25, perform TD-DFT
response calculations, allowing experiments to immediately compare with theory22,23.
Survey of mean polarizabilities of organic molecules have been performed26. Many
molecular calculations, such as excitations in small organic molecules26, in triphenyl47,
in transition metal molecules28 and complexes29,30, using nonempirical hy-
brid functionals25, have been studied. Closed-shell polyatomic asymmetric-harmonic
cations31 have been studied, as have open-shell molecules32, linear polyelectro-
ols33, liquid crystals with N,N bonds34, and substituted benzene in hexan and
solvent35. The optical response of organic dyes36 has been calculated and
experiments given of the color of 1,2-dihalo37, and the spectrum of sulfones38,
cromone39, and pyrazine3. Even aromatic radical cations3 have been studied.
Harmonic solutions are complex and of course unique36. Weakly hydrogen-bonded
species have also been studied37. Tests of various functionals for excitation ener-
gies on training sets of molecules are ongoing38, just as in the ground
state. One potential benefit is to combine spectral information with structural and
thermodynamical data as a more thorough test of DFT calculations, as in the case
of atoms, molecules, and clusters.

Higher order response has also been calculated. TD-DFT is now used for hyperpolarizabilities39,
such as in chiral molecules40. Both linear and magnetic circular dichroism have
been calculated41-47. The Rydberg states of propane have also been calculated
in conjunction with resonance energy multiphoton ionization experiments45. Reas-
cently, TD-DFT calculations showed that a candidate for strong nonlinear optical
response was less promising than experiment suggested46. Raman intensities have
also been calculated42,46. Not yet understood is the ability of TD-DFT to perform
well to even for states with significant delocalization character46.

Calculations are appearing with real biological significance, such as on chloro-
phyll A48 and free-base porphyrin49. A very important recent development is the
attempt to study charge transfer in biological molecules50-52. Fluorescence of 2-
aminophenol has been calculated53. Algorithmic developments are also occurring.
Under many circumstances, the Tamm-Dancoff approximation is sufficient50
for excitation energies. Fast algorithms for solving TDDFT equations can be immediate-
ly applied to ab initio TD-DFT calculations54,55. Geometric derivatives for excited
states have been compiled56.

Much of the earliest work on TD-DFT response was performed on metallic
clusters57. Clusters of ZnS have also been studied58.

In atomic and molecular physics, TD-DFT is being applied to problems of
j-tonal atoms in intense laser fields, including stabilization phenomena59, and
nonsequential multiple ionization60. Even the more demanding time-dependent
optimized effective potential (TDOPP)61 has been coded and applied to high har-
monic generation62. Some of these calculations apply the basic formalism within
the 4th theory63. Also, the original photoionization problem has been recently
been revisited using more accurate ground-state potentials64, while calculations for
molecules have also been done65. Clusters can now also be handled66. Energetic
collisions between atoms and ions are also being tackled67,68.

For extremely large calculations, involving thousands of electrons, even the
TDKS equations are too expensive to solve, and time-dependent Thomas-Fermi
approaches are used69-72.

In mesoscopic physics, TD-DFT has been used for quite a while to study the
optical response of quantum dots73. The applications mentioned have all been to finite systems. The exten-
sion 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 approxi-
mations to the exchange-correlation kernel \( f_{xc} \) in this case. To see this, simply
consider the Fourier transform of $f_{\vec{q}}$. The direct Coulomb interaction behaves as $\frac{q}{q^2}$, where $q$ is the wavevector corresponding to $-\vec{r}$. 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 GGA s. The ultra non-locality of the exchange-correlation kernel in extended systems has recently been emphasised \[35\].

There have been a few attempts to perform calculations on extended systems, such as in polymers \[33, 34\], and the optical response of solids \[35, 36\], 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 \[37\], in attempts to disentangle the dielectric effects from correlation, especially in the dispersion of the bulk plasma \[38\]. Recently, a spin response of magnetic metals \[39\] has been calculated using TDDFT. Also, electronic scattering at surfaces has recently been calculated using TDDFT \[40\].

At a conceptual level, the links between TDDFT and traditional many-body approaches for extended systems, such as GW, are only now being explored \[41\].

As extensions of ground state theorems \[42\] and the description of potentials in terms of wavefunction quantities \[43\] as opposed to functional derivatives.

2. Nine questions and some answers

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

As this volume is dedicated to Bob Parr on his 80th 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 its 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-polarized) electrons, the answer is yes. For example, one could deduce the ionisation energy $I$ from the tail of the density and also solve the one-electron problem for the external potential, yielding $E_i$. Then the two-electron ground-state energy is just $E_i - I$.

More generally, using a technique invented by Beliaev and others \[44\], one can, for any given density, construct the corresponding Kohn-Sham potential $v(r)$, i.e., find that single-particle potential for which that density is a ground-state density \[45\]. Then one can deduce the exchange-correlation potential $v_{xc}(r)$ by inverting its definition in Eq. (9). 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

$$E = T_e + U + \int d^3 r \, n(r) \, v_{xc}(r) + E_{xc},$$

(14)

where $T_e$ is the Kohn-Sham kinetic energy, $U$ is the Hartree energy, and $E_{xc}$ 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

$$E_{xc} + T_e = \int d^3 r \, n(r) \, v_{xc}(r),$$

(15)

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

Several years ago, one of the authors and Bob (with collaborators) \[46\] published back-to-back articles in Phys. Rev. A on this point, noting that the remaining piece of correlation energy, e.g., $E_{xc} + T_e$, is more amenable to approximation by many-body functional methods, so that use of the virial helps on the exact density reduction 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 $T_e \ll \langle \hat{N} \rangle$, one can use the virial once again to extract $E_{xc}$ 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 \[47\]

$$\dot{\hat{E}} = \{ \hat{H}, \hat{I} \} = \int d^3 r \, n(r) \, \dot{v}_{xc}(r),$$

(16)
i.e., the time-evolution of the energy is given exactly by the time-evolution of the one-particle perturbation. Integrating with respect to time shows that knowledge of \(v_{ex}(r)\) and \(n(r)\) is sufficient to determine the entire evolution of the energy, once the initial value is known, i.e.,

\[
E(t) = E(0) + \int_0^t dt' E(t').
\]

So, either 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 an approximation for its-functional derivative, the exchange-correlation potential \(v_{ex}(r)\) 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:

\[
\mathcal{A}[\Psi] = \int dt \langle \Psi | H | \Psi \rangle.
\]

Stationary points of \(\mathcal{A}\) with initial wavefunction \(\Psi(t)\), 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

\[
\mathcal{A}[\psi_1; \Psi] = \int d^3r \langle \psi_1 | \Psi \rangle \langle \Psi | H_0 | \psi_1 \rangle - \int d^3r \langle \psi_1 | \hat{V} | \psi_1 \rangle
\]

where \(\Psi\) is a functional of the density and the initial state \(\psi_1\). The potential \(\psi_1\) in the Hamiltonian \(H_0\) is given and fixed. The Euler equation \(\delta \mathcal{A}/\delta \psi_1 = 0\) would then specify the correct density. One can extract out a universal part of the action\(^{32}\), and a part that explicitly depends on the external potential. One can define a similar object for the Kohn-Sham action \(\mathcal{A}_K[\psi; \hat{V}]\), and comparing the two, extract an exchange-correlation action \(\mathcal{A}_ex[\psi; \hat{V}]\).
with Hamiltonian $H_{\text{e}}$. This is, however, not the case. So what has happened? To understand this point we must go back to the original variation Eq. (18) and 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 ($i\hbar \partial_t \Psi = -\frac{\nabla^2}{2m} \Psi$). We refer the reader to the recent review [99] for details, and here just state the results. Suppose the action $A$ is stationary for variations $\delta \phi$ around a certain $\Phi$. Then $\Phi$ satisfies the TDSE if the variations $\delta \Psi$ are such that

1. $\delta \Phi(t) = \delta \phi(t) = 0$ and the real and imaginary part can be varied independently,
2. or, alternatively, both $\delta \phi_1 = \delta \phi$ and $\delta \phi_2 = i \delta \phi$ are allowed variations for any $\delta \Phi$ [99].

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 density on the basis of the Kohn-Sham theorem together with the gauge condition $\psi \rightarrow \Phi$ for $\Phi \rightarrow \infty$ in the corresponding potential. We will refer to this set of wavefunctions $V$. To see if we can derive the TDSE from the restricted TDDFT action we must check that within the restricted set of wavefunctions $V$ 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. (20). The variations $\delta \phi$ within the set $V$ must always be generated by potential variations, i.e., if some $\Phi$ in this set satisfies a TDSE with Hamiltonian $\mathcal{H}$ then $\Phi + \delta \phi$ satisfies

$$ (i\hbar \partial_t - \mathcal{H}_c) \delta \phi = 0 \tag{24} $$

for some potential variation $\delta \mathcal{H}_c$. If we collect the first order terms we see that $\delta \phi$ must satisfy

$$ (i\hbar \partial_t - \mathcal{H}_c) \delta \phi = -i\hbar \delta \mathcal{H}_c(\Phi, \delta \mathcal{H}_c) \tag{25} $$

with the boundary condition $\delta \phi(t) = 0$ since we evolve all wavefunctions in the set $V$ from a fixed initial state $\psi$. Now it is clear that the real and imaginary part of $\delta \phi$ are not independent, they are both determined by the potential $\mathcal{H}_c$. Moreover, we see that Eq. (25) is first order in time and therefore $\delta \phi(t)$ is completely determined by the initial condition $\delta \phi(0) = 0$. We are therefore not allowed to put a second constant $\delta \mathcal{H}_c(t) = 0$ on the variation $\delta \mathcal{H}_c$. Therefore we cannot do the variations 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 $\delta \phi_1 = \delta \phi$ is a variation that satisfies Eq. (25) then the variation $\delta \phi_2 = i \delta \phi$ is produced by the potential $i \delta \mathcal{H}_c$, 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 cannot 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 $A$ that satisfies Eq. (23) if we can find such an action then we can construct the Legendre transform

$$ A[n] = -\int d^3x (\psi^*(t) \mathcal{H}_c(\Phi, \delta \mathcal{H}_c) \psi(t) - v_f(\psi(t))) \tag{26} $$

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

$$ \frac{\delta A}{\delta \mathcal{H}_c} = -\frac{\delta A}{\delta n} + \int d^3x \left( v_f(\Phi) - v_f(\Phi) \right) + n = n \tag{27} $$

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

$$ \frac{\delta A}{\delta \mathcal{H}_c} = n \tag{28} $$

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

$$ A[n] = -\int d^3x (\psi^*(t) \mathcal{H}_c(\Phi, \delta \mathcal{H}_c) \psi(t) - v_f(\psi(t))) \tag{29} $$

where $n$ must now be regarded as a functional of $A$. The question therefore is: is there a functional $\mathcal{A}$ 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 a functional derivative of some functional $\mathcal{A}$ of the
external potential. The answer is no if $\mathcal{A}$ is twice differentiable because then we could differentiate Eq. (38) again and obtain

$$\frac{d}{ds} \mathcal{A} = \frac{d\mathcal{A}}{ds}.$$  

The left-hand side of this equation is symmetric in the space-time arguments since we assumed that $\mathcal{A}$ 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 $t > s$). 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. (38). Consequently there is no functional of the density with the property Eq. (23). We therefore conclude that the external potential $\mathcal{V}_e$, $\psi_0$ of a many-body system with initial state $\psi_0$ and density $\rho$ 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 time-dependent density $\rho(t)$ 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 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 [11,34]. Let us finally answer the topical question posed 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 state

\[ \mathbf{J}(r) = -\frac{\partial}{\partial r} \rho(r). \]

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

\[ \mathbf{J}(r) = \frac{1}{2i} (\nabla - \nabla') \psi(r, r') \mathcal{J}_{\psi} \]

where $\gamma$ 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

\[ \mathbf{P}(t) = \int d^3r \mathbf{j}(r). \]

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

\[ \partial_t \rho(r) = -\nabla \cdot \mathbf{j}(r). \]

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

\[ j_n(r) = \frac{1}{\hbar} \sum_{\alpha} \langle \psi_{\alpha}(r) | \nabla \psi_{\alpha}(r) - (\nabla \psi_{\alpha}(r)) \rangle | \psi_{\alpha}(r) \rangle \]

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

\[ j_{xc}(r) = j_n(r) + j_n(r). \]

Let us now investigate what the equations we defined at the beginning of this section can tell us about $j_{xc}$. 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

\[ \nabla \cdot j_n(r) = \nabla \cdot j_n(r) - \nabla \cdot j_{xc}(r) = 0. \]

We see that $j_{xc}$ is a divergenceless or transverse vector field which can therefore be written in the form $j_{xc} = \nabla \times \mathbf{E}$ for some vector field $\mathbf{E}$. 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

\[ \mathbf{P}(t) = \int d^3r j_n(r) = \int d^3r \mathbf{P}(r). \]
From this equation we see that the Kohn-Sham system and the true system have the same momentum and so
\[ i \hbar \frac{\partial \psi(r)}{\partial t} = -\frac{1}{2} \nabla^2 \psi(r) + v_s(r) \psi(r). \] (37)

The continuity equation has therefore told us that \( j_x \) is a transverse vector field whose spatial average is zero. So far we have discussed some general relations which must be satisfied by \( j_x \). We now turn to some more specific cases. For one-dimensional systems in which there are no transverse vector fields \( j_x \) vanishes. For such systems the current is uniquely determined by the density from
\[ j_x(x) = -\int d^3 y \partial_t n(x,y). \] (38)

If the current vanishes at infinity, this equation immediately implies that for one-dimensional systems \( j = j_x \) and \( j_y = 0 \). It was conjectured \(^{21}\) that this holds true in general. The argument was based on the fact that systems with two different time-dependent scalar potentials \( v_1 \) and \( v_2 \) have a C(1) differing by more than a purely time-dependent function, yield two different currents \( j \neq j \). This follows immediately from the proof of the Ruppeiner theorem. Therefore the external potential is a well-defined functional \( v \) on the set of \( n \) representable currents. However, it was implicitly assumed that every current \( j \) produced by a scalar potential \( v \) in an interacting system can also be produced by a scalar potential \( v \) in a noninteracting system, i.e., the proof was based on an unproven noninteracting susceptibility assumption. One may object that such a conclusion 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 correlation of the external potential to the total energy is of the form of an integral over \( n \). 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 these arguments it seems unlikely that the noninteracting susceptibility assumption for the current can be justified.

Another argument which suggests that \( j_x \) is nonzero in general is provided by the following example. Consider a Kohn-Sham system with two particles in a singlet

state, doubly occupying one spatial orbital
\[ i \hbar \frac{\partial \psi}{\partial t} = -\frac{1}{2} \nabla^2 \psi + v_s \psi \]
\[ n(r) = 2 |\psi(r)|^2. \] (39)

The Kohn-Sham orbital can then always be written in the form
\[ \psi(r) = \sqrt{\frac{n(r)}{2}} e^{i \Phi(r)}. \] (40)

With this expression we obtain the following equation for the Kohn-Sham current
\[ j_x(r) = -n(r) \nabla \Phi(r). \] (41)

and we see that
\[ \nabla \cdot \frac{j_x}{n} = 0. \] (42)

If we assume that \( j = j_x \), then this implies that for any interacting two-electron system
\[ \nabla \cdot \frac{j}{n} = 0. \] (43)

This seems an unlikely property for an arbitrary two-electron system with rotating currents, such as an He 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 whole model systems are separable and have the special feature that they decouple exactly 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 \[ j_x = n(x) \Phi(\Phi) \] where \( \Phi(\Phi) \) 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
system cannot be reproduced by the current density of a spin-restricted Kohn-Sham system. However, if we relax the restriction that the Kohn-Sham system is in a doubly-occupied spin-orbital, and instead consider 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? Also, is this Kohn-Sham system unique? Is one-dimensional, 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 present semi-empirical XC energy functionals have potentials that do not resemble the exact XC potentials 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 $-1/r^4$, whereas the LDA and GGA decay exponentially. (How such functionals still yield good ground-state energies is an interesting question in itself[127].) This is not a difficulty for the ground-state theory, as the potential in the region where bond orbitals (in this case, just one) live is well approximated. But excited states, especially Rydberg states, are badly described. In fact, many 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 $-1/r^4$ tail in the asymptotic region. Several prescriptions for doing this have been suggested in the literature[128,129]. A statistical average of orbitals also produces an excellent potential in this regard[130].

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 orbitals are tiny[131].

These problems have recently been reviewed by Torder and Handy[20]. There is no noticeable error in the exponential 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.

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 He atom, the first transition from 2s to 2p is reasonably well LDA or GGA, but higher levels are bad. For many molecules and reactions of chemical 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 well correlated, then errors in the ground-state approximation become large, and difficulties arise for excitations. The H$_2$ molecule, stretched beyond the Coulson-Fischer 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
been recently studied from several different angles\textsuperscript{12,13,14,15}.

Assuming the ground-state potential is accurate, how about approximations to $f_{ex}$? In almost all applications at present, $f_{ex}$ is approximated adiabatically, by the second derivative of a ground-state XC energy functional. In recent work\textsuperscript{10}, some of us investigated the effect of different approximations. Using the single-particle 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 $f_{ex}$, typically a very small part of $E_{ex}$. This gives a functional explanation of why KS values are often good, but not always the best choice.

As the hybrid was designed simply to illustrate how insights into functionals could be used to improve accuracy in TDDFT calculations, its construction depended on the system being well described by having few electrons. It worked for He, but less well, and has been shown to yield no improvement for stretched H$_2$\textsuperscript{+}, or for the dispersion of the plasma in the uniform electron gas.

Very little exact information is known about the kernel. Even for exact exchange, relatively little practical is known\textsuperscript{15}, beyond the two-electron unimproved case. The frequency dependence of $f_{ex}$ for the uniform gas has been under constant study\textsuperscript{16,17,18,19,20,21,22}.

As for the question of which approximation – the one for $v_{ex}$ or the one for $f_{ex}$ – has a stronger influence on the calculated spectra, generally the effect of $v_{ex}$ 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 He atom resulting from various approximations for $v_{ex}$ and $f_{ex}$. For low-lying excitations, and especially for larger systems, often it is $f_{ex}$ which has the larger effect, as is seen in the $3s\to2p$ transition in the figure. These lower lying excitations are often the ones of photo-chemical interest.

![Image](image-url)

**Fig. 2.** Errors of singlet excitation energies from the ground state of He, calculated using the exact exchange-correlation potential obtained from an accurate wavefunction calculation, the DFT-SIC approximation and the X-only KLI approximation and with different approximations for the exchange-correlation kernel. The errors are given in millihartrees. To guide the eye, the errors of the discrete excitation energies were connected with thin, blue lines from Ref.\textsuperscript{10}.

2.5. When are Koopman transitions good approximations?

Early on, Calido\textsuperscript{2} showed how to recast Eq. (17) into common quantum chemical notation

$$K \Phi = \Omega \Phi \tag{44}$$

The eigenvalues are the squares of the physical excitation energies $\Omega$, and the eigenvector $\Phi$ determines the true oscillator strength of the corresponding transitions \textsuperscript{8}. Alternatively, these equations may be written\textsuperscript{18}:

$$\sum \omega (M_{\omega}(\Omega) + i \omega M_{\omega}(\Omega)) \beta_{\omega} = \Omega |\beta_{\omega}| \tag{45}$$
Here the matrix elements $M_{ij}(t; t') = \langle \psi_{j}(t') | H(t) | \psi_{i}(t) \rangle$, where $H(t)$ is the Hamiltonian, are expressed in terms of Kohn-Sham orbitals $\phi_{i}(x) = \langle \psi_{i}(x) | \phi_{i}(x) \rangle$. In the context of the Kohn-Sham formalism, these matrix elements are related to the one-electron density matrix elements.

To obtain a deeper understanding of the solutions to Eqs. (45) and (44), we first note that if $f_{c,i}$ is zero, the density matrix is diagonal, and both eigenvalues and eigenvectors will equal their KS counterparts. For weakly correlated systems, we expect $f_{c,i}$ to be small, some, 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 $f_{c,i}$ is frequency-independent, as is the case in most currently used approximations. We then use the method of continued fractions (CF), where solutions of linear equations in $q = 1$ orbital, and both eigenvalues and eigenvectors will equal their KS counterparts. For weakly correlated systems, we expect $f_{c,i}$ to be 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?

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2.6. What happens to atoms in strong laser fields?

TDDEFT 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)\(^{3,8,23,21,31}\), above-threshold ionization (ATI)\(^{3,9,12,14}\), or high-harmonic generation (HHG)\(^{3,9,38}\) 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\(^{3,7,23,38,39}\). For any time-dependent calculation within TDDFT there is, however, one important point to note: it is not sufficient to introduce 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-functional form for the observables. Usually the quantities of interest in a time-dependent calculation are some generalized cross sections like \( \sigma \) or \( T \) matrices in scattering processes, ionization yields, branching ratios for chemical reactions or absorption frequencies, to mention just a few. By virtue of the Range-Gross theorem all of these observables are functions 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 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 local volume has an intensity profile existing on different atoms to different intensities, these spectra are given by \( |\langle \alpha | \mu(n(r)) \rangle|^2 \). Here \( \mu(n) \) is the Fourier transform of the induced-time-dependent dipole moment of the

\[
\sigma(\omega) = \int d^3 r \ n(\mathbf{r})
\]

\[
T(\omega) = \int d^3 r \ n(\mathbf{r})
\]

\[
\frac{1}{2} \int d^3 r \ \langle \mathbf{r} | \mu(n(\mathbf{r})) | \mathbf{r} \rangle^2
\]

\[
P(\omega) = \int d^3 r \ n(\mathbf{r})
\]

\[
\frac{1}{2} \int d^3 r \ \langle \mathbf{r} | \mu(n(\mathbf{r})) | \mathbf{r} \rangle^2
\]

Note, since the time propagators are present in the ground state, both ionization yields \( P^{(1)}, P^{(2)} \) are functionals of the density only. For helium, the simplest

\[
\frac{1}{2} \int d^3 r \ |\langle \alpha | \mu(n(\mathbf{r})) \rangle|^2
\]

\[
\frac{1}{2} \int d^3 r \ \langle \mathbf{r} | \mu(n(\mathbf{r})) | \mathbf{r} \rangle^2
\]
approximation for the pair-correlation function is the exchange-only expression
\[ g_{el}(r) = \frac{1}{2} \frac{\hbar^2}{m} \frac{1}{r^3} \]

In this case the ionization probabilities \( P^{+1}, P^{+2} \) reduce to
\[ P^{+1} = 2p(1 - p) \]
\[ P^{+2} = (1 - p)^2, \]

where \( p(r) = \frac{1}{2} \int d^3r r(r) \). 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\(^{19}\) have performed numerically exact time propagations for a 1D soft-core model of helium in a laser field\(^{19}\). In the length gauge the Hamiltonian for their model system reads
\[ H = -\frac{1}{2} \frac{d^2}{dr^2} - 2V(r) + V(x_1, x_2) + (x_1 + x_2) E \text{ f}(t) s(\delta). \]

Here \( f(t) \) describes the envelope of the laser pulse and \( V(r) = 1/\sqrt{r^2} + 1 \) is the soft-core model potential. From the time-evolution of the two-electron wavefunction using the split-step method\(^{19}\), 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\(^{19}\) 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-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) recover 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\(^{19}\).

Thus more accurate exchange-correlation potentials, possibly including memory effects\(^{19}\), have to be studied in this case to obtain better approximations to the true time-evolving density.

2.7. What 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...
ten logical questions to time-dependent density functional theory

...functionals satisfy an important guide to understanding why various approximations work as they do, and indeed, to their construction. Exact conditions that the time-dependent functionals satisfy include Newton's Third Law, the harmonic potential theorem, behavior under uniform scaling, a virial theorem, and the memory formulas. For example, the violation of the harmonic potential theorem by the Gross-Kohn approximation for the exchange correlation kernel provided much of the motivation for a search for other approximations which do satisfy this theorem.

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 wavefunctions. 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. There 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

\[ H = \frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{1}{2} \int \frac{1}{r_1} \frac{1}{r_2} \, dt, \]

where the time-dependent force constant is

\[ \lambda(t) = \kappa - \cos(\omega t). \]

The one-electron version of this is the Mathieu oscillator. The dynamics is largely classical, because of the quadratic nature of the potential. If it were classically evolving a bunch of trajectories with the same initial phase-space distribution as the initial ground-state, describes the full quantum dynamics. But, for \( \kappa \) not too large, time-dependent perturbation theory tells us what frequencies appear in the dynamics. In Fig. 4, we plot the momentum-squared 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...
potential in terms of the evolving density. Once \( v_s(r) \) is known, the energy components \( \mathcal{E}(r_i) \), \( \mathcal{U}(r_i) \), and \( \mathcal{V}_{\text{int}}(r_i) \) may then be obtained with the help of the equations of motion. These energies contain global information about the potential \( v_s(r) \) and \( v_m(r) \). We shall describe a manifestation of this shortly.

The exact calculation may be compared with that of an exact adiabatic calculation (7). 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., \( \mathcal{E}^{(0)}(r) = E_s(r) - \mathcal{E}_{\text{eff}}(r) \). The exact ground-state value is obtained by a breaking 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 \( k_{\text{eff}}(r) \).

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 functional behaves qualitatively not the adiabatic approximation. We refer the reader to the paper 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-state cut off the dress is that \( \mathcal{E}_c(t) \) can become negative. No adiabatic a priori can capture this. In the time-dependent case there is of course no variational principle holding \( \mathcal{E}_c \) down zero and we found positivity in all of our runs. One can prove (7) that \( \mathcal{E}^{(0)}(r) \geq -T_{\text{eff}}(r) \), a negative number. In all the runs we considered we found \( \mathcal{E}^{(0)} \geq 0 \), always pulling up the negative ground-state value, but whether this is generally true, remains to be proved.

This graph also demonstrates the importance of memory effects (and now our poor ground-state recipe running). In the top panel is a plot of the value of \( \mathcal{E}_c(r) \) described earlier. This parameter completely identifies the density profile. The figure suggests that the correlation potential \( v_s(r) \) is a highly non-local functional of the density, meaning that \( v_s(r) \) depends not just the density at and around time \( t \), but rather on the entire history. The density profiles for a time range centered near \( t = 4.8 \) and centered near \( t = 26.6 \) are almost the same, yet the values of \( \mathcal{E}_c(r) \) near those times are hugely different. The density at times near \( t \) is not

\[\mathcal{E}_c(t) = \int d^3r \rho_0(r) \rho_0(\mathbf{r}) \] (57)

so that non-locality in \( \mathcal{E}_c \) directly implies non-locality in the correlation potential \( v_s(r) \). Clearly, \( \mathcal{E}_c(t) \) will also be a highly non-local functional of the density and this is also shown in the figure. Any adiabatic a priori calculation 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. We end this section by looking back to the linear response theory of the previous section. One can prove that although \( \mathcal{E}_{\text{eff}}^{(0)} \) vanishes in linear response, \( \mathcal{E}_{\text{eff}}^{(0)} \) and \( T^{(0)}_{\text{eff}} \) do not.
2.8. Can we always find a Kohn-Sham potential for an appropriate initial state?

The Kohn-Sham theorem proves that there is a 1:1 mapping between potentials and densities, much like in the ground-state case, but with one major difference: the mapping is unique only for a specified initial state. There may be 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 functions in use today completely ignore this initial-state dependence, partly because very little is known about it.

To tackle the problem of how functions depend on the initial state we might start 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. There is no initial-state dependence for one electron. The proof is very simple: the two Kohn-Sham wavefunctions must be related to each other by a phase, \( \phi (r) = e^{i\alpha(\mathbf{r})} \), in order to have the same density. If \( \alpha \) 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 derivative of the density \( \rho \), and which are well behaved in that their expectation values of the momentum-density tensor are finite, there exist two different potentials in which they evolve with the same density for all time. This holds also in the case of two different inter-particle interactions and so is a statement about non-interacting susceptibility. It is also shown 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. 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 to allow for the evaluation of the momentum density tensor with the Hamiltonian.

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 sufficient to completely determine all properties of the system at that time. The Kohn-Sham theorem says that this is overkill: knowing just the time-evolving density and just the initial wavefunction is enough to know everything about the system. In the ground-state case, by using in the 6N-variable wavefunction for the 3-variable density as its main player, and having to solve N non-self-adjoint Schrödinger's equations instead of the single 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, a fact which 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:
function evolved to at time \( t' \leq t \), we may equally well think of \( t' \) as the initial time, and the input to \( \rho_{t'} \) 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

\[
\rho_{t'}[\psi_{t'}, \phi_{t'}(r)] = \rho_{t'}[\psi_{t}, \phi_{t}(r)] \quad \text{for} \quad t \geq t',
\]

(58)

where

\[
\rho_{t'}(r) = n_{t'}(r) \quad \text{for} \quad t \geq t'.
\]

(59)

and \( n_{t'}(r) \) is defined for \( t' < t \). Eq. (58) is a very difficult condition for a approximate functionals to satisfy. Like other exact conditions, for example, the harmonic potential theorem \[30\] and the virial theorem \[31\], it may be used as a least tight 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 absorbed into 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 \( n(r) \), then

\[
\rho_{t'}[\psi_{t'}, \phi_{t'}(r)] = \rho_{t'}[n(r)] \quad \text{for} \quad t \geq 0.
\]

(60)

Here, the density \( n(r) = n_{t'}(r) \) for \( t \geq 0 \) is defined to be the density along a pseudo-prehistory which begins in some ground-state \( \psi_{t'} = \phi_{t'} \) for the Kohn-Sham system at some negative time \( t = -t' < 0 \) and evolves under some many-electron Hamiltonian that carries us to the true initial states \( \psi_{t} = \phi_{t} \) 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 \( \psi_{t'} \) and \( \phi_{t'} \) 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 \[31\], but there are plenty of initial states that can be.
3. Conclusions: Dante’s Inferno?

When we begin applying TDDFT to quantum mechanical systems, the image
response method looks very appealing, especially employing M Dick for $f_{\text{opt}}$. We
are the demons at the edge of the woods. But once we use things a little more
clumsily, we begin our descent through the various circles of Hell. So long as we
stay within linear response, we are always at variance 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 bears its
ugly head (similar to that of Bertrand’s Post) and we know we are in the inner
circle.

But there is more than just the inferno to Dante’s classic. There follow the
purgatorio and finally paradise, it is necessary to first pass through Hell, to achieve
the wisdom needed to reach the paradise. For TDDFT, we are on the way.

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