5-2015

Exploring Non-Equilibrium Dynamics in Time Dependent Density Functional Theory

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Exploring Non-Equilibrium Dynamics in Time Dependent Density Functional Theory

by

Kai Luo

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

2015
This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirements for the degree of Doctor of Philosophy.

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Abstract

Exploring Non-Equilibrium Dynamics in Time Dependent Density Functional Theory

by

Kai Luo

Advisor: Neepa T. Maitra

Time-dependent density functional theory (TDDFT) is a method of choice for calculations of excitation spectra and response properties in materials science and quantum chemistry. The many-body problem is mapped into a set of one-body Schrödinger equations, called the Kohn-Sham (KS) equations. In principle, the one-body potential can be chosen such that the density of the interacting system is exactly reproduced by the KS system. However, one component of the one-body potential has to be approximated and is typically “adiabatic”. Though in linear response regime adiabatic approximations give quite good spectra, it is important to explore their performances in non-equilibrium dynamics.

In this thesis, I will present the results of the explorations on non-equilibrium dynamics in TDDFT. For the first study, a decomposition of exact exchange-correlation potential into kinetic and interaction components is derived. We compare the components with that of “adiabatic” counterparts in non-perturbative dynamics and find that the interaction component is less poorly approximated adiabatically than the kinetic component. A salient feature is that step structures generically appear, of relevance in the second study. We prove that the step structures only appear in the non-linear response regime. We find an
exact condition which is typically violated by the approximations in use today. Spuriously
time-dependent spectra in TDDFT can be explained and we find that the more the condi-
tion is violated the worse the dynamics is. In last, we envision that orbital functionals are
able to incorporate the memory effects and compensate the deficiencies of the “adiabatic”
approximations.
Acknowledgements

Foremost, I would like to express my sincere gratitude to my advisor, Professor Neepa T. Maitra, for her guidance, support and friendship during all these years. Without her encouragement and understanding when in all kinds of stresses, I would not have gone this far in my research and life. I could not imagine having a better advisor and mentor for my Ph.D. study.

Besides my advisor, I would like to thank my thesis committee members, Prof. Mark Hillery, Prof. Vadim Organesyan, Prof. Michel Pavanello and Prof. Steven Greenbaum, for their willingness and precious time to read my thesis and serve on my committee and for their encouragement, insightful comments, and hard questions. My sincere thanks also go to Prof. Robert van Leeuwen, who helped me with his theoretical insight when I got stuck.

I thank my groupmates, students and friends whom I met at CUNY: Johanna I. Fuks, Ernesto D. Sandoval, Yin Cen, Arthur Parzygnat . . . , who I cannot enumerate all; I'm aslo grateful for the inumerous support I gained from Daniel Moy.

Lastly, my special thanks are given to my family. I thank my wife for the sacrifice she made to stay with me, the precious time she created, and the tough days she went through when missing her family; I thank my parents and sister for their forever love, care and support.
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Chapter 1

Introduction

1.1 Many Body Quantum Mechanics

The theory of quantum mechanics, tested and verified by innumerable precise experiments over last century, manifests itself as the most successful physical theory. The principles of quantum mechanics[16] are a set of laws which the microscopic world obeys. Particularly, the principle of the state evolution for non-relativistic quantum mechanics is expressed by the time dependent Schrödinger equation,

$$i\hbar \partial_t \Psi(t) = \hat{H} \Psi(t).$$

(1.1)

In general, electronic and nuclear degrees of freedom have to be treated equally by replacing \(p\) of a classical Hamiltonian with \(-i\hbar \nabla\) for each particle. We write the full Hamiltonian, \(\hat{H}\), as

$$\hat{H} = \hat{H}_{\text{BO}} + \hat{T}_n(\mathbf{R}) + \hat{V}_{\text{ext}}^e(\mathbf{r}, t) + \hat{V}_{\text{ext}}^n(\mathbf{R}, t),$$

(1.2)

where \(\hat{T}_n(\mathbf{R})\) is the nuclear kinetic energy operator, \(\hat{V}_{\text{ext}}^{e(n)}(\mathbf{r}(\mathbf{R}), t)\) is the external potential acting on the electrons(nuclei), and \(\hat{H}_{\text{BO}}\) is the traditional Born-Oppenheimer Hamiltonian that conventionally include nuclear-nuclear repulsion,

$$\hat{H}_{\text{BO}} = \frac{1}{2} \sum_{j \neq k}^{N_n} \frac{Z_j Z_k}{|\mathbf{R}_j - \mathbf{R}_k|} - \frac{\hbar^2}{2m_e} \sum_{\alpha = 1}^{N_e} \nabla^2 \alpha + \frac{1}{2} \sum_{\alpha \neq \beta}^{N_{e}} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \sum_{\alpha = 1}^{N_e} \sum_{j = 1}^{N_n} \frac{Z_j}{|\mathbf{R}_j - \mathbf{r}_\alpha|}.\)
The $\mathbf{R} = (R_1, R_2, \ldots, R_N)$ and $\mathbf{r} = (r_1, r_2, \ldots, r_N)$ are the nuclear and electronic coordinates. Here we use Greek letter for the electron index and Latin letter for the nucleus index. Symbols $R_j, r_\alpha, N_n, N_e$ are the nuclear coordinate, the electronic coordinate, the total number of nuclei and the total number of electrons. And we neglect spin for simplicity.

Under the Born-Oppenheimer approximation[6], the electronic Hamiltonian parametrically depends on the nuclear configuration, which can be written as

$$\hat{H}_e = \hat{T} + \hat{W} + \hat{V}$$  \hspace{1cm} (1.4)

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{W}$ is the instantaneous electron-electron coulomb interaction, and $\hat{V}$ includes both the nuclear attraction and any externally applied potential felt by the electrons. In general, electrons can be subject to the motion of nuclei and/or to an electric field, which leads to a time dependent external potential. In real space representation, it can be written as

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{\alpha=1}^{N_e} \nabla^2_{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta}^{N_e} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \sum_{\alpha=1}^{N_e} v_{\text{ext}}(\mathbf{r}_\alpha, t),$$  \hspace{1cm} (1.5)

where $m_e, e, N_e$ are the electron mass, the electron charge and the total number of electrons. All units are in the atomic units in the following text. For example, for a system illuminated by a laser beam in the dipole approximation and neglecting magnetic field, taking account of the moving nucleus we can write

$$v_{\text{ext}}(\mathbf{r}, t) = \sum_{j=1}^{N_n} \frac{-Z_j}{|\mathbf{r} - \mathbf{R}_j(t)|} - E(t)\mathbf{\alpha} \cdot \mathbf{r}.$$  \hspace{1cm} (1.6)

The electronic Hamiltonian, Eq. (1.4), is usually the starting point for first principles calculation, assumed by most ab initio electronic structure scientists.

In the early stage of solid state theory, the independent electron approximation, neglecting the $\hat{W}$ term, showed great success in explaining properties of metals. Detailed and
more precise experiments later revealed that electron-electron correlation is essential in
describing new physics, e.g. superconducting phenomena. To get a better understanding
of atoms, molecules and solids, it is desirable to make predictions from *ab initio* calcula-
tions. However, the task of getting the full wave function of Eq. (1.1) for a few electrons is
formidable and intractable. The complexity can be illustrated from the following consider-
ations.

First, let’s simulate the evolution of the many body state with brute force. Imagine a
system consisting of $N$ electrons living in $d$-dimensional space. It’s obvious that (classical)
computers can handle this task better than human labor. Certain discretization has to be
performed before we put on a computer. If we discretize each dimension in real space by
$k$ points, then the number of grid points, $M$, is $(d k)^N$. To get a sense of how large it could
be for a relatively small system, we consider neon atom with 10 electrons in a 3D cube
discretized by 33 points for each dimension. Then we have

$$M = (d k)^N = (3 \times 33)^{10} \approx 10^{10} \approx 10^{20}. \tag{1.7}$$

For each grid point, we assign a value of float type to it. In modern computer, a float type
has the size of 4B (B is short for *byte*). The total size of the wave function is $4 \times 10^{20} \text{B} 
\approx 4 \times 10^8 \text{ TB}$, which requires $10^{11}$ DVD discs to store it. A typical DVD disc weighs 15
grams and stores 4 GB. The total weight of those DVD discs is of order $10^6$ tons. For a 10
electron atom, the storage space is galactically large to afford, not to mention updating the
evolution. In fact, even we have clever ways to handle the wave functions, it is impractical
to obtain them when the number of electrons increases[43].

For most cases, the observables of particular interest is enumerable and it’s unnecessary to
obtain the full wave function. Knowing the wave function is knowing all the observables.
We may say wave function contains much more information than we need and that it is redundant for our needs. As quoted by Kohn [43] as the Van Vleck catastrophe, the wavefunction is no longer a legitimate scientific concept when $N$ exceeds $10^3$.

Instead, physicists have created mean field theories and effective theories to handle this challenging task. Among them are Hartree-Fock theory, density functional theory and dynamical mean field theory, to name a few. Density functional theory is widely accepted as an efficient computational tool for chemistry, physics and material sciences. Other methods dealing with strongly correlated systems, such as LDA+U, utilize local density functional approximation as the first round approximation due to the simplicity and low cost of DFT.

The need to go beyond the static theory to describe time dependent systems becomes intense and critical in the past decades. A system composed of hundreds of, even a few electrons interacting with light is difficult to model. Time-dependent density functional theory (TDDFT) has become one of the most promising theoretical tool for modeling and predicting spectroscopic experiments. TDDFT is in principle an exact reformulation of quantum mechanics that puts the many body effects into a one-body potential, a sum of external, Hartree and exchange-correlation (xc) potential. However, approximations for the xc potential have to be made to be practical. Most calculations in TDDFT rely on the so called “adiabatic approximation” where the instantaneous density is treated as a ground state density. Adiabatic approximations perform well in response of solids, non-perturbative electron dynamics[56]. Though the great success of TDDFT within adiabatic approximation cannot be denied, it is important to incorporate the memory dependence in double excitations and charge-transfer excitations for finite systems.
In the thesis, I will describe the basic theory of static DFT and TDDFT in Chapter 2. The essential object is the xc potential, which depends on both interacting and Kohn-Sham initial states and the history of the density. An exact decomposition of the xc potential shows the performance of the adiabatic approximation for each component, which is discussed in Chapter 3. A special feature is that these xc potentials display step structures, which are not captured adiabatically. However, adiabatic TDDFT(ATDDFT) linear response calculations typically give good spectra. Chapter 4 explores the step structures in the linear response regime, and shows that the steps only appear in the region where the density response is non-linear, illustrating why ATDDFT works. In Chapter 5, we derive a general response function for an arbitrary state and give an exact condition for the xc kernel to satisfy. The failure of usual approximate functionals to satisfy the condition leads to incorrect dynamics. It’s crucial to incorporate memory effects in the approximated functionals and we expect orbital functionals are worth exploring. A discussion on the frequency-dependent exchange-correlation kernel from an orbital functional is included in Chapter 6. Lastly, we conclude in Chapter 7.
1.2 Atomic Units

The use of atomic units (a.u.) is especially convenient for atomic physicists and we are going to use atomic units throughout the thesis without further declarations. Atomic units are a Gaussian system of units (by "Gaussian" it means that the vacuum dielectric constant has no dimensions and is set to be $\epsilon_0 = \frac{1}{4\pi}$), in which the numerical values of the Bohr radius, the electronic charge, the electronic mass, and the reduced Planck’s constant are set to one:

$$m_e = e^2 = a_0 = \hbar = 1.$$  \hspace{1cm} (1.8)

Note that the charge of electron, $-e$, should be negative, $-1$. We can deduce that the unit of energy is the potential energy in hydrogen atom,

$$E_{\text{hydrogen}} = \frac{1}{4\pi\epsilon_0 a_0} = 1,$$  \hspace{1cm} (1.9)

which is the first derived unit we often encounter. The next important one is the unit of time. The Planck constant has the dimension of time times energy (can be seen from Einstein relation $E = \hbar \omega$), which can be exploited to derive the unit of time:

$$\tau = \frac{\hbar}{E_{\text{hydrogen}}} = 4\pi\epsilon_0 \frac{a_0}{e^2} = 1.$$  \hspace{1cm} (1.10)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Value in SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e$</td>
<td>mass(electron)</td>
<td>$9.1094 \times 10^{-31} \text{ kg}$</td>
</tr>
<tr>
<td>$e$</td>
<td>charge(electron)</td>
<td>$1.6022 \times 10^{-16} \text{ C}$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>length(Bohr first radius)</td>
<td>$0.5292 \times 10^{-10} \text{ m}$</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>angular momentum</td>
<td>$1.0546 \times 10^{-34} \text{ J} \cdot \text{s}$</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity($\alpha c$)</td>
<td>$2.1877 \times 10^{+06} \text{ m} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$E$</td>
<td>energy($e^2/4\pi\epsilon_0 a_0$)</td>
<td>$4.3587 \times 10^{-18} \text{ J} = 27.2114 \text{ eV}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time($4\pi\epsilon_0 a_0/\hbar e^2$)</td>
<td>$2.4189 \times 10^{-17} \text{ s} \approx 24.2 \text{ attosecond}$</td>
</tr>
<tr>
<td>$d$</td>
<td>dipole($e a_0$)</td>
<td>$8.4788 \times 10^{-30} \text{ C} \cdot \text{m}$</td>
</tr>
</tbody>
</table>
Then the velocity can be directly written as

\[ v = \frac{a_0}{\tau} = \frac{1}{4\pi \epsilon_0} \frac{e^2}{\hbar} = \alpha c, \]  

(1.11)

where \( \alpha \) is the fine structure constant

\[ \alpha = \frac{1}{4\pi \epsilon_0 \hbar c} \approx \frac{1}{137}. \]  

(1.12)

The values in SI units of atomic units are listed in Table 1.1, which is handy when the conversion is necessary. All the numbers in this thesis are in atomic units.
Chapter 2

Static and Time-Dependent Density Functional Theory

2.1 Static Density Functional Theory

The seminal paper by Hohenberg and Kohn [39] establishes the existence proof of density functional theory, which revolutionized the understanding of quantum mechanics. It states that there exists a one-to-one mapping between the external potential $v(r)$ and the ground-state density $n(r)$. It reformulates quantum mechanics by pointing us to the search for the exact ground-state density, instead of the intractable wave function. For decades, DFT has been an active research area with ongoing work to build, improve and implement density functionals in physics, chemistry, materials science and computational biology.

2.1.1 The Hohenberg-Kohn Theorem

Before we proceed, let’s first define the density operator $\hat{n}(r)$ and the current density operator $\hat{j}(r)$ for later usage:

$$\hat{n}(r) = \sum_i \delta(r - r_i), \quad (2.1)$$

and

$$\hat{j}(r) = \frac{1}{2i} \sum_i \delta(r - r_i) \nabla_i + \nabla_i \delta(r - r_i). \quad (2.2)$$
In the following context, “different potential” is understood as “physically different potential”, meaning that two potentials are not simply connected by a constant, i.e. $v(r) \neq v'(r) + c$. Further, non-degenerate ground-states are considered here (although the theorems of DFT can be extended to degenerate ground-states[36]).

We prove that different external potentials $v(r)$ and $v'(r)$ yield different ground-state densities by neglecting the spin and note that the spin can be straightforwardly included. Clearly $\Psi'$ cannot be equal to $\Psi$ since they satisfy Schrödinger equations for different ground-state potentials. We denote them by unprimed symbols and primed symbols respectively. Assuming both systems have the same density $n(r)$ and proceeding by *reductio ad absurdum* from the variational principle for the ground state, we see that $E_0 = \langle \Psi | \hat{H} | \Psi \rangle$ and $E_0' = \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} + \hat{V}' - \hat{V} | \Psi \rangle$, namely

\[
E_0' < E_0 + \int dr \ [v'(r) - v(r)] n(r). \tag{2.3}
\]

where the electronic density is defined as

\[
n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle = N \int dr_2 \ldots \int dr_N |\Psi(r, r_2, \ldots, r_N)|^2. \tag{2.4}
\]

Interchanging the primed and unprimed symbols, we get

\[
E_0 < E_0' + \int dr \ [v(r) - v'(r)] n(r). \tag{2.5}
\]

Addition of Eq. (2.3) and Eq. (2.5) leads to *absurdum*. Thus a one-to-one mapping exists between the non-degenerate ground state density and the external potential. The mapping can be expressed briefly by $v[n](r)$, $v(r)$ being a functional of the ground state density. In other words, every density profile is associated with a unique external potential.
2.1.2 Constrained Search

From the variational principle, the ground state energy can be found by minimizing \( E = \langle \Psi | \hat{H} | \Psi \rangle \) over all antisymmetric N-particle wavefunctions. The corresponding wavefunction which delivers the minimum is the ground state wavefunction \( \Psi_{gs} \).

The proof by Levy allow us to actively search for the density to get the minima without explicit recourse to many-particle wavefunctions, known as “constrained search”[51]. First, for a given density find all possible wavefunctions which minimizes the energy. Define the minimizing wavefunction for the given density as \( \Psi_{min} \). Minimizing over all N-electron densities \( n(r) \) produces the ground state density, \( n_{gs} \). In mathematical language, we express the procedure as

\[
E = \min_n \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} + \hat{V}_{\text{ext}} | \Psi \rangle \right\}. \tag{2.6}
\]

A universal density functional \( F[n] \) is defined

\[
F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. \tag{2.7}
\]

since it is same for all different external potential \( v_{\text{ext}} \). It’s straightforward to see \( \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int dr \, n(r) v_{\text{ext}}(r) \). The variational principle yields the expression

\[
\delta \left\{ F[n] + \int dr \, (v_{\text{ext}}(r) - \mu) n(r) \right\} = 0, \tag{2.8}
\]

where the Lagrange multiplier \( \mu \) is inserted given that \( N \) is fixed. This variational expression from the constrained search leads to the Kohn-Sham equations.

2.1.3 Kohn-Sham Approach

The practical usage of DFT surges with Kohn-Sham(KS) approach[44], where a one-body local potential of the non-interacting system is introduced such that the interacting den-
sity is reproduced. One challenge of getting the total energy is to accurately approximate the kinetic energy, as the kinetic energy typically is a large portion. The introduction of Kohn-Sham system allows the calculation of the kinetic energy to include most of the true kinetic energy. It is computationally much cheaper for solving one-body Schrödinger equation compared to for solving a many-body one. Analogous to but different from Hartree’s method, the KS Hamiltonian is

$$\hat{H}_S = \sum_{\alpha=1}^{N_e} \left( -\frac{1}{2} \nabla_{\alpha}^2 + v_S(\mathbf{r}_\alpha) \right),$$

(2.9)

with the undetermined one-body potential $v_S(\mathbf{r})$, known as the KS potential. The non-interacting wavefunction takes the single-Slater determinant (SSD) form,

$$\Phi(x_1, \cdots, x_N) = \prod_{\alpha=1}^{N_e} \left| \varphi_1(x_1) \varphi_1(x_2) \cdots \varphi_1(x_N) \right| \left| \varphi_2(x_1) \varphi_2(x_2) \cdots \varphi_2(x_N) \right| \cdots \left| \varphi_N(x_1) \varphi_N(x_2) \cdots \varphi_N(x_N) \right|.$$  

(2.10)

where $x$ is short for $(\sigma, \mathbf{r})$ and $\sigma$ refers to the spin. If we define $F[n] = T_S[n] + U[n] + E_{XC}[n]$, the total energy, $E = \langle \Psi | \hat{H} | \Psi \rangle$, can be split into terms as

$$E[n] = \int v(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') + T_S + E_{XC}[n],$$

(2.11)

where $w(\mathbf{r}, \mathbf{r}')$ is the electron-electron interaction, usually $1/|\mathbf{r} - \mathbf{r}'|$, $T_S = \sum_i \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle$ is the non-interacting kinetic energy and $E_{XC}[n]$ is the central part of DFT, exchange-correlation (xc) energy. Typically, the xc energy is only a small fraction of the total energy but it is essential in accounting for the formation of molecules and solids, dubbed as “nature’s glue”[48]. From the stationary property of Eq. (2.11) we have, subject to the constraint that the total number of electrons is fixed, $\int n(\mathbf{r}) \, d\mathbf{r} = N$,

$$v(\mathbf{r}) + v_\mu(\mathbf{r}) + \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} = \mu_1,$$

(2.12)

while the KS system has

$$v_S(\mathbf{r}) + \frac{\delta T_s[n]}{\delta n(\mathbf{r})} = \mu_2.$$  

(2.13)
Eq. (2.12) and Eq. (2.13) are consistent if and only if

\[ v_S[n](r) = v(r) + v_H(r) + v_{XC}(r), \]  

(2.14)

where

\[ v_H(r) = \int n(r') w(r, r') \, dr' \]  

(2.15)

is the Hartree potential and

\[ v_{XC}(r) = \frac{\delta E_{XC}[n]}{\delta n(r)} \]  

(2.16)

is the xc potential. Note that the irrelevant constant \( \mu_2 - \mu_1 \) can be sucked into \( v_S \). The non-interacting electrons are obeying the one-particle Schrödinger equation, KS equation,

\[ \left[ -\frac{1}{2} \nabla^2 + v_S[n](r) \right] \varphi_j(r) = \epsilon_j \varphi_j(r), \]  

(2.17)

and we need to self-consistently solve the KS equations and sum over all the occupied orbital densities, \( n(r) = \langle \Phi | \hat{n}(r) | \Phi \rangle = \sum_j | \varphi_j(r) |^2 \). Up to this point, the theory is exact. The xc energy functional

\[ E_{XC}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle - U[n], \]  

(2.18)

in practice has to be approximated. The density obtained in the self-consistent calculation is the density resulting from the use of a certain approximate functional, not the exact density. The total energy may be written as

\[ E = \sum_j \epsilon_j - U[n] - \int dr \, n(r)v_{XC}(r) + E_{XC}[n], \]  

(2.19)

where the second and third terms on the right hand side removes the contributions to the first term which do not belong to the total energy.
2.1.4 Local, Semi-local and Non-local Functional

A paradigm model for an electronic system is called “jellium” model, where the electronic density are uniformly distributed among a positive background such that the net electric density are vanishing. The exchange energy per particle can be calculated by treating electron-electron interaction as a perturbation around non-interacting gas. For 3D, the exchange energy per particle is

$$e_x(n) = -\frac{3}{4\pi} (3\pi^2 n)^{1/3}. \quad (2.20)$$

The Seitz radius, denoted by $r_s$, the radius of a sphere which contains one electron is often used interchangeably with the density $n$, where $n = 3/4\pi r_s^3$. For low density limit, i.e. $r_s \to \infty$, the electron liquid become crystallized as the Wigner crystal. The analytic expressions for $e_c(n)$, the correlation energy are only known in high and low density limit[14, 28]. The numerical interpolation of the correlation energy for a general density $n$ is determined using Quantum Monte Carlo (QMC) method[13].

**Local Spin Density (LSD)**

The xc energy under LSD sums over all the energy of the volume element by treating the volume element as uniform electron gas locally.

$$E_{xc}^{LSD}[n_\uparrow, n_\downarrow] = \int d^3r \, n_r e_{xc}(n_\uparrow, n_\downarrow), \quad (2.21)$$

where $e_{xc}(n)$ is the exchange-correlation energy per particle for UEG. The spinless version is local density approximation (LDA). LDA is exact when the underlying physical system is UEG and performs well when the density varies slowly in space, by construction. The LSD is computationally cheap, direct and simple. It gives reasonable ground state energies.
and equilibrium geometries even in other cases. It satisfies several exact conditions. For example, the UEG xc hole density satisfies the sum rule \( \int d r' n_{xc}(r, r') = -1 \); the correct uniform scaling of \( E_x \) and LSD is size-consistent. One of the major drawbacks of the LSD is that the LSD xc potential has the wrong asymptote, which tends to overestimate the binding energy. It decays exponentially fast as \( v_{xc}^{LDA} \rightarrow -e^{-\alpha r} \) instead of \(-1/r\), when \( r \rightarrow \infty \).

**Generalized Gradient Approximation (GGA)**

The information of gradient of the density is built into the construction of the functionals and the general form of the GGA xc energy functional is

\[
E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int dr f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}).
\] (2.22)

One way of constructing this class of functionals is to satisfy as many of the known exact properties of \( v_{xc} \) as possible. For example, one of the most used GGA functionals, called PBE, was built in this spirit [57]. Again, GGA functionals decays too quickly as LSD.

**Hybrid Functional**

The idea of hybrid functional is to mix in some parts of exact exchange energy functional with GGA exchange and correlation. The simplest hybrid functional is

\[
E_{xc}^{hyb} = aE_{xc}^{exact} + (1-a)E_{xc}^{GGA} + E_{xc}^{GGA}.
\] (2.23)

where parameter \( a \) is picked empirically ranging from 0.2–0.4 such that the errors are less. Often used hybrid functionals are PBE0, HSE and B3LYP[3, 4, 37, 42, 58, 74]. Another type of hybrid functionals is the range-separated [85], where the Coulomb operator is partitioned into long range(LR) within Hartree-Fock(HF) exchange integral and short
range(SR) within DFT exchange,

\[
\frac{1}{r} = \frac{\alpha + \beta \text{erf}(\gamma r)}{r} + \frac{1 - (\alpha + \beta \text{erf}(\gamma r))}{r},
\]

with adjustable parameters \(\alpha, \beta, \gamma\). These parameters can be either empirical or chosen to satisfy exact constraints, such as Koopman’s theorem. Recently, it has been shown that the range-separated hybrid functional optimally-tuned per system can achieve comparable accuracy as computationally heavier many-body perturbation theory within GW approximation[66] for organic semiconductor applications.

We have introduced the theory for the ground state case. The following section is devoted to TDDFT, which greatly borrows the concepts in the static DFT.
2.2 Time-Dependent Density Functional Theory

TDDFT has become an increasingly important tool in first principles calculations including electronic spectra and real-time dynamics, due to its good balance between accuracy and computational cost [10, 56].

2.2.1 Runge-Gross Theorem

In 1984, Runge and Gross proved a one-to-one mapping between the time-dependent density and the external potential for a given initial state, which is known as Runge-Gross theorem[70]. Here, we present an alternative proof by van Leeuwen [81].

At \( t = t_0 \), the initial state is prepared as \(|\Psi_0\rangle\), which might be a non-stationary state. We remind ourselves the definition of the density operator Eq. (2.1) and the current density operator Eq. (2.2), where the corresponding observables are \( n(r) = \langle \Psi(t) | \hat{n}(r) | \Psi(t) \rangle \) and \( j(r) = \langle \Psi(t) | \hat{j}(r) | \Psi(t) \rangle \).

The derivative of an operator can be expressed as the derivative of its mean value(see Landau and Lifshitz [49]), namely

\[
\frac{df}{dt} = \frac{1}{i} [\hat{f}, \hat{H}],
\]

(2.25)

where the hermicity of the Hamiltonian is used and we assume \( \hat{f} \) is time-independent.

Considering the Hamiltonian of Eq. (1.5) and Eq. (2.1), Eq. (2.2), we arrive at

\[
\frac{\partial}{\partial t} n(r) + \nabla \cdot j(r) = 0
\]

(2.26)

and

\[
\frac{\partial}{\partial t} j(r) = - n(r) \nabla v_{ext}(r) - F(r)
\]

(2.27)
where we define a generalized force as

$$F(rt) = \int d^3r' \nabla w(r, r') P(r', r, t) - \frac{1}{4} (\nabla - \nabla_{r'}) (\nabla^2_{r'} - \nabla^2) \rho(r', r, t)|_{r'=r}, \quad (2.28)$$

which will be derived in Section 3.2. The pair density is

$$P(r', r, t) = \langle \Psi | \sum_{k \neq j} \delta(r - r_k) \delta(r' - r_j) | \Psi \rangle = \frac{N(N-1)}{2} \int dr_3... \int dr_N |\Psi(r, r', r_3, r_N; t)|^2, \quad (2.29)$$

and the one-body density matrix (we will use $\rho(r, r', t)$ throughout this thesis for $\rho_1(r, r', t)$ for simplicity) is

$$\rho(r, r', t) = N \int dr_2... \int dr_N \Psi^*(r, r_2...r_N; t) \Psi(r', r_2...r_N; t). \quad (2.30)$$

Note that if no explicit subscript of $\nabla$ is shown, it defaults to $\nabla_r$. Taking the divergence of Eq. (2.27) and using the continuity equation Eq. (2.26) leads to the local force equation

$$\frac{\partial^2}{\partial t^2} n(rt) = \nabla \cdot [n(rt) \nabla v_{ext}(rt)] + q(rt), \quad (2.31)$$

in which $q(rt) = \nabla \cdot F(rt)$, the divergence of a local force field.

Assuming another system (primed) with possibly different electron interaction $\hat{W}'$ and a different external potential $\hat{V}'$ of Hamiltonian $\hat{H}' = \hat{T} + \hat{V}' + \hat{W}'$ has the same density $n(rt)$ always, then similar equation to Eq. (2.31) exists,

$$\frac{\partial^2}{\partial t^2} n(rt) = \nabla \cdot [n(rt) \nabla v'_{ext}(rt)] + q'(rt). \quad (2.32)$$

Subtracting Eq. (2.31) from Eq. (2.32), we get

$$\nabla \cdot [n(rt) \nabla \nu(rt)] = \zeta(rt), \quad (2.33)$$

where $\nu(rt) = v_{ext}(rt) - v'_{ext}(rt)$ and $\zeta(rt) = q'(rt) - q(rt)$.

Firstly, the initial wavefunctions have to be related such that they evolve with the same density. If so, the second order differential equation demands that the initial density must
be the same, namely,

$$\langle \Psi_0 | \hat{n}(r) | \Psi_0 \rangle = \langle \Psi'_0 | \hat{n}(r) | \Psi'_0 \rangle ,$$

(2.34)

and the first derivative in time for $n(rt)$ is also same $\dot{n}(rt) = \dot{n}'(rt)$, i.e.

$$\langle \Psi_0 | \nabla \cdot \hat{j}(r) | \Psi_0 \rangle = \langle \Psi'_0 | \nabla \cdot \hat{j}(r) | \Psi'_0 \rangle .$$

(2.35)

Next, we will ask if another external potential $v'_\text{ext}$ is determined for a given density evolution of the original external potential $v_{\text{ext}}$. At $t = t_0$, we have

$$\nabla \cdot [n(r_{t_0}) \nabla \nu(r_{t_0})] = \zeta(r_{t_0}),$$

(2.36)

where a unique $\nu(r_{t_0})$ can be obtained if $\zeta(r_{t_0})$ and the boundary conditions are given by virtue of the Sturm-Liouville type equation. Equivalently, $v'_\text{ext}(r_{t_0}) = v_{\text{ext}}(r_{t_0}) + \nu(r_{t_0})$ is determined. If we take the time derivative of Eq. (2.33) at $t = t_0$, we have

$$\nabla \cdot [n(r_{t_0}) \nabla \nu^{(1)}(r_{t_0}) + n^{(1)}(r_{t_0}) \nabla \nu(r_{t_0})] = \zeta^{(1)}(r_{t_0}),$$

(2.37)

where the superscript denotes the order of time derivative. Rearrange the equation

$$\nabla \cdot [n(r_{t_0}) \nabla \nu^{(1)}(r_{t_0})] = \zeta^{(1)}(r_{t_0}) - \nabla \cdot [n^{(1)}(r_{t_0}) \nabla \nu(r_{t_0})],$$

(2.38)

where $\zeta^{(1)}(r_{t_0})$ can be calculated from $v'_\text{ext}(r_{t_0})$. As before, $\nu^{(1)}(r_{t_0})$ can be obtained. Repeat the procedure and we have the equation for the $k$th derivative of $\nu^{(k)}(r_{t_0})$,

$$\nabla \cdot [n(r_{t_0}) \nabla \nu^{(k)}(r_{t_0})] = \zeta^{(k)}(r_{t_0}) - \sum_{l=0}^{k-1} C_k^l \nabla \cdot [n^{(k-1-l)}(r_{t_0}) \nabla \nu^{(l)}(r_{t_0})].$$

(2.39)

In this way, we collect all orders of $\nu^{(k)}(r_{t_0})$ and hence $v'_\text{ext}(r_{t_0})$. Within the convergence radius of the Taylor expansion, we are able to construct the Taylor expandable series for $v'_\text{ext}(r_t)$,

$$v'_\text{ext}(r_t) = \sum_{k=0}^{\infty} \frac{1}{k!} v^{(k)}_{\text{ext}}(r_{t_0})(t - t_0)^k.$$
For time $t_1 > t_0$ within the convergence radius, a propagation of $\Psi'(t_0)$ to $\Psi'(t_1)$ is possible with the known $v'_{\text{ext}}(rt)$. Recurrence of the steps enables us to reproduce $v'_{\text{ext}}$ for all times. It could be seen that $v'_{\text{ext}}(rt)$ is determined up to a purely time-dependent function.

Note that this proof assumes that both the external potentials and the density are time-analytic about $t_0$. Original Runge-Gross proof assumed only that the external potential time-analytic (which is actually much less severe given the cusp from the Coulomb interaction causes density to be non-time-analytic)[22, 54].

To summarize, we prove that for an initial state $\Psi'_0$ of interaction $\hat{W}'$, the external potential $v'_{\text{ext}}$ is determined if a given density evolution $n(rt)$ is prescribed. Two direct consequences of the proof:

- For cases where $\hat{W}' = \hat{W}$ and $\Psi'_0 = \Psi_0$, it amounts to say that there is a unique external time potential (up to a purely time-dependent function) that yields the given density evolution, which is known as the Runge-Gross theorem.

- For cases where $\hat{W}' = 0$, there is a non-interacting system with proper initial state $\Phi_0$, which reproduces the same density evolution as the interacting system.

### 2.2.2 Memory Dependence

In contrast to static DFT where the variable is the ground state density, $n_{\text{gs}}(r)$, TDDFT is based on the one-to-one mapping between the density $n(r,t)$ and the external potential $v_{\text{ext}}(rt)$, for a given initial state. From van Leeuwen’s proof, we are able to choose $v_S$ such that the time-dependent density is reproduced through time-dependent KS equations,

$$\left[i \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2 - v_S(rt)\right] \varphi_i(rt) = 0,$$  \hspace{1cm} (2.41)
where we have again an analogous definition, \( v_s(t) = v_{\text{ext}}(t) + v_H(t) + v_{\text{XC}}(t) \). In particular, xc potential has extra dependence

\[
v_{\text{XC}}[n(t'), \Psi_0, \Phi_0](r, t) = v_s[n, \Phi_0](rt) - v_{\text{ext}}[n, \Psi_0](rt) - v_H[n](rt).
\] (2.42)

The dependence on the density \( n(t' < t) \) means the previous evolution is relevant, called *history dependence*, while the dependence on both the interacting and KS initial states is called *initial state dependence*. They follow from the Runge-Gross proof, which we refer them together as *memory dependence*. Almost all functionals in use today have no memory dependence (see Subsection 2.2.3).

### 2.2.3 Adiabatic Approximation

In TDDFT, *adiabatic approximation* has been extensively and successfully used, which establishes TDDFT as a useful theory for calculations of atoms, molecules and solids. As stated before, the xc functional depends on the whole density evolution as well as the initial states. The simplest treatment is to regard the instantaneous density as a ground state density and to plug it into a ground state functional neglecting the memory dependence,

\[
v_{\text{XC}}^{\text{adia}}[\Psi_0, \Phi_0, n](t) = v_{\text{XC}}^{\text{gs}}[n(t)],
\] (2.43)

which is called the *adiabatic* approximation. For instance, one typical approximation for \( v_{\text{XC}}(r, t) \) is *adiabatic local density approximation* (ALDA),

\[
v_{\text{XC}}^{\text{ALDA}}(r, t) = \left. \frac{d}{dn} [n \, e_{\text{XC}}(n)] \right|_{n=n(r,t)}.
\] (2.44)

Errors of adiabatic approximation come from the approximation of ignoring all memory dependence and from a certain approximated ground state functional, e.g. LDA.

When the ground state functional becomes an exact one, we call it *adiabatically-exact* (AE) approximation. For AE approximation, the density is treated as a ground state density
\[ n_0(r) = n(rt). \] For the initial state being the ground state, the exact xc potential shows memory at any time \( t \). The initial state is a functional of the ground state density which means that only density dependence is necessary. It is a nonlocal functional of the density at all previous times, i.e., \( v_{xc}^{ex}(rt) = v_{xc}^{ex}[n(r', t')] (rt) \) where \( t' \leq t \). The definition of the AE xc potential following standard DFT is

\[ v_{AE}^{xc}(r) = v_{AE}^{S}(r) - v_{H}(r) - v_{AE}^{ext}(r). \] (2.45)

The KS potential, \( v_{AE}^{S} \) is the local potential which gives \( n_0 \) while the interacting potential, \( v_{AE}^{ext} \), is the local potential which yields \( n_0 \) as the solution of the interacting Schrödinger equation. This allows to numerically define the AE xc potential for few-electron systems. No exact ground state functional has been formulated except for simple models[22, 52]. It is worth pointing out that the AE approximation can disentangle the errors due to adiabatic approximation from that due to the approximation used for the ground-state functional, which we explore this in Chapter 3 and Chapter 4.

2.2.4 Linear Response Theory in TDDFT

Consider a perturbation is switched on at \( t = 0 \) assuming the unperturbed system begins in its ground state. The change of the external potential is denoted as \( \delta v_{ext}(rt) \). The density responds to the perturbation,

\[ n(rt) = n_{\infty}(r) + n_1(rt) + n_2(rt) + \cdots, \] (2.46)

where the first order term \( n_1(rt) \) is of particular interest and the whole point of the linear response theory. The density response can be computed from the density-density response function \( \chi_{nn} \) (for simplicity we use \( \chi \) instead) as

\[ \delta n(rt) = n_1(rt) = \int_0^\infty dt' \int dr' \chi(rt, r't') \delta v_{ext}(r't'), \] (2.47)
where
\[ \chi(rt, r't') = \frac{\delta n(rt)}{\delta v_{\text{ext}}(r''t')} . \] (2.48)

Following time-dependent perturbation theory in the interaction picture yields[29]
\[ \chi(rt, r't') = -i\theta(t - t') \langle \Psi_0|\hat{n}_{H_0}(rt), \hat{n}_{H_0}(r't')|\Psi_0 \rangle , \] (2.49)

where \( H_0 \) is the unperturbed Hamiltonian, \( \hat{n}_{H_0} = \exp[iH_0t]\hat{n}(r)\exp[-iH_0t] \) and \( \theta(x) \) is the Heaviside function (or step function). Inserting the completeness relation, \( \sum_k |\Psi_k\rangle \langle \Psi_k| = 1 \) into \( \chi \) and Fourier transforming with respect \( t - t' \) leads to the "Lehmann representation":
\[ \chi(r, r', \omega) = \sum_k \left[ \frac{\langle \Psi_0|\hat{n}(r)|\Psi_k \rangle \langle \Psi_k|\hat{n}(r')|\Psi_0 \rangle}{\omega - (E_m - E_0) + i\eta^+} - \frac{\langle \Psi_0|\hat{n}(r')|\Psi_k \rangle \langle \Psi_k|\hat{n}(r)|\Psi_0 \rangle}{\omega + (E_m - E_0) + i\eta^+} \right] . \] (2.50)

This is typically hard to calculate since we don’t have the eigen-energies and eigenfunctions and we resort to TDDFT to see how it can be obtained via the KS system. Since KS system is formally exact in reproducing the time-dependent density of the system, we can calculate the density linear response as
\[ n_1(rt) = \int_0^\infty dt' \int dr' \chi_S(rt, r't') \delta v_S(r't') , \] (2.51)

where KS response function is
\[ \chi_S(rt, r't') = \frac{\delta n(rt)}{\delta v_S(r't')} . \] (2.52)

Analogously to Eq. (2.50), the Lehmann representation of the KS response function can be written as
\[ \chi_S(r, r', \omega) = \sum_{k,j} (f_k - f_j)^\omega \frac{\varphi^*_k(r)\varphi_j(r)\varphi^*_j(r')\varphi_k(r')}{\omega - (\epsilon_j - \epsilon_k) + i\eta^+} , \] (2.53)

where \( f_k \) is the Fermi occupation number in the ground state and \( \varphi_j \) are the KS eigen-orbitals that solve Eq. (2.17). If we define a xc kernel \( f_{\text{xc}} \) by the functional derivative of the xc potential
\[ f_{\text{xc}}[n_{gs}](rt, r't') = \left. \frac{\delta v_{\text{xc}}(rt)}{\delta n(r't')} \right|_{n=n_{gs}} . \] (2.54)
From the change in the KS potential, we have

$$\delta v_s(rt) = \delta v_{\text{ext}}(rt) + \delta v_H(rt) + \delta v_{\text{XC}}(r,t).$$  \hspace{1cm} (2.55)$$

where the potential change relates to the density change as

$$\delta v_H(rt) = \int d'r' n_1(r't) w(r,r'), \quad \delta v_{\text{XC}}(r,t) = \int_0^\infty dt' \int d'r' f_{\text{XC}}[n_{gs}](rt,r't') n_1(r't').$$  \hspace{1cm} (2.56)$$

Equating Eq. (2.50) and Eq. (2.53) with the substitution of Eq. (2.55), we arrive at a Dyson-like equation for $\chi$:

$$\chi(rt,r't') = \chi_S(rt,r't') + \int dt_1 dt_2 dr_1 dr_2 \chi_S(rt,r_1 t_1) f_{\text{HXC}}(r_1 t_1, r_2 t_2) \chi(r_2 t_2, r't').$$  \hspace{1cm} (2.57)$$

where the Hartree-exchange-correlation kernel is

$$f_{\text{HXC}}(r_1 t_1, r_2 t_2) = \delta(t_1 - t_2) w(r_1, r_2) + f_{\text{XC}}[n_{gs}](r_1 t_1, r_2 t_2).$$  \hspace{1cm} (2.58)$$

The Hartree potential behaves electrostatically and thus the Hartree kernel is proportional to a delta function in time and to the electron-electron interaction in space. The adiabatic xc kernel is instantaneous in the density, namely local in time. Consequently, $f_{\text{XC}}$ has no frequency dependence, i.e. $f_{\text{XC}}(\omega = 0)$.

2.2.5 Orbital Dependent Functional

One idea to incorporate some memory is to use orbital functionals, since the instantaneous KS orbital incorporates some KS memory. This class of xc functionals are “implicit” density functionals but “explicit” orbital functionals, which we write $v_{\text{XC}}$ in short as $v_{\text{XC}}[\{\varphi_j\}]$. In self-consistently solving the KS equation, we are able to see the meaning of “implicit” in a moment. The KS orbitals $\varphi_j$ are obtained via the KS equation, where the $v_{\text{XC}}$ depends on the density. Thus, $\varphi_j$’s are dependent of the density $n(t)$, such that we may write
$\varphi_j[n(t)]$. In this sense $v_{xc}$ constructed with KS orbitals is an implicit density functional. The method to construct these functionals in TDDFT is via “time-dependent optimized effective potential” (TDOEP) [79, 80] for a xc energy or action. The most well-know orbital functional is the exact-exchange functional, where the energy is taken from the Fock expression, but using KS orbitals. The TDOEP method gives the corresponding exact “exact exchange” potential in TDDFT. The correct asymptotic behavior is easily achieved with in TDOEP, which are important in many applications. In the linear response regime, TDOEP within the Slater approximation leads to the PGG kernel [59], which gives good optical spectra of atoms. The hybrid functionals also include some KS memory within generalized KS theory.
Chapter 3

Kinetic and Interaction Components of XC Potential

TDDFT is today increasingly stepping into the fascinating playground of time-resolved dynamics in the presence of external fields, and has already proven to have made useful predictions for a number of phenomena, e.g. coherent phonon generation[73], photovoltaic design[21, 60], dynamics of molecules in strong laser fields[5], including coupling to ions[8], and attosecond control[11]. Despite significant success in obtaining excitation spectra and response of molecules and solids, the reliability of TDDFT[10, 56, 70] for dynamics beyond the perturbative regime remains somewhat cloudy. Little is known about the performance of adiabatic functionals for non-perturbative dynamics, even for cases where the adiabatic approximation is known to perform satisfactorily within the linear response regime. Beyond the linear response realm one must consider the full time-dependent xc potential, not just perturbations of it around the ground-state. To this end, there has recently been considerable effort in finding exact xc potentials for non-equilibrium dynamics [18, 25, 65, 69, 78], with the hope that analysis and understanding of their main features would lead to understanding errors in the commonly used approximations, and eventually to the development of improved functional approximations. In
this chapter, we will study some exactly-solvable systems and analyze the exact xc potential for this reason. The present chapter focuses on a decomposition of the exact xc potential into kinetic and interaction components, in particular the analysis of step-like features that appear in them, the effectiveness of the adiabatic approx, and exploring the relation of these features to natural orbital occupation numbers. This work was published in Ref.[53].

About 25 years ago in ground-state density-functional theory, decompositions of the exact ground-state xc potential into kinetic and potential (hole) and response components began to be considered [9, 32, 33, 35], for the purpose of analysis of the xc potential in cases where it could be calculated exactly, or highly accurately. It was found that the potential component due to the Coulomb potential of the xc hole tends to be important in atoms and molecules in most regions, while the kinetic and response components play more of a role in intershell and bonding regions especially for “stretched” molecules, displaying step and peak features.

We perform a similar decomposition for the time-dependent xc potential, particularly with a view to appraise the performance of the adiabatic approximation. We ask, can a decomposition into kinetic and potential contributions in the time-domain provide us with insight and understanding of the time-dependent xc potential? Recent work [18, 25, 38, 65] has shown the prevalence of dynamical step features in the correlation potential in non-linear dynamics that require non-local dependence on the density in both space and time; these features appear far more generically than in the ground-state case, and are not associated with fractional charge prevention, ionization, or electric fields, as has been the case with steps found previously in time-dependent xc potentials. The physics of the time-
dependent screening that the step feature, and accompanying peak, represent, have yet
to be understood, and motivates the present study. Which terms in the decomposition of
\( v_{XC}(t) \) are largely responsible for their appearance? Although it has been shown that an
adiabatic approximation completely misses the dynamical step feature – even in an AE
approximation where an exact ground-state potential is used adiabatically (Section 2.2.3)
– are adiabatic approximations to any of the individual components in the time-dependent
decomposition adequate? In the ground-state, the step structure is a signature of static
correlation, and we ask whether this is true also for the dynamical step. That is, is the
dynamical step an indication that the system is evolving “significantly away” from a single-
Slater determinant (SSD)? To this end, we investigate the dynamics of the time-dependent
natural orbital occupation numbers of the interacting spin-summed density-matrix. More
generally, we will use the decomposition to try to gain a better understanding of time-
dependent correlation, steps or no steps. For example, when the system is in an excited
state, there is large non-adiabatic correlation: is the kinetic or potential component largely
responsible for this? How do the kinetic and potential components look in cases where the
density of the \( N \)-electron system is a sum of \( N \) spatially-separated but time-evolving one-
electron densities?

Before diving into the study, we will discuss the background including the computational
details, Rabi dynamics, generic step structures and the theory of natural orbital and nat-
ural occupation number.
3.1 Background

3.1.1 Computational Details

The main program for real-time TDDFT calculations is octopus [1, 12], a pseudopotential real-space package aimed at the simulation of the electron-ion dynamics of one-, two-, and three-dimensional finite systems subject to time-dependent electromagnetic fields.

In Chapter 3, the components of the \( v_c \), depend on \( \rho(r, r', t) \) and \( n_{xc}(r, r', t) \), which are calculated using Mathematica by feeding in the exact wavefunctions. In order to compute the exact wavefunction, the time-dependent Schrödinger equation is solved by first mapping the Hamiltonian of two interacting electrons in 1D onto the Hamiltonian of one electron in 2D. The AE counterparts are found with the iterative scheme mentioned early (see Subsection 2.2.3) by plugging in interacting wavefunction of density \( \Psi_{gs}[n(t)] \), and KS orbitals \( \varphi(r) = \sqrt{\frac{n(r_t)}{2}} \). The AE quantities \( \rho^{AE}, \rho^{AE}_S, n^{AE}_{xc} \) are formed accordingly.

In Chapter 4, the calculations are performed with a grid of size 40.00 and grid spacing of 0.1. The approximated enforced time-reversal symmetry method was used in the propagation, with a time-step of 0.001. The results still hold when we decrease the grid spacing and increase the size of the simulation box. The densities and current densities are then extracted and a standard finite-difference scheme is used get the time derivative of the velocity in Eq. (3.10) and Eq. (3.12).

In Chapter 5, the “kick” spectrum is obtained from a total time \( T = 1000 \) propagation in the local one-electron soft-helium model. The energy resolution depends on the total time of the propagation, \( \Delta E = 2\pi/T \).

In Chapter 6, the total time of propagation for the modelling of the charge transfer dynam-
ics is $T = 5000$, where the grid size is 100.00 and the spacing is 0.1. The time propagation uses a time step 0.005. It allows us to discern the energy $\Delta E = 2\pi/5000 = 0.00126$.

### 3.1.2 Rabi Dynamics

For a two-level quantum system driven by an oscillatory field, the populations of both states have a cyclic feature, known as Rabi dynamics[61].

Consider two eigenstates of $\hat{H}_0$, $|\psi_a\rangle$ and $|\psi_b\rangle$ with eigenvalues $E_a = \omega_a$ and $E_b = \omega_b$. The general wave function for this system within two-level approximation may be written as

$$|\Psi(t)\rangle = c_a(t) |\psi_a\rangle + c_b(t) |\psi_b\rangle .$$

(3.1)

Normalization condition, $\langle \Psi(t)|\Psi(t)\rangle = 1$, requires that $|a(t)|^2 + |b(t)|^2 = 1$, since $\langle \psi_a|\psi_b\rangle = 0$. If the system is coupled to a weak electric field, $\alpha \varepsilon(t)$, where $\alpha$ is a unit vector, then the full Hamiltonian in the dipole approximation is $\hat{H} = \hat{H}_0 - \alpha \cdot r \varepsilon(t)$, written as a matrix of

$$
\begin{pmatrix}
\langle \psi_a|H|\psi_a\rangle & \langle \psi_a|H|\psi_b\rangle \\
\langle \psi_b|H|\psi_a\rangle & \langle \psi_b|H|\psi_b\rangle
\end{pmatrix} =
\begin{pmatrix}
E_a - d_{aa}\varepsilon(t) & -d_{ab}\varepsilon(t) \\
-d_{ba}\varepsilon(t) & E_b - d_{bb}\varepsilon(t)
\end{pmatrix} .
$$

(3.2)

Therefore, Eq. (1.1) can be recast as

$$i\partial_t
\begin{pmatrix}
c_a(t) \\
c_b(t)
\end{pmatrix} =
\begin{pmatrix}
E_a - d_{aa}\varepsilon(t) & -d_{ab}\varepsilon(t) \\
-d_{ba}\varepsilon(t) & E_b - d_{bb}\varepsilon(t)
\end{pmatrix}
\begin{pmatrix}
c_a(t) \\
c_b(t)
\end{pmatrix} ,
$$

(3.3)

where $d_{ij} = \langle \psi_i|\alpha \cdot r|\psi_j\rangle$ is the transition dipole moment. If the field is expressed as $\varepsilon(t) = \varepsilon \cos(\omega t)$ and $d_{aa} = d_{bb} = 0$, this is setting for the standard Rabi dynamics[75]. This can be generalized to the case where the initial or final state dipole is not zero, which has been discussed in Ref.[7]. In other words, $d_{aa} \neq 0$ or $d_{bb} \neq 0$, which is the case of charge-transfer dynamics. If we redefine our coefficients $c_a(t) = a(t)e^{-i\omega_a t}$ and $c_b(t) = b(t)e^{-i\omega_b t}$, Eq. (3.3)
Figure 3.1: This plots shows the population of the state $b$ for different $\Delta$. When $\Delta = 0$, the full population inversion can be achieved. The case where $\Delta \neq 0$ (we choose $\Delta = 0.8\Omega_R$) is called detuned Rabi.

can be simplified as

$$
\dot{a}(t) = \frac{id}{2} \left[ e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t} \right] b(t) \tag{3.4a}
$$

$$
\dot{b}(t) = \frac{id}{2} \left[ e^{-i(\omega-\omega_0)t} + e^{i(\omega+\omega_0)t} \right] a(t) \tag{3.4b}
$$

where we take $d_{ab} = d_{ba} \equiv d$ and $\omega_0 = \omega_b - \omega_a$. For $\omega$ is close to $\omega_0$, then $\Delta = \omega - \omega_0$ varies slowly compared to $\omega + \omega_0$.

The fast oscillation of $\omega+\omega_0$ compared to that of $|\omega-\omega_0|$ is averaged out to zero. Ignoring the fast part and maintaining the slow oscillation is called rotating wave approximation (RWA).

Further calculations lead to an analytical solution to the coefficients, $a(t)$ and $b(t)$, as follows:

$$
a(t) = -\frac{1}{d\epsilon} e^{\frac{1}{2}i\Delta t} \left[ (\Delta - \Omega_R)A e^{\frac{1}{2}i\Omega_R t} + (\Delta + \Omega_R)B e^{-\frac{1}{2}i\Omega_R t} \right] \tag{3.5a}
$$

$$
b(t) = e^{-\frac{1}{2}i\Delta t} \left[ A e^{\frac{1}{2}i\Omega_R t} + B e^{-\frac{1}{2}i\Omega_R t} \right], \tag{3.5b}
$$
in which $A$ and $B$ are determined from the initial conditions. In Eq. (3.5), Rabi frequency and Rabi period are defined as

$$\Omega_R = \sqrt{\Delta^2 + (de)^2} \quad \text{and} \quad T_R = 2\pi/\Omega_R. \quad (3.6)$$

From Eq. (3.5), we can invert it and write the unknown $A, B$ in terms of, say, initial conditions $a(0), b(0)$.

$$A = \frac{1}{2} b(0) + \frac{\Delta}{2\Omega_R} b(0) + \frac{de}{2\Omega_R} a(0) \quad (3.7a)$$

$$B = \frac{1}{2} b(0) - \frac{\Delta}{2\Omega_R} b(0) - \frac{de}{2\Omega_R} a(0) \quad (3.7b)$$

If the initial state is $\psi_a$, in other words, $|c_a(0)|^2 = |a(0)|^2 = 1$, $|c_b(0)|^2 = |b(0)|^2 = 0$, then $A = -B = de/2\Omega_R$. The solution for this initial condition is

$$a(t) = e^{+i\Delta t} \left( \cos \frac{1}{2} \Omega_R t - i \frac{\Delta}{\Omega_R} \sin \frac{1}{2} \Omega_R t \right) \quad (3.8a)$$

$$b(t) = e^{-i\Delta t} \frac{de}{\Omega_R} i \sin \frac{1}{2} \Omega_R t \quad (3.8b)$$

The populations in Figure 3.1 are $P_a(t) = |c_a(t)|^2 = (\Delta/\Omega_R)^2 + (de/\Omega_R)^2 \cos^2(\Omega_R t/2)$ and $P_b(t) = |c_b(t)|^2 = (de/\Omega_R)^2 \sin^2(\Omega_R t/2)$. When $\Delta \neq 0$, only partial population can be pumped to the other state, named as detuned Rabi dynamics. For the resonant Rabi, i.e. $\Delta = 0$, at $t = T_R/4$, the state is a 50:50 mixture of two states, and at $t = T_R/2$, the state has been pumped from $\psi_a$ to $\psi_b$.

The dipole dynamics can be sufficiently accurate while the dynamics of the density is erroneous which has been discussed in Ref. [68]. One has to be cautious of the applicability of few-level approximations within TDDFT in dynamics. We don’t impose few-level system in our dynamics but instead use Rabi as a guide.
3.1.3 Generic Step Structures

In Ref. [18] it was argued that, in the two-electron case, the step structures appear at peaks of the acceleration, with magnitude given by the spatial integral of the acceleration: in the expression for the KS potential, there is a term \( \int x \partial_t (j(x', t)/n(x', t)) \, dx' \) which is responsible for the dynamical step. In general, the exact KS potential is usually hard to find. In a two-electron spin singlet state, this becomes feasible. The KS wavefunction thus becomes \( \Phi(r, r', t) = \varphi(rt) \varphi(r't) \), which gives the density \( n(rt) = 2|\varphi(rt)|^2 \). The KS orbitals can written as

\[
\varphi(rt) = \sqrt{\frac{n(rt)}{2}} e^{i\alpha(rt)}
\]

With Eq. (2.17), the KS potential can be inverted

\[
v_S(rt) = \frac{\nabla^2 n(rt)}{4n(rt)} - \frac{[\nabla n(rt)]^2}{8n^2(rt)} - \frac{1}{2} |\nabla \alpha(rt)|^2 - \frac{\partial \alpha(rt)}{\partial t},
\]

where

\[
\nabla \cdot [n(rt)\nabla \alpha(rt)] + \frac{\partial n(rt)}{\partial t} = 0.
\]

In 1D, \( \alpha(xt) \) can be obtained

\[
\alpha(xt) = \int_{-\infty}^{x} dx' u(x'), \quad u(x) = \frac{j(x)}{n(x)},
\]

in which \( u(x) \) can be regarded as the “local” velocity field. For the cases where the interacting state reaches an eigenstate, then the exact KS potential can be inverted directly from the corresponding density (unless there is a node in the density, typically for few electrons, then some care is needed).

The soft-Coulomb model is commonly used in analyzing functionals, since it is numerically straightforward to find the exact time-evolving wavefunction, and then extract the exact
exchange and correlation potentials for comparison with approximations[2, 24, 46, 50, 76–78, 82, 83]. The system in this section is a one-dimensional(1D) model of the He atom; the Hamiltonian can be written as

\[
\hat{H} = \hat{H}_0 + \hat{H}_1(t) = \hat{T} + \hat{V}(t) + \hat{W},
\]

(3.13)

where \(\hat{T} = \sum_i -\frac{1}{2} \frac{\partial^2}{\partial x_i^2}\) is the kinetic energy, \(\hat{V}(t) = \sum_i [-2/\sqrt{x_i^2 + 1} - x_i \mathcal{E}(t)]\) is the external potential, and \(\hat{W} = 1/\sqrt{(x_1 - x_2)^2 + 1}\) is the soft-Coulomb electron-electron interaction[41]. The sums go over two fermions. The field \(\mathcal{E}(t)\) here is weak but resonant with \(E_e - E_g\), the energy difference between the ground state and 1st excited state. We consider a superpo-

![Graphs showing correlation potentials at different times](image)

Figure 3.2: The exact correlation potential(solid black line) at times indicated for the two state example(Eq. (3.14)). The local acceleration(dotted red line) and \(-\int x \partial_t u(x',t) \, dx' - v_{\text{ext}}\) (dashed purple line) are shown. The adiabatically exact correlation potential is plotted(dash-dotted blue line). This figure is taken from Elliott et al. [18] with permission.

transition state of ground and first excited state of soft-coulomb helium atom. We express the

33
\[
\Psi(x, x', t) = \frac{1}{\sqrt{2}} \left[ e^{-iE_g t} \Psi_g(x, x') + e^{-iE_e t} \Psi_e(x, x') \right].
\] (3.14)

As shown in Figure 3.2, the exact KS potentials at different times are shown. Specifically, we are able to show the correlation part in the 2-electron system by noticing that 
\[v_x(x) = -v_H(x)/2 \quad \text{and} \quad v_C(x) = v_g(x) - v_{nx}(x).\] The step, not captured by the adiabatic approximations, requires a spatially nonlocal density dependence in the correlation functional.

### 3.1.4 Natural Orbital Occupation Numbers

Another aspect of the dynamics we will investigate is the relation between the dynamical step structures and the time-dependent natural orbital occupation numbers (NOONs). By diagonalizing the one-body time-dependent density-matrix of the interacting system, \(\rho_1(r, r', t)\) introduce in Eq. (2.30), we will investigate the connection between the time-dependent NOONs and the dynamical step. In each example, we will diagonalize the interacting \(\rho_1\):

\[
\int \rho_1(r, r', t) \varphi_j^*(r', t) \, dr' = \eta_j(t) \varphi_j(r, t).
\] (3.15)

The eigenfunctions \(\varphi_j\)'s are called natural orbitals (NOs) and the eigenvalues \(\eta_j\)'s are the NOONs. For an SSD, the occupation numbers are 2, 0, 0, ..., which means essentially one orbital is sufficient. It is straightforward to show that in the general \(N\)-electron case,

\[
\partial_t \left( \frac{j(x, t)}{n(x, t)} \right) = \sum_k \eta_k(t) \left( \frac{\partial_{j_k} j(x, t)}{n(x, t)} - \frac{j(x, t)}{n^2(x, t)} \partial_t n_k(x, t) \right) + \sum_k \dot{\eta}_k(t) \left( \frac{j_k(x, t)}{n(x, t)} - \frac{j(x, t)}{n^2(x, t)} n_k(x, t) \right)
\] (3.16)

where

\[
n_k(x, t) = |\varphi_k(x, t)|^2, \quad (3.17)
\]
and

\[ j_k(x,t) = \frac{1}{2i} [\varphi_k^*(x,t) \nabla \varphi_k(x,t) - \varphi_k(x,t) \nabla \varphi_k^*(x,t)]. \]

(3.18)

The spatial integral of the right-hand-side of Eq. (3.16) gives the dynamical step structure expressed in terms of time-dependent natural orbitals and NOONs. The relation is far from trivial, and suggests that the relation between the dynamical step and the time-dependent NOONs is not as straightforward as that between the ground-state step structures and the ground-state NOONs (see shortly in Section 3.3). We will plot the NOONs \( \eta_k(t) \) for the different dynamics and see if any trends can be identified.
3.2 Derivation of the Decomposition

In this section, we will decompose the exact xc potential into two parts, called kinetic potential and interaction potential respectively. Making use of the fact that the density of the KS system has to be the same as the interacting system and that the time derivative of the current density is related to the gradient of the external potential, we can derive the decomposition.

3.2.1 Continuity Equation

As seen in the proof of Runge-Gross theorem, we have made use of the equation of motion for the density, i.e. the continuity equation. Now we give a detailed derivation. First, following Eq. (2.25) we see time derivative of the density is

\[ i \frac{\partial}{\partial t} n(r_t) = \langle \Psi(r_1...r_N; t) | \hat{n}(r), \hat{H} | \Psi(r_1...r_N; t) \rangle \]  

(3.19)

where the commutator

\[ [\hat{n}(r), \hat{H}] = \left[ \sum_{k=1}^{N} \delta(r - r_k), -\frac{1}{2} \sum_{i=1}^{N} \hat{\nabla}_i^2 + \frac{1}{2} \sum_{i \neq j} w(r_i, r_j) + \sum_{i=1}^{N} v_{\text{ext}}(r_i; t) \right], \]  

(3.20)

should be evaluated. It can be seen easily that the last two terms commutes with delta-function operator. What’s left is only the kinetic operator, pretty simple:

\[ \left[ \sum_{k=1}^{N} \delta(r - r_k), -\frac{1}{2} \sum_{i=1}^{N} \hat{\nabla}_i^2 \right] = -\frac{1}{2} \sum_{k,i} \hat{\nabla}_i \cdot \left[ \delta(r - r_k), \hat{\nabla}_i \right] + \left[ \delta(r - r_k), \hat{\nabla}_i \right] \cdot \hat{\nabla}_i. \]  

(3.21)

What should be evaluated is \[ \left[ \delta(r - r_k), \hat{\nabla}_i \right] \].

\[ \left[ \delta(r - r_k), \hat{\nabla}_i \right] = -\delta_{ki} \nabla_k \delta(r - r_k) = \delta_{ki} \nabla \delta(r - r_k). \]  

(3.22)
Notice: the hat on $\nabla$ is removed to denote it only operates on the function right next to it while $\hat{\nabla}$ denotes the operator product when it operates on its neighbor. Hence,

$$\left[ \hat{n}(r), \hat{H} \right] = \left[ \sum_{k=1}^{\infty} \delta(r - r_k), -\frac{1}{2} \sum_{i=1}^{\infty} \hat{\nabla}_i^2 \right] = -\frac{1}{2} \sum_k \hat{\nabla}_k \cdot \nabla \delta(r - r_k) + \nabla \delta(r - r_k) \cdot \hat{\nabla}_k \quad (3.23)$$

On the other hand,

$$i \frac{\partial}{\partial t} n(rt) = -\frac{1}{2} \langle \Psi \left| \sum_k \hat{\nabla}_k \cdot \nabla \delta(r - r_k) + \nabla \delta(r - r_k) \cdot \hat{\nabla}_k \right| \Psi \rangle = -i \nabla \cdot j(rt) \quad (3.24)$$

where $\nabla$ is taken out, being not influencing the integral and the commutativity of dot product is used. We arrive at the continuity equation,

$$\frac{\partial n}{\partial t} + \nabla \cdot j = 0 \quad (3.25)$$

3.2.2 Equation of Motion of the Current

Next, we further decompose the terms to help clarify the derivation to see how the current changes in time. First, we denote the current as $j(r) = \sum_k j_k(r)$, where $j_k(r) = 1/(2i) \hat{\nabla}_k \delta(r - r_k) + \delta(r - r_k) \hat{\nabla}_k$, so that we have

$$\left[ j(r), \hat{H} \right] = \sum_k \left[ j_k(r), \hat{H} \right] \quad (3.26)$$

Then, we are further decomposing the terms to have detailed derivation.

$$\sum_k \left[ j_k(r), \hat{H} \right] = -\frac{1}{2} \sum_{i,k} \left[ j_k(r), \hat{\nabla}_i^2 \right] + \frac{1}{2} \sum_k \sum_{i \neq j} \left[ j_k(r), w(r_i, r_j) \right] + \sum_{i,k} \left[ j_k(r), v_{ext}(r_i, t) \right] \quad (3.27)$$
The simplest one, actually, is the last term. Let’s evaluate \( \hat{j}_k(r) \) first. Plugging in the expression \( \hat{j}_k(r) \) yields

\[
\sum_{i,k} \left[ \hat{j}_k(r), v_{\text{ext}}(r_i, t) \right] = \frac{1}{2i} \sum_{i,k} \left[ \hat{\nabla}_k \delta(r - r_k) + \delta(r - r_k) \hat{\nabla}_k, v_{\text{ext}}(r_i, t) \right] \\
= \frac{1}{i} \sum_{i,k} \delta(r - r_k) \delta_{ik} \nabla v_{\text{ext}}(r, t) \\
= -i \sum_k \delta(r - r_k) \nabla v_{\text{ext}}(r, t) \\
= -i \hat{n}(r) \nabla v_{\text{ext}}(r, t)
\]

which gives the 3rd term as

\[
\langle \Psi | \sum_{i,k} \left[ \hat{j}_k(r), v_{\text{ext}}(r_i, t) \right] | \Psi \rangle = -i \ n(r, t) \nabla v_{\text{ext}}(r, t) .
\] (3.28)

The next complicated one would be the second term.

\[
\frac{1}{2} \sum_k \sum_{i \neq j} \left[ \hat{j}_k(r), w(r_i, r_j) \right] \\
= \frac{1}{2i} \sum_k \sum_{i \neq j} \left[ \hat{\nabla}_k \delta(r - r_k) + \delta(r - r_k) \hat{\nabla}_k, w(r_i, r_j) \right] \\
= \frac{1}{2i} \sum_k \sum_{i \neq j} \delta(r - r_k) \left[ \hat{\nabla}_k, w(r_i, r_j) \right] \\
= \frac{1}{2i} \sum_k \sum_{i \neq j} \delta(r - r_k) \left[ \delta_{ik} \nabla w(r_k, r_j) + \delta_{jk} \nabla w(r_i, r_k) \right] \\
= \frac{1}{2i} \sum_{k \neq j} \delta(r - r_k) \left[ \nabla w(r, r_j) + \nabla w(r_j, r) \right] \\
= \frac{1}{i} \sum_{k \neq j} \delta(r - r_k) \nabla w(r, r_j)
\]

where in the 2nd last step the dummy index \( i \) is switched to \( j \) and pair interaction term \( w(r, r') \) is invariant with respect to the exchange of \( r \) and \( r' \). Furthermore, we can introduce \( \delta(r' - \hat{r}_j) \) above so that we can have the pair density operator \( \hat{P}(r', r, t) = \sum_{k \neq j} \delta(r - r_k)\delta(r' - \hat{r}_j) \).
\[ \frac{1}{i} \sum_{k \neq j} \delta(r - r_k) \nabla w(r, r_j) = \frac{1}{i} \int dr' \sum_{k \neq j} \delta(r - r_k) \delta(r' - r_j) \nabla w(r, r'). \tag{3.29} \]

Now, take the expectation value of the operator

\[ \langle \Psi | \frac{1}{2} \sum_k \sum_{i \neq j} \left[ j_k(r), w(r_i, r_j) \right] | \Psi \rangle = \frac{1}{i} \int dr' \nabla w(r, r') P(r', r, t) \tag{3.30} \]

in which the pair density is defined in Eq. (2.29). Eventually, the complicated part is the 1st term:

\[ -\frac{1}{2} \sum_{i,k} \left[ j_k(r), \nabla_i^2 \right] = -\frac{1}{4i} \sum_{i,k} \left[ \nabla_k \delta(r - r_k) + \delta(r - r_k) \nabla_k, \nabla_i^2 \right]. \tag{3.31} \]

Again, it can be seen easily that only \( i = k \) terms can survive,

\[ \left[ \nabla_k \delta(r - r_k) + \delta(r - r_k) \nabla_k, \nabla_i^2 \right] \]

\[ = \nabla_k \delta(r - r_k) \nabla_k^2 - \nabla_k^3 \delta(r - r_k) - \nabla_k^2 \delta(r - r_k) \nabla_k. \]

Inserting \((-i)^2\) in the first term due to the hermicity of momentum operator \(-i \nabla_i\), yields

\[ -\frac{N}{4i} \int dr_1 \ldots dr_N \Psi^*(r_1 \ldots r_N; t) \left[ -i \nabla_1 \right] \delta(r - r_1) \nabla_i^2 \Psi(r_1 \ldots r_N; t) \]

\[ = -\frac{N}{4i} \int dr_1 \ldots dr_N i [-i \nabla_1 \Psi(r_1 \ldots r_N; t)]^* \delta(r - r_1) \nabla_i^2 \Psi(r_1 \ldots r_N; t) \]

\[ = -\frac{N}{4i} \int dr_1 \ldots dr_N i [i \nabla_1 \Psi^*(r_1 \ldots r_N; t)] \delta(r - r_1) \nabla_i^2 \Psi(r_1 \ldots r_N; t) \]

\[ = \frac{N}{4i} \int dr_1 \ldots dr_N \nabla_i \Psi^*(r_1 \ldots r_N; t) \delta(r - r_1) \nabla_i^2 \Psi(r_1 \ldots r_N; t) \]

\[ = \frac{N}{4i} \int dr_1 \ldots dr_N \nabla \Psi^*(r_1 \ldots r_N; t) \nabla^2 \Psi(r_1 \ldots r_N; t) \]

Similar for the other terms, the sum of 4 terms is

\[ \frac{N}{4i} \int dr_1 \ldots dr_N \left[ -\Psi \nabla^3 \Psi^* - \Psi^* \nabla^3 \Psi + \nabla \Psi \nabla^2 \Psi^* + \nabla \Psi^* \nabla^2 \Psi \right], \tag{3.32} \]

where the arguments are compressed to avoid clutter. Notice that 1-body reduced density matrix is defined in Eq. (2.30). The different orders of gradient are

\[ \nabla^{(k)} \rho_1(r, r', t) = N \int dr_2 \ldots dr_N \nabla^{(k)} \Psi^*(r, r_2 \ldots r_N) \Psi(r', r_2 \ldots r_N), \tag{3.33} \]
which are also similar for $\nabla^{(k)}_{r'}$. If associate $r$ with $\nabla$ and $r'$ with $\nabla'$, we get

$$\frac{1}{4i} N \int dr_2 \ldots dr_N \left[ -\Psi \nabla^3 \Psi^* - \Psi^* \nabla^3 \Psi + \nabla \Psi \nabla^2 \Psi^* + \nabla \Psi^* \nabla^2 \Psi \right]$$

$$= \frac{1}{4i} \left( \nabla^3 - \nabla'^3 + \nabla^2 \nabla'^2 + \nabla' \nabla^2 \right) \rho_l(r, r', t) \bigg|_{r'=r}$$

$$= \frac{1}{4i} \left( \nabla - \nabla' \right) (\nabla'^2 - \nabla^2) \rho_l(r, r', t) \bigg|_{r'=r}$$

(3.34)

Putting all the terms together (Eq. (3.28), Eq. (3.30), Eq. (3.34)), we have

$$\frac{\partial j(rt)}{\partial t} = -n(rt) \nabla v(rt) - \int dr' \nabla w(r, r') P(r, r', t) - \frac{1}{4i} (\nabla - \nabla') (\nabla'^2 - \nabla^2) \rho_l(r', r, t) \bigg|_{r'=r} \ (3.35)$$

which is the central result for this part. A similar derivation has been called the differential virial theorem (DVT)[71].

### 3.2.3 Decomposition of the Exact $v_{xc}$

With the equation of motion for the density Eq. (2.26) and the current density Eq. (2.27) of the interacting and the KS systems, then we arrive at the equation Eq. (2.32), where the term $q'(rt)$ is calculated for the KS system. The pair density can be written as

$$P(r, r', t) = n(rt) \left( n(r't) + n_{xc}(r, r', t) \right), \quad (3.36)$$

which defines $n_{xc}$, the xc hole density, satisfying the sum rule, $\int dr' n_{xc}(r, r', t) = -1$.

Notice that for KS system a trivial term, $w(r, r') = 0$, leads to a vanishing integration against the KS pair density Eq. (2.28). Writing the Eq. (2.33) explicitly with substitution of Eq. (2.28), we have

$$\nabla \cdot [n(rt) \nabla (v_s(rt) - v_{ext}(rt))] = \nabla \cdot \left\{ \int dr' \nabla w(r, r') P(r', r, t) + \mathbb{D}_{r,r'} \rho_c(r', r', t) \bigg|_{r'=r} \right\} \quad (3.37)$$

where we have seen the defined operator $\mathbb{D}_{r,r'} = \frac{1}{4i} (\nabla - \nabla') (\nabla'^2 - \nabla^2)$ and $\rho_c(r, r', t) = \rho(r, r', t) - \rho_s(r, r', t)$. Putting in Eq. (3.36), we notice that the first term (under the $\nabla$) on
right hand side can be recognized

\[ n(rt) \int dr' \nabla w(r, r') (n(r't) + n_{xc}(r, r', t)) = n(rt)\nabla v_h(rt) + n(rt) \int dr' \nabla w(r, r') n_{xc}(r, r', t). \]

(3.38)

Therefore, taking away both Hartree terms from each side yields

\[ n(rt)\nabla v_{xc}(rt) = n(rt) \int dr' \nabla w(r, r') n_{xc}(r', r, t) + \nabla \times \widetilde{C}(r, t) \]

(3.39)

where the last term is a gradient free vector. For 3D, this term can be determined through the Sturm-Liouville type equation given a boundary condition. Note that in 1D, we have thrown away a term of the form \( g(t)/n(x, t) \), where \( g(t) \) is the integration constant of the outer \( \nabla \). We do so because \( g(t) \) is actually zero, due to satisfaction of boundary conditions: at the boundary of a finite system, the density decays exponentially, so to avoid the field \( \nabla v_{xc} \) diverging exponentially, the integration constant \( g(t) \) must be taken to be zero. We invert it to derive the exact xc potential. Eq. (3.39) can be easily solved for the xc field, defined as the gradient of the xc potential:

\[ \frac{d}{dx} v_{xc}(xt) = \frac{1}{n(x, t)} \left[ \left. \nabla \rho_C(x, x', t) \right|_{x' = x} + \int dx' n_{xc}(x, x', t) \frac{\partial}{\partial x} w(x, x') \right]. \]

(3.40)

We now write \( v_{xc}(xt) = v_{C}^{T}(xt) + v_{xc}^{W}(x, t) \) and define the kinetic contribution \( v_{C}^{T} \) from the first term on the right of Eq. (3.40):

\[ v_{C}^{T}(x, t) \equiv \int dy \frac{1}{4n(y, t)} \left( \frac{d}{dx'} - \frac{d}{dy} \right) \left( \frac{d^2}{dy^2} - \frac{d^2}{dx'^2} \right) \left( \rho(x', y, t) - \rho_s(x', y, t) \right) \bigg|_{x' = y}, \]

(3.41)

since it arises from differences in kinetic/momentum aspects of the KS and interacting systems. Further, we denote it as a correlation contribution (hence the c subscript), since correlation generally refers to the deviation from single-Slater determinant behavior. The second term in Eq. (3.40) gives a potential-like contribution arising directly from the electron-
interaction $W$, which we denote $v_{\text{xc}}^W(x, t)$. We further decompose $v_{\text{xc}}^W$ as:

$$v_{\text{xc}}^W(x, t) = v_{\text{xc}}^\text{hole}(x, t) + \Delta v_{\text{xc}}^W(x, t),$$  \hspace{1cm} (3.42)

where $v_{\text{xc}}^\text{hole}$ is the Coulomb potential of the xc hole,

$$v_{\text{xc}}^\text{hole}(x, t) = \int \! dx' n_{\text{xc}}(x', x, t) w(x, x'),$$  \hspace{1cm} (3.43)

while the remaining term, $\Delta v_{\text{xc}}^W$, is

$$\Delta v_{\text{xc}}^W(x, t) = - \int_0^x \! dy \int \! dx' w(y, x') \nabla n_{\text{xc}}(y, x', t).$$  \hspace{1cm} (3.44)

Before proceeding, we consider a simple example. Consider a system of non-interacting electrons evolving from an initial state $\Psi_0$ in some potential $v(x, t)$. We may then ask whether we can find a potential in which the same non-interacting electrons evolve in with exactly the same density but beginning in a different initial state $\Phi_0$ \cite{19, 20}. Assuming such a potential may be found, we see that the potential that the second system evolves in is given by $v(x, t) + v_{\text{xc}}^T(x, t)$. That is the kinetic part of the potential contains the entire difference. From this simple argument, we might expect that $v_{\text{xc}}^T$ in the general interacting case contains a large part of the initial-state dependent effects. In fact, in our examples that do not start from the ground-state, we shall see $v_{\text{xc}}^T$ is indeed the predominant term in the initial correlation potential.
3.3 A Ground State Case Study

A similar decomposition in the ground-state has led to insights for ground-state potentials in various cases [9, 32, 33, 35]. There, the exact ground-state xc potential is decomposed into a kinetic contribution $v_{\text{kin}}^C$, the Coulomb potential due to the xc hole $v_{\text{hole}}^\text{XC}$, and two response terms that depend on the functional derivatives of these two potentials with respect to the density, denoted together as $v_{\text{resp}}^\text{XC}$:

$$v_{\text{XC}}^\text{T}(r) = v_{\text{kin}}^C(r) + v_{\text{hole}}^\text{XC}(r) + v_{\text{resp}}^\text{XC}(r).$$

In atoms and molecules at equilibrium, it is expected that $v_{\text{hole}}^\text{XC}$ is the important contribution to $v_{\text{XC}}^\text{T}$ in most regions [9, 32, 33, 35]. The kinetic potential tends to give peaks in intershell regions in atoms and bonding regions in molecules, while the response potentials may have step structures related to different decays of the dominant orbitals. These steps and peaks do however become more prominent in molecules stretched to large bond-lengths and are associated with static correlation.

An example on a 1D model of a LiH molecule is shown in Figure 3.3, where two fermions, interacting via soft-Coulomb potential $1/\sqrt{1 + (x_1 - x_2)^2}$ live in a double well potential (see Tempel et al. [76] for details)

$$v_{\text{ext}}(x) = -1/\sqrt{2.25 + (x + R/2)^2} - 1/\sqrt{0.7 + (x - R/2)^2}.$$

Moving from equilibrium separation of $R = 1.6$ to larger bond lengths, a salient feature is the build-up of the step and peak structures in $v_{C}^T$. These features are essential to prevent dissociation of the molecule into fractional charges, and to lead to the correct atomic-densities in the infinite separation limit. The kinetic component $v_{C}^T$ gives the correlation potential an ultra-non-local in space character, while the hole potential, $v_{C}^{\text{hole}}$ is quite local [32, 76]. For the two electrons cases, the exchange potential $v_{X} = -v_{H}/2$ and
Figure 3.3: Ground-state potential components for a 1D model of the LiH molecule [76] for equilibrium $R = 1.6$ (left) and stretched $R = 7.0$ (right) geometries. Top panels: density (red solid), external potential (green dashed) and Kohn-Sham potential (blue dotted). Lower panels: $v_C^W$ (blue dotted), $v_C^T$ (green dashed) and $v_C^{\text{hole}}$ (pink dotted) contributions to the total correlation potential $v_C$ (red solid).

we can focus on the correlation part and its components. In the general case, approximations in use today do a better job of capturing $v_C^{\text{hole}}$ than of $v_C^T$ and $\Delta v_C^W$, which require the correlation potential to have spatially non-local density-dependence.

The step structure in the ground-state potential indicates strong correlation in the system, with NOONs significantly away from their SSD values (see Section 3.1.4). For example, the largest occupation numbers in the equilibrium geometry in the model of the LiH molecule in Fig. 3.3 are 1.9551, 0.0412, 0.0035..., indicating a weakly correlated system, while for the stretched molecule at $R = 7$ they are 1.0996, 0.8996, 0.0008... As the separation increases further, the two largest occupation numbers approach one, with others becoming zero, indicating a strong deviation from SSD behavior for which one occupation number
would be 2 while all others are zero.

### 3.4 Components of Time Dependent Correlation Potential in Dynamics

To find the exact xc potential Eq. (3.40), we must not only solve for an exact solution for the interacting wavefunction, from which we extract \( \rho(x, x', t) \) and \( n_{XC}(x, x', t) \), but we also need a method to find the exact KS density-matrix \( \rho_S(x, x', t) \). In general, this is not a trivial task. However, for two electrons in a singlet state, assuming one starts the KS calculation in a SSD, then simply requiring the doubly occupied KS orbital to reproduce the exact density \( n(x, t) \), yields

\[
\varphi(x, t) = \sqrt{\frac{n(x, t)}{2}} \exp \left[ i \int x' j(x', t) \frac{1}{n(x', t)} dx' \right] \tag{3.46}
\]

and \( \rho_S(x, x', t) = 2 \varphi^*(x, t) \varphi(x', t) \)(see Subsection 3.1.3).

#### 3.4.1 1D He: Rabi dynamics to local excitations

Here we consider a 1D model of the He atom \( v_{\text{ext}}(x, 0) = -2/\sqrt{x^2 + 1} \), and apply a weak resonant field \( \mathcal{E}(t) = 0.00667 \cos(0.533t) \) to induce local Rabi oscillations between the ground and the lowest singlet excited state of the system. (The Rabi frequency from Eq. (3.6) is \( \Omega_R = 0.00735 \)). This example was also considered in works\[18, 24, 68\]. Figure 3.4 plots the exact KS potential at four times during a half-Rabi cycle, along with the density. Step and peak structures are clearly present during the time-evolution. The step actually oscillates on the time-scale of the optical cycle, with magnitude and direction varying significantly.

We investigate the role of the different components \( v^T_C, v^W_C \), and \( v^\text{hole}_C \) and compare these components with their AE approximations(see Subsection 2.2.3). In Figure 3.5, we find
Figure 3.4: 1D He model: snapshots of density $n$ (red solid) and exact KS potential $v_s$ (black dashed) during a half-Rabi cycle (excited state is reached at $T_R/2$).

Here (top right and lower left panels) that both $v_{C,AE}^{T}$ and $v_{C,AE}^{W}$ do display a small step feature, that exactly cancel once added.

Although $v_{C,AE}$ does a poor job in approximating $v_C$, the AE approximation is noticeably better for the hole component: $v_{C,AE}^{\text{hole}}$ does somewhat capture $v_C^{\text{hole}}$ as shown in the lower right panel, reasonably capturing the well structure. Neither the exact nor the AE $v_C^{\text{hole}}$ component displays any step structure.

These observations appeared to hold generally; for example, see Figure 3.6, where the components are shown at $T_R/4$. There, the step is considerably larger than at $T_R/8$, and the dominant component to the step appears in $v_{C}^{T}$, while at $T_R/8$, the contributions from $v_{C}^{W}$ and $v_{C}^{T}$ are comparable. Again, the $v_{C}^{T}$ and $v_{C}^{W}$ components of the AE approximation each display a (much smaller) step, but which cancel each other; again the AE approximation
Figure 3.5: 1D He Rabi dynamics at $T_R/8$: exact (red solid) and AE (blue dashed) components of $v_C$ as indicated.

does a better job for $v_C^\text{hole}$ than for the other components.

At the time when the excited state is reached, the dynamical step wanes: as $T_R/2$ is reached, the electron dynamics slows down, and the local acceleration in the system decreases to zero. As was seen in Eq. (3.10) (see Elliott et al. [18] and in Subsection 3.1.3) the dynamical step arises from a spatial integral of the acceleration through the system, so consequently this goes to zero; the oscillations over the optical cycle become increasingly gentle and eventually vanish to zero. Figure 3.7 shows that still, the AE correlation potential is dramatically different from the exact potential, and that the dominant behavior is contained in the kinetic component $v_C^T$. The AE approximation does not do well for any of the components, but is particularly bad for $v_C^T$. This can be understood from realizing that underlying the AE approximation is the assumption that both the interacting and KS
states are ground-states. This is obviously not the case at half a Rabi cycle, when the true state has reached the first excited state of the system. The KS state on the other hand does have a ground-state nature (although is not the ground-state of the 1D-He potential), as it consists of a doubly-occupied node-less wavefunction.

Although the dynamical step structures look rather stark, they do tend to appear in regions where the density is small, although not negligible. A question is then, what is their impact on the dynamics? Figure 3.8 plots the exact dipole, compared with three TDDFT calculations using approximate functionals; in all calculations the same field is applied, that is resonant with the exact transition frequency. These approximations do quite poorly, as has also been observed in the past for Rabi dynamics [24, 68]. One can also understand the poor performance of the approximate methods from the errors in their resonant frequencies: for exact exchange(Exx), the local density approximation (LDA) and
the self-interaction corrected LDA (LDA-SIC), the linear response (LR) resonances lie at $\omega_{\text{LR}}^{\text{EXX}} = 0.549$, $\omega_{\text{LR}}^{\text{LDA-SIC}} = 0.528$ and $\omega_{\text{LR}}^{\text{LDA}} = 0.475$, whereas the exact resonance is at $\omega = 0.533$. In Figure 3.8 the performance of the different approximate functionals in a self-consistent KS propagation are shown. The failure is evident and is worse for the approximations with poor LR resonances. For LDA, in addition to the bad LR frequency the ionization threshold lies already below $\omega = 0.5$, so the LDA dipole begins to probe the continuum and there is no dominant frequency. In order to assess the impact of the adiabatic approximation itself independently of the choice of the ground state approximation it would be desirable to run an AE calculation self-consistently.

We now come to the question of the relation between the dynamical step and the NOONs. Figure 3.9 shows the NOONs plotted over a half-Rabi cycle: as might be anticipated, two
Figure 3.8: Dipole moment $d(t) = \int dx x n(x, t)$ during a half-Rabi cycle for the 1D He model. The same field is applied in all cases, $E(t) = 0.00667 \cos(0.533 t)$. Exact (top panel), LDA (second panel), LDA-SIC (third panel), and EXX (fourth panel).

dominate. One starts out close to 2 while the other is close to 0, and both approach 1 as the excited state is reached at $T_R/2 \approx 430$. In particular, we note that, in contrast with the ground-state case, there is no direct relation with the deviation from SSD and the size of the step, e.g. as we approach a half-Rabi cycle, when the interacting system is farthest from a SSD, the size of the dynamical step decreases and eventually vanishes. Instead, it seems to be related more to the local oscillatory behavior of the NOONs: Figure 3.10 shows the step at various times in an optical cycle near $T_R/4$ while the inset shows the corresponding NOONs. We observe that there is a correlation between the oscillations of
the step and those of the NOONs. The largest (smallest) step size during the optical cycle appears to occur at local minima (maxima) of NOONs. This feature also holds when we zoom in to optical cycles centered around other times. The adiabatic NOONs, computed from diagonalizing the one-body density matrix of the interacting ground-state wavefunction of instantaneous density \( n(x,t) \), have a much smaller variation. They begin at the exact values \((1.9819, 0.0166, 0.0014...)\), make a gentle dip to \((1.8437, 0.0899, 0.0668...)\) at \( T_{R}/2 \) before rising back up: in the AE approximation the underlying ground-state remains weakly correlated throughout, as it is the ground-state of a relatively localized density.

![Figure 3.9: The two largest time-dependent NOONs over a half-Rabi cycle for the 1D He model. All other NOONs are negligible.](image)

### 3.4.2 1D He: Field-Free Evolution of a Non-Stationary State

In this example, we prepare the field-free evolution of a 50:50 mixture of the ground and first excited state in the 1D He atom,

\[
|\Psi(t)\rangle = \left( e^{-iE_{g}t}|\Psi_{g}\rangle + e^{-iE_{e}t}|\Psi_{e}\rangle \right) / \sqrt{2}.
\]  

(3.47)
Figure 3.10: 1D He Rabi dynamics: The dynamical step at snapshots over one optical cycle near $T_R/4$, i.e. at times 0.13, 0.25, 0.38, 0.5, 0.63 $T_{opt}$ after $T_R/4$, as indicated in the inset. The dominant time-dependent NOON is shown in the inset.

First in Figure 3.11, we plot the exact KS potential and the density at four times within the first half-period of the motion (the period of the dynamics is $2\pi/(E_e - E_g) = 11.788$). Dynamical steps are once again clearly evident, and particularly prominent at the initial time and every half-period of the evolution. There it dominates the xc potential. Figure 3.12 shows the correlation potential at the initial time, as well as its components $v_C^T$, $v_C^W$, and $v_C^{hole}$, and the AE approximation to these terms. We notice that the step is the over-riding feature of the correlation potential at this time, and is largely contained in the kinetic component $v_C^T$. This is consistent with the expectation expressed in Subsection 3.2.3, that initial-state effects are largely contained in the kinetic component of the correlation potential. At the same time, it represents an electric field, $\nabla v_C$, that is quite localized, although large, in a region of small but appreciable density. The AE approximation fails miserably
Figure 3.11: The exact Kohn-Sham potential (black dashed) and density (red solid) in the field-free evolution of Eq. (3.47) in 1D He at times indicated.

to capture it, but does a much better job in capturing the gentle undulations of $v^W_C$ and even more so $v^\text{hole}_C$. The $v^W_C$ does appear to display a small step, and is fairly captured by the AE approximation at this time. At time $t = 2$ in Figure 3.13, although the overall step size is less, the AE approximation captures neither the step in $v^T_C$ nor in $v^W_C$. The AE again does a reasonable job of capturing $v^\text{hole}_C$ although not getting all its structure correct, similar to the case of the local Rabi excitation in Section 3.4.1.

3.4.3 1D H$_2$: Resonant Energy Transfer Dynamics

We now consider a case where an excitation transfers over a long distance but without charge transfer. We place our two soft-Coulomb interacting electrons in a 1D model of the H$_2$ molecule:

$$v_{\text{ext}}(x) = -1/\sqrt{(x-R/2)^2} + 1 - 1/\sqrt{(x+R/2)^2} + 1$$ (3.48)
and take $R = 16$. The exact ground-state of this molecule has a Heitler-London nature in the limit of large separation, 

\[ \Psi_{g,s}(x,x') = \frac{(\phi_L(x)\phi_R(x') + \phi_R(x)\phi_L(x'))}{\sqrt{2}} \]

(3.49)

while the lowest two singlet excitations become:

\[ \Psi^{(1)}(x,x') = \frac{(\phi_L(x)\phi_R^*(x') + \phi_R^*(x)\phi_L(x'))}{\sqrt{2}} \]

(3.50)

\[ \Psi^{(2)}(x,x') = \frac{(\phi_L(x)\phi_R^*(x') - \phi_R^*(x)\phi_L(x'))}{\sqrt{2}} \]

where $\phi_{L,R}$ denote the ground-state hydrogen orbitals on the left and right atoms, and $\phi_{L,R}^*$ denote the excited state atomic orbitals. The charge-transfer resonances, $\text{H}^+\text{H}^- + \text{H}^-\text{H}^+$ (in the large separation limit), are found at higher energies in this model. We begin with an initial excitation localized in the right-hand-well, which is specifically a 50:50 combination
of the first two excited states, $\Psi(0) = (\Psi^{(1)} + \Psi^{(2)}) / \sqrt{2}$. The density is essentially that of a local excitation on the right atom and the ground-state on the left and is compared with the hydrogen atom ground and first excited state densities on each atom in Figure 3.14.

The electrons are then allowed to evolve, as in the previous section, with no external field applied.

As the right-hand well de-excites, the density in the left-hand-well gets excited; the excitation transfers back and forth while the density remains integrated to one electron on each well at each time. The density and full KS potential are plotted in Figure 3.15 at two times during the energy transfer; $T$ is the period of the dynamics, $T = 2\pi/(E^{(2)} - E^{(1)}) = 5374.84$.

After $T/2$ the excitation has transferred completely to the other atom and the pictures at times between $T/4$ and $T/2$ are the same as those between 0 and $T/4$ but flipped around the $x$-axis. The system seems to be essentially two one-electron systems in each well, each
Figure 3.14: Initial density in the 1D H₂ molecule (red solid line), compared with the ground-state density of a hydrogen atom on the left (green points) and the excited state density of a hydrogen atom on the right (blue points).

getting excited then de-excited; so one might expect that Hartree-xc effects are minimal, at least locally in each well and that the KS potential would revert to the external potential in the one-electron regions around each well. (Certainly, for a time-dependent truly one-electron system, $v_S = v_{\text{ext}}, v_C = 0, v_X = -v_H$). Turning to the lower panels in Figure 3.15 we see this is not in fact the case for the exact $v_H + v_{\text{XC}}$. The AE $v_H + v_{\text{XC}}$ does show the above described behavior, i.e. it becomes flat in the region in each well in the large separation limit and only the intermolecular midpoint peak remains. This midpoint peak is similar to the peak in the ground-state potential in H₂ that appears as the ground-state molecule dissociates [34, 76] and is a feature of the kinetic component to the correlation potential, $v_C^T$ (see shortly). However the exact $v_H + v_{\text{XC}}$ is certainly nowhere near becoming flat locally around each well! The interacting system cannot be thought of as solving a one-electron Schrödinger equation in each well: although locally the density is a one-electron density,
the system cannot be described by one orbital in each well. To see this more precisely, take a look at the NOONs plotted in Figure 3.16 and the NOs themselves, plotted in Fig. 3.17. At the initial time and every half-period, there are two NOs that are equally occupied: in fact these have a bonding and antibonding structure across the molecule, and are identical up to a sign locally in each well, as can be seen from the top left panel of Fig 3.17. At these times therefore one orbital describes the dynamics in each well, and the problem resembles the stretched H$_2$ molecule (Heitler-London). In fact at $t = 0, T/2$, the exact $v_H + v_{XC}$ does become flat locally in the region of each atom.

Figure 3.15: Top panels: exact KS potential (black dashed) and density (red solid) at times shown during the resonant energy transfer in the H$_2$ molecule. Lower panels: The exact Hartree-xc potential, $v_H + v_{XC}$ (red solid) and its AE approximation (blue dashed).

Away from the initial time and half-periods, more than two natural orbitals are significantly occupied. At a quarter-period, when there is equal excitation on both wells, four natural orbitals are equally occupied and these are shown on the right panels of Fig. 3.17. Around each well, two of the four largest natural orbitals have essentially identical densi-
ties; pairwise, they have the structure of \( f_1(x) \pm f_2(x) \) where \( f_{1,2}(x) \) is a function localized on the left(right), but, importantly, different pairs have different \( f_i(x) \). This means that the electron localized in one well is being described by four orbitals, which are pairwise essentially identical, but quite distinct from the other pair. That is, each electron is locally described by two distinct functions with comparable weights: definitely not a one-electron dynamics, despite being a one-electron density. As a result the exact \( v_{Hi} + v_{XC} \) does not vanish locally around each well as would be the case for one-electron systems (time-dependent or ground-state), see Figure 3.17. The excitation–de-excitation process in each well cannot be described by a pure state \( (a_1 \phi_1 + a_2 \phi_2) \). Note that the AE NOONs stay constant and extremely close to 1. The AE NOs (not shown) also have the symmetric/antisymmetric combination structure \( g_1(x) \pm g_2(x) \), but around each well the two orbitals are essentially identical, like for the exact case at the initial time. Each electron in the AE approximation is therefore described by one function around each well, and so the system does behave...
Figure 3.17: At $t = 0$ and $t = T/4$, the natural orbitals (real parts) and orbital densities with significant occupation numbers are shown. The real part of the natural orbitals show, pairwise, the structure of $f_1(x) \pm f_2(x)$ as discussed in the text, and the bottom panel shows the orbital densities.

locally as a one-electron system, and hence in the AE approximation the Hartree-xc potential vanishes locally around each well.

Figure 3.18 and Figure 3.19 plot the correlation potential and its components $v^T_C, v^W_C, v^\text{hole}_C$ at two times during the energy transfer. We observe that the AE approximation is consistently essentially exact for the potential contributions $v^W_C$, and $v^\text{hole}_C$, which in fact exactly cancel the Hartree-exchange potential locally: $v^\text{W,AE}_C = v^W_C$ and $v_H + v_X + v^W_C = 0$ locally in each well. We can understand this, since being a one-electron density in the well, there should be no self-interaction from the Coulomb interaction, so the potential contribution $v^W_C$ must just cancel the Hartree and exchange potential. (Although locally a one-electron system, globally we have a two-electron systems so $v_X = -v_H/2$ instead of completely canceling Hartree; $v^W_C$ then steps in to complete the job, which is called a static correlation.
effect and also occurs in the ground-state of stretched molecules [34, 76]). The entire non-trivial structure of \( v_C \) is in its kinetic component \( v_C^{T} \), and is due to the effect discussed in the last paragraph, and is completely missed by the AE approximation, \( v_C^{T,AE} = 0 \) locally in each well. Similar behavior appears at other times not shown.

No dynamical step across the system is observed, which we can understand from the idea that due to the excitation–de-excitation nature of the dynamics in each well, local accelerations on each side of the system are in opposite directions. Given that the step arises from the spatial-integral of the acceleration, any local step structure would cancel out across the system.

![Figure 3.18: Components of \( v_C \) at \( t = T/8 \) for the resonant energy transfer model.](image)

In this chapter, we have discussed the decomposition of the exact xc potential and compared the adiabatically-exact counterparts in Rabi dynamics, field-free evolution and resonant energy transfer situations. The relation between the NOONs and steps is also discussed for the ground state case and the time-dependent case. Next, we will explore these
Figure 3.19: Components of $v_c$ at $t = T/4$ for the resonant energy transfer model.

steps in the linear response regime.
Chapter 4

Absence of Step Structure in Linear Response Regime

A question to ask is “what is the relevance of these step structures in linear response calculations”. Since adiabatic TDDFT typically gives good spectra, then what happens to these steps in the linear response regime: are they linear or non-linear phenomena? This is what we will answer soon after we introduce the natural orbital occupation numbers as a measure of SSD, as it’s related to the step structures.

We will apply weak off-resonant fields (different from the field in Subsection 3.1.3), to stimulate linear response of the system, as will be detailed below.

For two electrons in a spin-singlet, choosing the initial KS state as a doubly-occupied spatial orbital, $\varphi(r,t)$, means that the exact KS potential for a given density evolution can be found easily as Eq. (3.10): in 1D, we have

$$v_S(x,t) = -\frac{(\partial_x n(x,t))^2}{8n^2(x,t)} + \frac{\partial^2 n(x,t)}{4n(x,t)} - \frac{1}{2} u^2(x,t) - \int_x^\infty \frac{\partial u(x',t)}{\partial t} \, dx'.$$  \hfill (4.1)

We numerically solve the exact time-dependent two-electron wavefunction, obtain the one-body density and current-density, and insert them into Eq. (4.1). The exchange-potential in this case is simply minus half the Hartree potential, $v_X(x,t) = -v_H(x,t)/2$, with Hartree
potential \( v_H(x, t) \) in Eq. (2.16), in terms of the two-particle interaction \( w(x', x) \). Therefore, we can directly extract the correlation potential using

\[
v_C(x, t) = v_S(x, t) - v_{\text{ext}}(x, t) - \frac{v_H(x, t)}{2},
\]

where \( v_{\text{ext}}(x, t) \) is the external potential applied to the system.

### 4.1 Dynamics in a Gaussian-Shaped Pulse

The examples of previous chapters began in the ground state and either applied a weak resonant field or a strong arbitrary field to the system, or began in a superposition of a ground and excited state. None of these situations are the territory of linear response. Instead here, we apply a weak off-resonant field, but with an envelope such that a number of excitations fall under it. To this end, we apply a weak electric field \( \mathcal{E}(t) \) with the following Gaussian envelope:

\[
\mathcal{E}(t) = \epsilon_\alpha e^{-\left(\frac{t - T_0}{\sqrt{2}T_0}\right)^2} \cos(\Omega_0 t),
\]

where \( T_0 = 2\pi/\Omega_0 \) is the period corresponding to the central frequency, and \( \epsilon_\alpha \) is the peak field strength (see below). Figure 4.1 shows the power spectrum for strength \( \epsilon_1 \); excitations of the 1D He model of frequency \( 0.533, 0.672, 0.7125 \ldots \) lie in its bandwidth. Here we have chosen \( \Omega_0 = 0.7 \), but our conclusions are independent of this value. We choose a weak field strength \( \epsilon_1 = 0.0067 \) such that the predominant response of the system is linear. We then apply weaker fields, \( \epsilon_\alpha \), of strengths: \( \epsilon_{0.50} = \epsilon_1/2 \) and \( \epsilon_{0.25} = \epsilon_1/4 \). The top left panel of Figure 4.2 shows that the density response, defined as \( \delta n_\alpha(x, t) = n_\alpha(x, t) - n(x, 0) \), predominantly scales linearly with the field strength: plots of \( \delta n_\alpha/\alpha \) lie essentially on top of each other. The correlation potential response, in the lower left panel, in region \( \approx (-5, 5) \) also scales linearly with the applied field but deviates from linearity outside this region.
region, displaying step and peak structures; these are also evident in the full correlation potential plotted in the top right panel. Zooming into the tail regions of the densities (see e.g. inset of top panel), we see in fact the density response is not linear in these regions. The steps and peaks in the non-linear region do not scale with the field strength; we do not expect them to, as the response is not linear, and they also do not have any higher-order consistent scaling behavior with the field strength.

We have checked that the step features are not numerical artifacts: they are converged with respect to the size of the box and grid-spacing. Changing these parameters may change the details of the noise in the small oscillations visible in $\delta v_c$ (much smaller scale than the scale of the step itself) but do not change the overall structure.

To quantify the deviation from linearity we next define a measure, which we plot in the lower right panel. Since the weakest strength is closest to the ideal linear response limit,
Figure 4.2: Densities and correlation potentials at time $t = 22.440$. The top-left shows the scaled density response $\delta n_\alpha(x, t)/\alpha$ for the three values of $\alpha$ indicated. The inset zooms in on the scaled density response in the outer region. The top-right shows the correlation potentials at different field strengths. The bottom-left panel plots the scaled correlation potential response, $\delta v^c_\alpha(x, t)/\alpha$. The steps of the correlation potentials occur where the density response is non-linear. The lower right panel plots the deviation from linearity, $M_\alpha$, of Eq. (4.4).

we define the deviation relative to this strength, and define:

$$M_\alpha = \frac{|\delta n_\alpha - 4\alpha \delta n_{0.25}|}{|\delta n_\alpha| + 4\alpha|\delta n_{0.25}|}. \quad (4.4)$$

If the density response at field strength $\alpha$ was truly linear, the numerator would vanish (within the approximation that when $\alpha = 0.25$ the system response is linear); and it is trivially zero when $\alpha = 0.25$. The measure takes values from 0 to 1, growing as the degree of non-linearity grows. Note that when the signs of $\delta n_\alpha$ and $\delta n_{0.25}$ are opposite, the measure takes the value of 1. In the lower right panel in Figure 4.2, we see that, aside from a sharp peak structure near $x = 0$, $M_\alpha$ is small in the region $x \approx (-5, 5)$, then grows outside this region, peaking and remaining large after the peak. The sharp structure near $x = 0$ occurs due to the density responses themselves going through zero near the origin. The step structures in the correlation potential appear only in the outer region, where the
measure is appreciable, i.e. the density response is significantly non-linear.

Figure 4.3: Densities and correlation potentials at time \( t = 26.929 \). See caption of Figure 4.2 for details.

Figure 4.3 and Figure 4.4 show the density responses and correlation potentials plotted in the same way, at two different times, \( t = 26.929 \) and \( t = 31.417 \). The same conclusions can be drawn as for the earlier time, and in fact for all the different times throughout the time propagation that we analyzed: step structures appear only in regions where the system’s response is nonlinear. We did not find a single time at which steps occurred in a region where the density response is linear. The step structures do not scale in any consistent way with the field strength. (Where the system response is linear, the correlation potential response scales linearly with the field, as expected). There are times at which the step is abnormally large: this tends to happen in close-to-nodal structures of the density, and is likely a feature only of two-electron systems.

We note that regions of non-linear system response are typical in linear response calculations: essentially, the term representing the field in Hamiltonian \( H_0 + \mathcal{E}(t)x \) gets larger
than the field-free term for large $x$, so a perturbative treatment of it in that region is no longer valid. However, such a calculation is still considered to be in the linear response regime, since these regions contribute negligibly to practical observables extracted from the system dynamics.

### 4.2 Dynamics under a “delta-kick”

A common way to obtain linear response spectra from real-time dynamics is to apply a “delta-kick” to the system at the initial time, and measure the subsequent free evolution [84]. That is, $\mathcal{E}(t) = k\delta(t)$, so that we can write $\Psi(t = 0^+) = e^{ikx}\Psi(t = 0)$. For small enough kick strengths $k$, the system response is linear in $k$. Fourier transforming the time-dependent dipole moment yields the spectrum shown in Figure 4.5, where a value of $k = 0.01$ was used. The peaks correspond to the singlet excited states of odd parity as these are dipole-allowed. The peak-frequencies shown can be confidently assigned to these states only up to about $\omega \sim 0.73$, because the excited states of energies higher than this
have spatial extent too large for the size of the box in our calculation (we have checked convergence with respect to box size for the lower excitations). Now we consider the same

![Graph of dipole power spectrum](image)

Figure 4.5: The dipole power spectrum obtained from solving the time-dependent Schrödinger equation. Vertical dashed lines indicate the dipole-allowed singlet transition energies, which agree with the energy spectrum. (Note the relative oscillator strengths are not accurate because the propagation time was not long enough.)

analysis as in the previous case: we halve $k$ and study the response of the correlation potential and density, looking for the step feature. The main difference from the Gaussian pulse field is that now all the dipole-allowed singlet excited states are equally stimulated: the power spectrum for the delta-kick is uniform.

Figures 4.6 and 4.7 show the response densities and correlation potentials at two snapshots of time 400 and 1400, respectively. Similar graphs appear at the other times we looked at. We again see steps and (sometimes large and oscillatory) peak-like structures, but, again, they appear only in the region of non-linear density-response; regions that contribute negligibly to the linear response observables. Once again, these structures are fully non-linear, in that there is no consistent scaling of their size with the field strength.
Figure 4.6: At time 400 after the kick is applied, the response densities and correlation potentials are shown; please refer to Figure 4.2 for the details of the panels.

4.3 Linear Terms in $v_C$ in Field-Free Evolution of a Perturbed Ground-State

The dynamical step that was found in typical non-linear dynamics situations arises from the fourth term of Eq. (4.1). Here we analyze that term, as well as the full correlation potential, in a linear response situation, by explicitly finding the terms that scale linearly with the deviation from the ground-state.

We consider field-free evolution of a perturbed ground state, for example, as would occur in the delta-kicked propagation of the previous section. We can then expand the wavefunction at time $t$ in terms of the eigenstates, $\Psi_m$, of the unperturbed system, as

$$\Psi(t) = e^{-iE_0t} \left( \Psi_0 + \sum_m c_m e^{-i\omega_m t} \Psi_m \right)$$

(4.5)

where $\Psi_0$ is the ground-state, $\omega_m = E_m - E_0$ are excitation frequencies, and $c_m$ are expansion coefficients, to be considered the small parameter. For example, in the delta-kick of the previous section, $c_m = ik\langle \Psi_0 | \hat{x} | \Psi_m \rangle$ (where, for the two electron case $\hat{x} = x_1 + x_2$). (Note
that in the general case, $c_0$ need not be zero). Then we may write, to first order in the $c_m$,

$$n(x, t) = n_0(x) - 2i \sum_m c_m \sin(\omega_m t)n_{0m}(x)$$  \hspace{1cm} (4.6)

where $n_0(x)$ is the ground-state density and $n_{0m}(x) = 2 \int dx' \Psi_0(x, x')\Psi_m(x, x')$ is the $m$th transition density. Also, we have, to linear order in $c_m$,

$$j(x, t) = i \sum_m c_m \cos(\omega_m t)j_{0m},$$  \hspace{1cm} (4.7)

where $j_{0m}(x) = 2 \int dx' [\Psi_m \partial_x \Psi_0/\partial x - \Psi_0 \partial_x \Psi_m/\partial x]$. So, to linear order in the $c_m$,

$$\int^x \partial_t u(x', t) \, dx' = -i \sum_{m \neq 0} c_m \omega_m \sin(\omega_m t) \int^x j_{0m}(x') \, dx'. \hspace{1cm} (4.8)$$

If there is any step in the correlation potential that appears at linear order, it must appear in this term. From computing just the excited state wavefunctions and their energies, the right hand side can easily be computed. Further, expanding all terms in Eq. (4.1) to linear
order, and using Eq. (4.2), we get the response of the correlation potential to first order as:

\[ \delta v_C = \sum_{m \neq 0} \left\{ i c_m \sin(\omega_m t) \left( \frac{\partial_x n_0}{2n_0} \left( \frac{\partial_x n_{0m}}{n_0} - \frac{n_{0m}}{n_0} \right) - \frac{\partial_x^2 n_0}{2n_0} \left( \frac{\partial_x^2 n_{0m}}{\partial_x n_0} - \frac{n_{0m}}{n_0} \right) \right) \right\} \\
+ \sum_{m \neq 0} \left\{ \omega_m \int x \, j_{0m}(x') \frac{n_{0m}(x')}{n_0(x')} \, dx' + \int \frac{n_{0m}(x')}{\sqrt{(x - x')^2 + 1}} \, dx' \right\} . \tag{4.9} \]

(Note that the \( c_m \) are pure imaginary, and the correlation potential is indeed purely real).

Plotting these terms for the delta-kicked soft-Coulomb well, where \( c_m = 2i k d_{0m} \), there is no step seen; as one moves out to larger \( x \) the terms can grow very large, but there is no step-structure. Figure 4.8 plots the response correlation potential arising from the lowest three dipole-accessible states (which are the first, third, and fifth excitations) in the sum of Eq. (4.9); the contributions from higher order terms decrease rapidly, due to the decreasing oscillator strength. Moreover, carrying out the expansion to second-order in \( k \) there is also no evidence of step-like structure. This is consistent with results of previous section; the regions where there is a step are in fact where such an expansion does not hold, and the response of the system is fully non-linear.

Figure 4.8: The correlation responses from first 3 terms are plotted.
The results so far show that the dynamical step feature does not appear in linear response. That is, the lack of the non-adiabatic step feature in approximations does not affect the success of the approximations in predicting linear response, because this feature only appears in situations where the system response is non-linear. This conclusion has been based on the model 1D He atom, and we expect it to go through for the general three-dimensional $N$-electron case. A question might arise about systems that have states of multiple-excitation character in their linear response spectra: it is known that for TDDFT to capture such states the exchange-correlation kernel must have a frequency-dependence [55], indicating the underlying linear response exchange-correlation potential has an essentially non-adiabatic character. For the He atom (1D or 3D), such states however lie in the continuum and, although they can be accessed by the delta-kick perturbation [77], they contribute much less to the spectrum than the bound states and are outside the range of frequencies for which our dynamical simulations can be trusted. A better model to explore states of multiple-excitation character is a 1D model of a quantum dot: the Hooke’s atom, where two soft-coulomb interacting fermions live in a harmonic potential. The lowest singlet excitation is predominantly a single-excitation (excitation of the electronic center of mass coordinate), but the 2nd and 3rd excitations are (largely) mixtures of one single-excitation and one double-excitation [19, 55]; one is the second excitation of the center of mass coordinate while the other is an excitation in the electronic relative coordinate. A dipole perturbation applied to such a system can only couple to the lowest excitation in linear response, a result that can be interpreted in terms of the harmonic potential theorem[17]. A quadratic kick however does excite the 2nd and 3rd
excitations, and this is what we will consider now: we take

$$V(x, t) = \sum_{i=1}^{2} \frac{1}{2} (1 + k\delta(t)) x_i^2$$  \hspace{1cm} (4.10)

so that in Eq. (4.5), $c_m = i\epsilon(\Psi_0|\hat{x}^2|\Psi_m)$. In Figure 4.9, we plot the contribution to the first-order correlation potential of Eq. (4.9) of the two states of double-excitation character mentioned above. Once again, there is no step structure evident. The non-adiabaticity required to capture states of double-excitation in linear response is unrelated to the dynamical step feature uncovered in Ref. [18].

### 4.4 Conclusion

These results therefore explicitly justify the expectation expressed in Ref. [18] that the nonadiabatic nonlocal step feature that was generically found there in the time-dependent correlation potential is a feature of nonlinear dynamics and is related to having appreciable population in excited states. This explains why adiabatic approximations can usefully
predict linear response spectra in general, while these same approximations may, in many cases, give incorrect time dynamics in the non-perturbative regime.
5.1 Attosecond Transient Absorption Spectroscopy

In 1999, Ahmed Zewail was awarded the Nobel Prize in Chemistry for his studies of the transition states of chemical reactions using femtosecond spectroscopy[86, 87]. Ultrafast spectroscopies facilitate the study of molecular processes on the femtosecond scale. The advances over last two decades in laser technology provide ultrashort pulses of few tens of attoseconds, giving us the unprecedented resolution to unveil the electron dynamics[30, 45]. One of the typical spectroscopies is called “attosecond transient absorption spectroscopy” (ATAS), our main focus here.

In the ATAS, two lasers, as in other pump-probe experiments, are applied to the target with a delay between pump and probe. The pump sometimes has to be strong so that the relevant states are largely populated. After the pump, the system is left in a superposition state, where both electrons and ions are moving. The duration of the probe should be short enough to resolve the motion. After the probe passes through the system, the intensity profile will be lowered than the original probe. The amount of reduction is due to the absorption. The temporal overlap between the pump and the probe determines if the
probe is done in the presence of a strong field. We will consider the case of no temporal overlap.

## 5.2 Generalized Linear Response Function

The well-established ground state linear response theory is not appropriate for the description of non-stationary state that is probed in the ATAS experiments, as in the pump-probe experiment. We will generalize the linear response theory around an arbitrary state and see how the KS description behaves. Before we dive into that, the interaction picture will be discussed, which is helpful in calculations of the response function.

### 5.2.1 Interaction Picture

The switching into *interaction picture* (a.k.a. Dirac picture) in many-body quantum mechanics facilitates the calculations, often in the perturbative regime. Two other pictures are definitely useful before we introduce the interaction picture: Schrödinger picture (SP) and Heisenberg picture (HP)[31, 49, 72].

In the SP, the quantum state but not the operator with no time-dependence evolves in time according to TDSE, and vice versa for the HP. We distinguish the pictures by using the leading letters of subscripts.

**Schrödinger Picture**

State evolves according to TDSE,

\[
i \frac{\partial}{\partial t} \psi_S(t) = \hat{H} \psi_S(t), \tag{5.1}\]
where $\hat{H}$ can be time-dependent in general. We can link the state at $t$ with the initial state by an evolution operator $\hat{U}_S$, $\psi_S(t) = \hat{U}_S(t)\psi_S(t = 0)$. Inserting back to Eq. (5.1), we obtain the motion of $\hat{U}_S$.

$$i \frac{\partial}{\partial t} \hat{U}_S(t) = \hat{H}(t)\hat{U}_S(t).$$ (5.2)

Integration of both sides gives

$$\hat{U}_S(t) = 1 + (-i) \int_0^t \hat{H}(t_1)\hat{U}_S(t_1)dt_1$$

$$= 1 + (-i) \int_0^t dt_1 \hat{H}(t_1) + (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2) + \cdots$$

$$= \sum_{n=0}^\infty (-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2) \cdots \hat{H}(t_n)$$ (5.3)

With the time-ordering operator $\mathcal{T}$, we can use a short notation $\hat{U}_S(t) = \mathcal{T}\exp[-i \int_0^t \hat{H}(t')dt'].$

In the case of time-independent $\hat{H}$, we have $\hat{U}_S(t) = \exp[-i \hat{H}t]$. **Heisenberg Picture**

Operators are defined $\hat{O}_H(t) = \hat{U}_S^\dagger(t)\hat{O}_S\hat{U}_S(t)$ and states are static. With the complex conjugate of Eq. (5.2) and the unitarity of $\hat{U}_S$, we get

$$i \frac{\partial}{\partial t} \hat{O}_H(t) = i \frac{\partial \hat{U}_S^\dagger(t)}{\partial t} \hat{O}_S\hat{U}_S(t) + i\hat{O}_S \frac{\partial \hat{U}_S(t)}{\partial t} = [\hat{O}_H, \hat{H}].$$ (5.4)

Note that in the last step we used $\hat{H}_H = \hat{U}_S^\dagger(t)\hat{H}\hat{U}_S(t) = \hat{H}$. **Interaction Picture**

We consider writing the total Hamiltonian into two parts, $\hat{H} = \hat{H}_0 + \hat{V}(t)$. The interaction picture is then defined such that the time-dependence of the states reflects that only of $\hat{V}(t)$, while the time-dependence arising from $\hat{H}_0$ is absorbed into the operator evolution.

If we require that $\psi_I(t) = \exp[i \hat{H}_0 t]\hat{U}_S(t)\psi_S(0)$ and $\hat{O}_I(t) = \exp[i \hat{H}_0 t]\hat{O}_S \exp[-i \hat{H}_0 t]$. Any
quantity is the same for all pictures, which can be seen from

\[ O_I(t) = \langle \psi_I(t) | \hat{O}_I(t) | \psi_I(t) \rangle = \langle \psi_S(0) | \hat{U}_S^\dagger \hat{O} \hat{U}_S | \psi_S(0) \rangle = O_S(t). \quad (5.5) \]

The equation of motion for \( \hat{U}_I(t) \) is

\[ i \frac{\partial}{\partial t} \hat{U}_I(t) = i e^{i \hat{H}_0 t} \hat{U}_I(t) + e^{i \hat{H}_0 t} \hat{H}(t) \hat{U}_S(t) = \hat{V}_I(t) \hat{U}_I(t) \quad (5.6) \]

which has a solution \( \hat{U}_I(t) = T \exp[-i \int_0^t \hat{V}_I(t') dt'] \). Also note that a time independent \( \hat{V} \) simplifies a bit.

### 5.2.2 Generalization of Linear Response Function

Analogous to classical mechanics, we understand the quantum system by probing with a weak perturbation and observing the induced change\[47\]. The probe as a perturbation is expressed as \( \hat{V} = F(t) \hat{B} \), an external field \( F(t) \) coupled to an operator \( \hat{B} \). It’s turned on at time \( t_0 \), and we will measure the changes in observable \( A \) at time compared to time \( t_0 \). Note that for a general non-stationary state this change has contributions from free evolution as well as due directly to the probe. The change for quantity \( A \) is \( \Delta A(t) = A_F(t) - A(t) = \langle \psi_F(t) | \hat{A} | \psi_F(t) \rangle - \langle \psi(t) | \hat{A} | \psi(t) \rangle \). The induced change for quantity \( \hat{A} \) of linear order in \( F \) is of particular interest in the theory of linear response.

In the interaction picture, both operator and state evolves, expressed as \( \hat{O}_I = e^{i \hat{H}_0 t} \hat{O} e^{-i \hat{H}_0 t} \) and \( |\psi(t)\rangle = \hat{U}_I(t) |\psi(0)\rangle \), with \( \hat{U}_I(t) = e^{i \hat{H}_0 t} \hat{U}_S(t) \). To linear order in \( V \),

\[ \hat{U}_I(t) = 1 + (-i) \int_0^t d\bar{t} \hat{V}_I(\bar{t}) + \mathcal{O}(V^2). \quad (5.7) \]
Substituting the first two terms in \( \hat{U}_I \) and only keeping the linear order, we obtain

\[
A_F(t) = \langle \psi(0) | \left( 1 + i \int_0^t \hat{V}_I(i) \, dt \right) \hat{A}_I(t) \left( 1 - i \int_0^t \hat{V}_I(i) \, dt \right) | \psi(0) \rangle
\]

\[
= \langle \psi(0) | \hat{A}_I(t) \hat{A}_I(t) | \psi(0) \rangle - i \int_0^t \, d\tilde{t} \, \langle \psi(0) | [\hat{A}_I(t), \hat{V}_I(i)] | \psi(0) \rangle + \mathcal{O}(V^2)
\]

\[
= A(t) - i \int_0^t \, d\tilde{t} \, \langle \psi(0) | [\hat{A}_I(t), \hat{V}_I(i)] | \psi(0) \rangle + \mathcal{O}(V^2)
\]

(5.8)

In the case of \( \hat{V} = F(t)\hat{B} \), \( \Delta A(t) = (-i) \int_0^t \, d\tilde{t} \, \langle \psi(0) | [\hat{A}_I(t), \hat{B}_I(i)] | \psi(0) \rangle F(i) \). Now we write

\[
\Delta A = \int_0^\infty \, d\tilde{t} \, \chi^{AB}_R(t, \tilde{t}) F(\tilde{t}).
\]

(5.9)

The retarded response function is defined

\[
\chi^{AB}_R(t, \tilde{t}) \equiv (-i)\theta(t - \tilde{t}) \langle \psi(0) | [\hat{A}_I(t), \hat{B}_I(\tilde{t})] | \psi(0) \rangle
\]

\[
= (-i)\theta(t - \tilde{t}) \sum_m \sum_n \sum_k c^*_{m} c_{n} e^{i(E_m - E_n)t} \left[ e^{i(E_m - E_k)(t - \tilde{t})} A^{m_k} B_{kn} - e^{i(E_k - E_n)(t - \tilde{t})} B^{mk} A_{kn} \right]
\]

\[
= \frac{1}{2\pi} \int_{-\infty}^{\infty} \, d\omega \, \frac{e^{-i\omega(t - \tilde{t})}}{-i \omega + i \eta} \sum_m \sum_n \sum_k c^*_{m} c_{n} e^{i(E_m - E_n)t} \left[ e^{i(E_m - E_k)(t - \tilde{t})} A^{m_k} B_{kn} - e^{i(E_k - E_n)(t - \tilde{t})} B^{mk} A_{kn} \right],
\]

where we have evaluated

\[
\langle \psi(0) | [\hat{A}_I(t), \hat{B}_I(\tilde{t})] | \psi(0) \rangle
\]

\[
= \sum_m \sum_n \sum_k c^*_{m} c_{n} \langle \psi_m | e^{i\hat{H}_0 t} A^{\hat{H}_0} e^{i\hat{H}_0 \tilde{t}} B^{\hat{H}_0} e^{-i\hat{H}_0 \tilde{t}} - e^{i\hat{H}_0 \tilde{t}} B^{\hat{H}_0} e^{-i\hat{H}_0 \tilde{t}} A^{\hat{H}_0} e^{-i\hat{H}_0 t} | \psi_n \rangle
\]

\[
= \sum_m \sum_n \sum_k c^*_{m} c_{n} \langle \psi_m | e^{i\hat{H}_0 \tilde{t}} A^{\hat{H}_0} e^{-i\hat{H}_0 \tilde{t}} | \psi_k \rangle \langle \psi_k | e^{i\hat{H}_0 \tilde{t}} B^{\hat{H}_0} e^{-i\hat{H}_0 \tilde{t}} | \psi_n \rangle - (A \leftrightarrow B, t \leftrightarrow \tilde{t})
\]

\[
= \sum_m \sum_n \sum_k c^*_{m} c_{n} \langle \psi_m | e^{i(E_m - E_n)\tilde{t}} + iE_k(\tilde{t} - t) A^{m_k} B_{kn} - (A \leftrightarrow B, t \leftrightarrow \tilde{t})
\]

\[
= \sum_m \sum_n \sum_k c^*_{m} c_{n} \langle \psi_m | e^{i(E_m - E_n)\tilde{t}} \left[ e^{i(E_m - E_k)(t - \tilde{t})} A^{m_k} B_{kn} - e^{i(E_k - E_n)(t - \tilde{t})} B^{mk} A_{kn} \right]
\]

in which \( a \leftrightarrow b \) means switching the variable \( a \) and \( b \) for the other preceding term. An expansion for \( \psi(0) \) for an arbitrary non-stationary state,

\[
\psi(0) = \sum_n c_n \psi_n.
\]

(5.10)
and the identity
\[
\theta(\tau) = \lim_{\eta \to 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-i\omega'\tau}}{\omega' + i\eta} d\omega'.
\] (5.11)
are used above as well. Fourier transforming in terms of \(\tau = t - \bar{t}\),
\[
\chi_{AB}^{AB}(\tau, \bar{t}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \chi_{AB}^{AB}(\omega, \bar{t}) e^{-i\omega\tau},
\] (5.12)
allows us the identification of
\[
\chi_{AB}^{AB}(\omega, \bar{t}) = \sum_{m,n,k} c_m^* c_n e^{i(E_m - E_n)\bar{t}} \left[ \frac{A_{mk}B_{kn}}{\omega + (E_m - E_k) + i\eta} - \frac{B_{mk}A_{kn}}{\omega - (E_n - E_k) + i\eta} \right]
\] (5.13)
In the summation, we can split these terms into two groups, one with \(n = m\) and one with \(n \neq m\). We have for \(n = m\),
\[
\sum_{n,k} |c_n|^2 \left[ \frac{A_{nk}B_{kn}}{\omega + (E_m - E_k) + i\eta} - \frac{B_{mk}A_{kn}}{\omega - (E_n - E_k) + i\eta} \right]
\] (5.14)
and for \(n \neq m\)
\[
\sum_{m \neq n, k} c_m^* c_n e^{i(E_m - E_n)\bar{t}} \left[ \frac{A_{mk}B_{kn}}{\omega + (E_m - E_k) + i\eta} - \frac{B_{mk}A_{kn}}{\omega - (E_n - E_k) + i\eta} \right].
\] (5.15)
When \(\hat{A} = \hat{n}(r)\) and \(\hat{B} = \hat{n}(r')\), the density-density response function can be cast as
\[
\chi_{nn}(\omega, \bar{t}) = \sum_{m,n,k} c_m^* c_n e^{i(E_m - E_n)\bar{t}} \left[ \frac{f_m(r) f_n(r')}{\omega + (E_m - E_k) + i\eta} - \frac{f_m(r') f_n(r)}{\omega - (E_n - E_k) + i\eta} \right]
\] (5.16)
in which \(f_{ij}(r) = \langle \Psi_i | \hat{n}(r) | \Psi_j \rangle\). A special case is that when and the system stays in ground state for all times before the applied field, e.g. \(c_n = \delta_{n0}\). The \(\bar{t}\)-dependence in
\[
\chi_{nn}(\omega) = \sum_{k} f_{0k}(r) f_{k0}(r') \left[ \frac{f_0(r) f_{k0}(r')}{\omega - (E_k - E_0) + i\eta} - \frac{f_0(r') f_{k0}(r)}{\omega + (E_k - E_0) + i\eta} \right]
\] (5.17)
disappears, which reduces to the zero-temperature limit of the usual ground state linear response function.

Typically, a weak field off-resonant field is applied to calculate the linear response observables and \(\delta\)-kick is particularly important in TDDFT linear response calculations[84].
5.3 Non-stationary State Linear Kick Spectra

To obtain the absorption spectrum, the dynamical polarizability has to be calculated since the optical absorption cross-section is related to the dynamic polarizability \[40\] via

\[
\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \alpha(\omega)
\] (5.18)

In \textit{octopus}[1, 12], the dynamic polarizability can be obtained by propagating in real time. The response of the dipole moment in the \textit{i} direction to a dipole perturbations in \textit{j} direction,

\[
\delta v_{\text{ext}}(r, \omega) = -r_j k(\omega),
\]

\[
\delta \langle \hat{r}_i \rangle (\omega) = -k(\omega) \int dr \, r_i \delta n(r, \omega)
\]

is given by

\[
\delta \langle \hat{r}_i \rangle (\omega) = -k(\omega) \int dr \, \int dr' \, r_i \chi(r, r', \omega) r'_j.
\]

We define the dynamical polarizability \(\alpha_{ij}(\omega)\) as the quotient of dipole moment in the direction \textit{i} with that applied in direction \textit{j}, which is

\[
\alpha_{ij}(\omega) = -\int dr \, \int dr' \, r_i \chi(r, r', \omega) r'_j.
\]

For the “kick” case, we have \(k(\omega) = k\), equal for all frequencies. Then

\[
\alpha_{ij}(\omega) = \frac{\delta \langle \hat{r}_i \rangle (\omega)}{k} = \frac{1}{k} \int dr \, r_i \delta n(r, \omega)
\]

For one dimension, the diagonal element of the absorption cross section tensor is

\[
\sigma(\omega) = \frac{1}{k} \frac{4\pi\omega}{c} \int dx \, x \, \text{Im} \, \delta n(x, \omega)
\]

The strength function,

\[
S(\omega) = \frac{c}{2\pi^2} \sigma(\omega) = \frac{2\omega}{\pi k} \int dx \, x \, \text{Im} \, \delta n(x, \omega).
\]
In a “δ-kick” setup, we apply one weak impulsive electric field to the system, $v_{\text{ext}}(rt) = I\delta(t)r_\nu$, where $I$ is a small magnitude of the impulse, such as to stay in linear response regime. In classical mechanics, all the electrons in the system pick up an initial velocity $v = I/m$, where $I$ acts as a momentum. In quantum mechanics, the orbitals pick up a phase of planewave, since

$$\varphi_i(0^+) = \exp \left\{ \frac{i}{\hbar} \int_{0^-}^{0^+} dt \left[ h + I\delta(t)r_\nu \right] \right\} \varphi_i(0^-) = e^{ikr_\nu} \varphi_i(0^-)$$

(5.23)

where the wave vector $k = I/\hbar$.

Now consider an arbitrary state of the system described by the interacting wavefunction, which can be expanded in terms of the eigenstates, $|\Psi_n\rangle$, complete and orthonormal, of the static Hamiltonian $\hat{H}_0$, with $\hat{H}_0 |\Psi_n\rangle = E_n |\Psi_n\rangle$.

Before the kick, a non-stationary state can be written as

$$|\Psi(t = 0^-)\rangle = \sum_n c_n |\Psi_n\rangle ,$$

(5.24)

where the expansion coefficients $c_n$ can be complex and time-independent. With a weak kick of strength $k$ applied, the phase picked up is $\exp(ik \sum_i x_i)$. It changes the expansion coefficients into

$$|\Psi(t = 0^+)\rangle = \sum_n f_n |\Psi_n\rangle ,$$

(5.25)

where $f_n$’s can be related to $c_n$’s through

$$f_n = \langle \Psi_n |\Psi(t = 0^+)\rangle = \sum_m c_m \langle \Psi_n |e^{ik \sum_i x_i} |\Psi_m\rangle .$$

(5.26)

If $k << 1$, then $e^{ikx} = 1 + ikx + O(k^2)$. In the following, all the higher order of $k$ will be ignored in the linear response context. Making use of the orthonormal condition $\langle \Psi_n |\Psi_m\rangle = \delta_{nm}$ yields

$$f_n = \sum_m c_m \left( \langle \Psi_n |\Psi_m\rangle + ik \langle \Psi_n |\sum_i x_i |\Psi_m\rangle \right) = c_n + ik \sum_m d_{nm} c_m$$

(5.27)
in which we defined the transition dipole $d_{nm} = \langle \Psi_n | \sum x_i | \Psi_m \rangle$. From $t = 0^+$ on, the evolution of the state is

$$|\Psi(t)\rangle = \sum_n f_n e^{-iE_nt} |\Psi_n\rangle.$$  

(5.28)

In density functional theory, we are particularly interested in the density-density response function. We now focus on the density evolution. Again, using Eq. (2.1), we have

$$n(r, t) = \langle \Psi(t) | \hat{n}(r) | \Psi(t) \rangle = \sum_{n,m} f_n^* f_m \rho_{nm}(r) e^{i\omega_{nm}t},$$  

(5.29)

where $\rho_{nm} = \langle \Psi_n | \hat{n}(r) | \Psi_m \rangle$ is the transition density and $\omega_{nm} = E_n - E_m$ is the resonant frequency between state $n$ and state $m$.

Now consider two simplest cases:

1. Starting with an eigenstate $|\Psi_r\rangle$:

$$c_n = \delta_{nr};$$

2. Starting with a superposition of two eigenstates $|\Psi_s\rangle$ and $|\Psi_t\rangle$:

$$c_n = c_s \delta_{ns} + c_t \delta_{nt}.$$

5.3.1 “Kick” around an Eigenstate

In the first case, $f_n = \delta_{nr} + ik d_{nr}$:

$$f_n^* f_m = \delta_{nr} \delta_{mr} + ik (d_{mr} \delta_{nr} - d_{nr} \delta_{mr})$$  

(5.30)

Keeping terms only up to linear order in $k$ and plugging back to Eq. (5.29) and changing the dummy index yields

$$n(r, t) = \rho_{rr}(r) + ik \sum_m d_{mr} \rho_{mr}(r) \left( e^{i\omega_{mr}t} - e^{-i\omega_{mr}t} \right)$$  

(5.31)
where we exploited the equation $\rho_{ab}(r) = \rho_{ba}(r)$ due to the reality of the states. It can be seen that at $t = 0^-$, $n(rt) = \rho_{rr}(r)$. The change in density is thus

$$\delta n(rt) = n(rt) - n(r0^-) = ik \sum_m d_{mr} \rho_{mr}(r) \left( e^{i\omega_{mr}t} - e^{-i\omega_{mr}t} \right).$$

(5.32)

The Fourier transform of $\delta n(rt)$ is

$$\delta n(r\omega) = \int_0^\infty dt \delta n(rt) e^{i(\omega + i\eta)t}.$$

(5.33)

Notice that

$$\int_0^\infty dt e^{i(\omega + y + i\eta)t} = \frac{1}{i(\omega + y + i\eta)} = \frac{1}{\omega + y + i\eta},$$

(5.34)

and

$$\frac{1}{\omega + y + i\eta} = \mathcal{P} \frac{1}{\omega + y} - i\pi\delta(\omega + y).$$

(5.35)

With Eq. (5.34), we express

$$\delta n(r\omega) = i^2 k \sum_m d_{mr} \rho_{mr}(r) \left( \frac{1}{\omega - \omega_{mr} + i\eta} - \frac{1}{\omega + \omega_{mr} + i\eta} \right).$$

(5.36)

The imaginary part of it is

$$\text{Im} \delta n(r\omega) = k \pi \sum_m d_{mr} \rho_{mr}(r) \left[ \delta(\omega - \omega_{mr}) - \delta(\omega + \omega_{mr}) \right].$$

(5.37)

In this case, the strength function is

$$S(\omega) = 2\omega \sum_m |d_{mr}|^2 \left[ \delta(\omega - \omega_{mr}) - \delta(\omega + \omega_{mr}) \right].$$

(5.38)

where we observe the identity $d_{mr} = \int dx x \rho_{mr}(x)$. We can understand the strength function in the following way. On one hand, considering state $r$ as a ground state, then the peak, $\omega_{mr} > 0$, of transition from a lower state to an higher excited state $m$ has a relative size of $\omega_{mr}|d_{mr}|^2 > 0$, which plotted in the positive frequency range exhibits a positive peak indicating absorption.
Figure 5.1: This plot shows the linear “kick” spectra, starting from the ground state of energy $E_0 = -1.483436$ and the 1st excited state of energy $-0.772169$. The states are calculated from the exact Schrödinger equation in the soft Coulomb helium potential, $v_{\text{ext}}(x) = -2/\sqrt{x^2 + 1}$. The transition dipole between them is $d_{01} = 0.807916$. It can be seen that the strength function peaks located around $\omega = E_1 - E_0 \approx 0.711$ have the same height and opposite sign, which agrees with the statement. The highest peak in the red dotted line shows the transition between the 1st excited state and 2nd excited state, with a larger transition dipole. Note that other transitions are noticeable when starting from the 1st excited state. The total propagation time is $T = 1000$, and time step is 0.002.

On the other hand, the amplitude of the transition from an excited state $r$, to a lower state $m$, $\omega_{mr} < 0$, is $(-)^2\omega_{mr}|d_{mr}|^2 < 0$, which corresponds to a negative peak indicating emission. The statement above is best illustrated by Figure 5.1.

### 5.3.2 “Kick” around a Superposition State

In the second case, $f_n = (c_s \delta_{ns} + c_t \delta_{nt}) + ik(d_{ns}c_s + d_{nt}c_t)$, which gives

$$f_n^* f_m = (c_s^* \delta_{ns} + c_t^* \delta_{nt})(c_s \delta_{ms} + c_t \delta_{mt})$$

$$+ ik [(c_s^* \delta_{ns} + c_t^* \delta_{nt})(c_s d_{ms} + c_t d_{mt}) - (c_s \delta_{ms} + c_t \delta_{mt})(c_s^* d_{ns} + c_t^* d_{nt})].$$
Well, the essential point is that the first line is of order $O(1)$ in the perturbation, while the second line is of linear order in the perturbation; the second line signifies the linear response of the system to the perturbation.

From the terms of $O(1)$ in the perturbation the density $n_0$ is

\[
n_0(rt) = \sum_{n,m} (c_s^* \delta_{ns} + c_t^* \delta_{nt})(c_s \delta_{ms} + c_t \delta_{mt}) \rho_{nm}(r)e^{i\omega_{nt}t} \\
= \rho_{ss}(r) + \rho_{tt}(r) + \rho_{ts}(r)(c_s c_t^* e^{i\omega_{ts}t} + c_t c_s^* e^{-i\omega_{ts}t}).
\]

which is not part of the response due to the kick. The second part is a bit more involved. The coefficients in the summation are

\[
(f_{n,m})_1 = ik \left[ |c_s|^2 (d_{ms} \delta_{ns} - d_{ns} \delta_{ms}) + |c_t|^2 (d_{mt} \delta_{nt} - d_{nt} \delta_{mt}) \\
+ c_s c_t^* (d_{ms} \delta_{nt} - d_{nt} \delta_{ms}) + c_t c_s^* (d_{mt} \delta_{ns} - d_{ns} \delta_{mt}) \right],
\]

which leads to the density $n_1(rt)$:

\[
i k \sum_m |c_s|^2 d_{ms} \rho_{ms}(r) \left[ e^{-i\omega_{ms}t} - e^{i\omega_{ms}t} \right] + |c_t|^2 d_{mt} \rho_{mt}(r) \left[ e^{-i\omega_{mt}t} - e^{i\omega_{mt}t} \right] \\
+ d_{ms} \rho_{mt}(r) \left[ c_s c_t^* e^{-i\omega_{ms}t} - c_t c_s^* e^{i\omega_{ms}t} \right] + d_{mt} \rho_{ms}(r) \left[ c_t c_s^* e^{-i\omega_{mt}t} - c_s c_t^* e^{i\omega_{mt}t} \right].
\]

Fourier transforming $n_1(rt)$ leads to

\[
n_1(r,\omega) = -\pi k \sum_m |c_s|^2 d_{ms} \rho_{ms}(r) \left[ \frac{1}{\omega - \omega_{ms} + i\eta} - \frac{1}{\omega + \omega_{ms} + i\eta} \right] \\
+ |c_t|^2 d_{mt} \rho_{mt}(r) \left[ \frac{1}{\omega - \omega_{mt} + i\eta} - \frac{1}{\omega + \omega_{mt} + i\eta} \right] \\
+ d_{ms} \rho_{mt}(r) \left[ \frac{c_s c_t^*}{\omega - \omega_{ms} + i\eta} - \frac{c_t c_s^*}{\omega - \omega_{ms} + i\eta} \right] \\
+ d_{mt} \rho_{ms}(r) \left[ \frac{c_t c_s^*}{\omega - \omega_{ms} + i\eta} - \frac{c_s c_t^*}{\omega - \omega_{ms} + i\eta} \right].
\]

Then assuming the principle part does not give peak structures, we get the absorption
cross section with Eq. (5.22),

\[ \sigma(\omega) \propto \text{Im} \int dx \, n_1(x, \omega) \]

\[ = k \sum_m |c_s|^2 d_{ms}^2 [\delta(\omega - \omega_{ms}) - \delta(\omega + \omega_{ms})] \]
\[ + |c_t|^2 d_{mt}^2 [\delta(\omega - \omega_{mt}) - \delta(\omega + \omega_{mt})] \]
\[ + d_{ms} d_{mt} [\text{Re}(c_s c_t^*) \delta(\omega - \omega_{mt}) - \text{Re}(c_s^* c_t) \delta(\omega + \omega_{mt})] \]
\[ + d_{mt} d_{ms} [\text{Re}(c_t c_s^*) \delta(\omega - \omega_{ms}) - \text{Re}(c_t^* c_s) \delta(\omega + \omega_{ms})] . \]

When one of the coefficients vanishes, say \( c_t = 0 \), then it reduces to Eq. (5.37) in the case of Subsection 5.3.1. For example, the peaks corresponding to the transition between \( m \)(not equal to \( s \) or \( t \)) and \( s \) are proportional to the sum of \( d_{ms}^2 |c_s|^2 + d_{mt} d_{ms} \text{Re}(c_t c_s^*) \). The way we determine the coefficients is to choose \( m \) such that in the delta function \( \delta(x - \omega_0) \), where \( \omega_0 \) corresponds to the transition frequency between state \( t \) and state \( s \), which we call \( t \) and \( s \) are “paired up”.

When \( \omega_{st} < 0 \), the height of the peak around \( \omega_{ts} \) in the positive range is

\[ |c_s|^2 d_{ts}^2 - |c_t|^2 d_{ts}^2 - \text{Re}(c_s^* c_t) d_{ss} d_{ts} + \text{Re}(c_t c_s^*) d_{tt} d_{ts} . \]  \( (5.40) \)

It’s not difficult to generalize to a more complicated case where \( c_n = \sum_i \delta_{ni} c_i \).

### 5.4 Spurious Time Dependent Resonances

It is clear that the positions of the resonances will not change for a non-stationary state when the field is off. There may be more or less of them, and they may change in magnitude and sign, but their positions are invariant. If we now turn to the KS-TDDFT description, we shall find this is not true for approximate functionals. The appearance of spurious time
dependent resonances is a challenge for the usual approximate functionals to model the ATAS experiments[27].

Recall that the ATAS experiment in Section 5.1. After the pumping field excites the system, it is turned off. Considering the nuclei are clamped, the electronic state is freely evolving in a static potential. The onset of the free evolution is denoted by $T$. The probe is applied at various times to obtain the time-resolved spectra. The spectral description now requires the generalized density-density response function in Eq. (5.16).

The KS description, however, is not as straightforward as the interacting system. We assume the non-equilibrium KS response function at time $t = T$,

$$\tilde{\chi}_S[n_T^{(0)}, \Phi(T)](r, r', t, t') = \left. \frac{\delta n(r, t)}{\delta v_S(r', t')} \right|_{n_T^{(0)}, \Phi(T)},$$

(5.41)

has poles in its $(t-t')$-Fourier transform that define the KS response frequencies, and these are typically $T$-dependent (for either exact or approximate functionals). The functional dependence on $n_T^{(0)}$ and $\Phi(T)$ can be seen from the Runge-Gross theorem for the KS system.

Note that the $n_T^{(0)}$ evolves in time, which renders a time-dependent KS potential $v_S[n_T^{(0)}, \Phi(T)]$. This leads to a time-dependent KS Hamiltonian. Because the interaction picture here involves a time-dependent $H_S^{(0)}(t)$, the density-operators involve time-ordered exponentials and a simple interpretation of its Fourier transform with respect to $(t-t')$, $\tilde{\chi}_S(r, r', \omega, t')$, in terms of eigenvalue differences of some static KS Hamiltonian is generally not possible.

Still, from the fact that the physical and KS systems yield the same density-response as for the ground state case in Subsection 2.2.4, we can derive a Dyson-like equation linking the two response functions:

$$\tilde{\chi}^{-1}(\omega, t') = \tilde{\chi}_S^{-1}(\omega, t') - \tilde{f}_{\text{HXC}}(\omega, t')$$

(5.42)
dropping the spatial arguments and functional dependencies to avoid clutter. Here we have defined the generalized Hartree-\(xc\) kernel as 
\[
\tilde{f}_{HXC} = \frac{1}{|r - r'|} + \tilde{f}_{XC},
\]
where
\[
\tilde{f}_{XC}[n_T^{(0)}; \Psi(T), \Phi(T)](r, r', t, t') = \frac{\delta v_{XC}(r, t)}{\delta n(r', t')} \bigg|_{n_T^{(0)}, \Psi(T), \Phi(T)}. \tag{5.43}
\]
Compared to linear response from a ground-state, there is an additional facet to the task of the generalized kernel: it not only has to shift the response frequencies of the KS system to that of the interacting system but must do it in a way that cancels the \(T\)-dependence of the KS frequencies. We can now state the exact condition: Let \(\omega_i\) be a pole of \((\tilde{\chi}^{-1}_s[n_T^{(0)}, \Phi(T)] - \tilde{f}_{HXC}[n_T^{(0)}, \Psi(T), \Phi(T)])^{-1}\), then \(\omega_i\) should be invariant with respect to \(T\):
\[
\frac{d\omega_i}{dT} = 0. \tag{5.44}
\]
This gives a strict condition that is particularly important in time-resolved spectroscopic studies and in resonant dynamics: sometimes more important than accuracy in the actual values of the predicted response frequencies is their invariance with respect to \(T\). Approximate kernels may shift the poles of the KS response function towards the true ones, but unless they cancel the \(T\)-dependence of them, they will give erroneously \(T\)-dependent spectra.

This has implications even in the cases where the nuclei cannot be considered as clamped. There, in the physical system, the electronic excitations couple to ionic motion, so that the potential \(v_{ext}^{(0)}\), which depends on the nuclear positions, depends on \(T\) and on the time delay between pump and probe. The time-resolved resonance spectrum can then be interpreted as “mapping out” the potential energy surfaces of the molecule. Time-dependence should arise purely from ionic motion: spurious time-dependence in approximate TDDFT simulations arising from violation of condition, Eq. (5.44), in the limit of clamped ions will
muddle the spectral analysis in the moving-ions case, and could be mistaken for changes in the nuclear configuration.

5.4.1 Spuriously Time-Dependent Spectra Observed in Real systems

From the analysis above, adiabatic TDDFT will give spuriously time-dependent spectra in theory. Recent studies on real systems have shown time-dependent spectra in adiabatic real-time TDDFT calculations[15, 63, 64]. For example, in the work by Raghunathan and Nest [63], a sequences of ultrashort pulses, separated by long intervals of field free evolution, are applied to two molecules, Li₂C₂ and LiCN. After each pulse, a comparatively long free evolution is performed between the pulses and the dipole moment during the free evolution is Fourier transformed to obtain the spectra. The height of the peaks in the spectra may change because the occupations of the populated states vary due to the energy pumped into the system but their positions should not change. They found that the positions of the peaks are shifted after each pulse. This phenomenon is present regardless of the functional used, although the amount and direction of shift depended on the approximate functional. We can understand this result since the adiabatic kernel is not able to cancel the time-dependent KS bare frequencies, which lead to spurious time-dependence in the spectra.

5.5 Impact on Dynamics

Resonant charge-transfer(CT) beginning in the ground-state provides an example of dramatically changing KS resonances, even for the exact KS potential. Here we study a model system \( v_{\text{ext}}(x) = -2/\sqrt{(x + R/2)^2 + 1} - 2.9/\cosh^2(x + R/2) - 1/\cosh^2(x - R/2) \) with \( R = 7\text{au} \).

The ground-state has two electrons in the left well, and the exact initial KS potential \( v_s^0 \) is
Figure 5.2: Dipole moments calculated from the center of the double-well: exact (black), EXX (red), LSD (green) and SIC-LSD (blue), driven at resonant $\omega$ for each. The initial and target-final KS potentials are shown as insets, exact in the top panel, and in EXX in the lower panel. Top panel: CT from the ground-state. Lower panel: CT from the “photo-excited” state.

shown on the left in the top panel in Figure 5.2.

The KS CT excitation frequency is $\omega_S = 2.2348$ which happens to equal the true (interacting) CT excitation, up to the 5th decimal place. If the exact KS system is driven by a weak-enough resonant field, it achieves the exact density of the true CT excited state via a doubly-occupied KS orbital after half a Rabi cycle. The exact KS potential at this final time, $v_S^f$ (on the right of top panel of Figure 5.2), looks very different: it displays a step, which, in the limit of large separation[25], results in “aligning” the lowest level of each well. Therefore the KS response frequencies are completely different than those at the initial time: $\omega_S^f = 0.0007$.

$\tilde{f}_{\text{HXC}}$ plays an increasingly crucial role in maintaining constant TDDFT response frequencies of Eq. (5.44), $\omega^i = \omega^f = 2.2348$: at first its effect is small but as the charge transfers,
its correction to the KS response frequency increases dramatically. The dipole dynamics for field \( E(t) = 0.05 \sin(2.2348t) \) is shown.

Now turning to approximations: the approximate KS resonances also change in time significantly, but the approximate kernel corrections are typically small, resulting in grave violations of condition(Eq. (5.44)). For example, in exact-exchange (EXX) \( \omega_{ss}^f = 2.2340 \) while again \( \omega_{ss}^i \) tends to zero, with the \( f_{\text{HX}} \) correction in the fifth decimal place in both the initial and final states. As a consequence, the EXX dipole dynamics driven at its resonance completely fails to charge transfer, as seen in the top panel of Figure 5.2.

Other recent works have noted the failure of adiabatic functionals in TDDFT (including the adiabatically-exact) to transfer charge across a long-range molecule[23, 25, 26, 38, 62, 67], even when their predictions of the CT energies are very accurate [23, 26], as computed from the ground-state response. The resonant frequencies predicted by the functional in the initial state and in the target CT state are significantly different from each other. This is due to having one delocalized KS orbital describing the final CT state, resulting in static correlation in the targeted final KS system, and a grossly underestimated CT frequency when computed via the response of the target CT state. The CT frequency computed in the initial ground-state, on the other hand, can be quite reasonable, as seen above.

We next consider CT from a singly-excited state where the KS system involves more than one orbital, and the transferring electron is not tied to the same orbital that the non-transferring electron is in.

We consider a “photoexcitation” in our model molecule that takes the interacting system to its 4th singlet excited state, localized on the left well. We then apply a weak driving field, \( E(t) = 0.0067 \sin(\omega t) \), at frequency \( \omega = 0.289 \), that is resonant with a CT state that has
Table 5.1: Bare KS and TDDFT-corrected photo-excited CT frequencies computed in the
initial, targeted final, and ground states. The exact CT frequency is \( \omega = 0.289 \). The
TDDFT values were obtained via linear response to a \( \delta \)–kick perturbation\[84\] and “–”
indicates no peak was discernible in the spectra, but we expect \( \omega^i \approx \omega^i_S \). Calculations were
performed using the octopus code [1, 12]: a box of size 50, grid spacing 0.1, and time-step
0.005 were used.

<table>
<thead>
<tr>
<th></th>
<th>( \omega^i_S )</th>
<th>( \omega^f_S )</th>
<th>( \omega^{k=\infty}_S )</th>
<th>TDDFT ( \omega^i )</th>
<th>TDDFT ( \omega^f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXX</td>
<td>0.286</td>
<td>0.286</td>
<td>0.288</td>
<td>0.287</td>
<td>0.287</td>
</tr>
<tr>
<td>LSD</td>
<td>0.247</td>
<td>0.094</td>
<td>0.482</td>
<td>–</td>
<td>0.091</td>
</tr>
<tr>
<td>SIC-LSD</td>
<td>0.287</td>
<td>0.236</td>
<td>0.267</td>
<td>0.287</td>
<td>0.237</td>
</tr>
</tbody>
</table>

essentially one electron in each well (see lower panel of Figure 5.2. For this case, \( v^i_S \) and
\( v^f_S \) within EXX are shown; the exact ones are similar. The exact dipole Figure 5.2 shows
almost complete CT.

We now consider TDDFT simulations of this process, using three functionals: EXX, local-
spin-density approximation (LSD), and self-interaction corrected LSD (SIC-LSD). For each,
we begin the calculation in the 4th excited KS state, as would be done in practise to model
the process above. However, we first relax the state via an SCF calculation to be a KS
eigenstate, so that there is no dynamics until the field is applied, as in the exact prob-
lem. We then apply a weak driving field of the same strength as applied to the interacting
problem, but at the CT frequency of the approximate functional, computed from the initial
state, \( \omega^i \). In Table 5.1 one can contrast this with the values for the CT frequency computed
from the target final CT state, \( \omega^f \), as well as the bare KS eigenvalue differences, \( \omega^i_S \) and
\( \omega^f_S \). The approximate TDDFT corrections to the bare KS values for CT are very small, as
expected.

Most notable is that the CT TDDFT EXX frequency computed in the initial and CT states
is identical up to the third decimal place, while there is significant difference amongst the
SIC-LSD values, and even more amongst LSD. In light of the exact conditions (5.44), we
expect EXX to resonantly CT well, while SIC-LSD would suffer from spurious detuning, and LSD even more. Indeed, this speculation is borne out in Figure 5.2: EXX captures the exact dynamics remarkably well. SIC-LSD begins to CT but ultimately fails due to its response frequencies continually changing during the dynamics, as reflected in the initial and final snapshots of the frequencies given in the table. LSD, with its even greater difference in the initial and targeted-final response frequency, indeed fails miserably. Note that, as in practical calculations, spin-polarized dynamics is run from the initial singly-excited KS determinant, with the idea that results would be spin-adapted at the end.

Why does EXX not suffer from spuriously time-dependent response frequencies here? For the special case of two electrons in a spin-symmetry-broken state, \( v_{\text{XC}}^{\text{EXX},\uparrow} = -v_{\text{H}}[n_{\uparrow}] \), so \( v_{\text{S}}^{\text{EXX},\uparrow} = v_{\text{ext}} + v_{\text{H}}[n_{\downarrow}] \). Driving with a weak field resonant with the \( \uparrow \)-electron excitation, where the \( \uparrow \) is promoted in the initial state, causes only a gentle jiggling of the \( \downarrow \)-electron, so that the \( \uparrow \) sees an almost static potential; in this sense EXX mimics the exact functional, that keeps the response frequencies static. So, absorption and emission peaks are on top of each other. For general dynamics, we do not advocate EXX, even for two-electron systems (see previous example); it works in this example because of the conditions above that lead to the nearly constant KS potential.
Chapter 6

Towards Developing Improved Functionals and Kernels: Orbital Functionals

To improve the functionals in use today, memory dependence has to be contained in the xc potential in some form. Orbital functional is a special class of xc potentials where the explicit dependence on the orbitals local in time implies non-local dependence on the density. Orbital functional is promising to go beyond the adiabatic approximation. In the linear response regime, xc kernel derived from an orbital functional, in principle, should has frequency dependence, which is important in capturing double excitations, charge transfer excitations and non-perturbative dynamics. Which kind of orbital functional has frequency dependence and which do not? In order to answer it, we derive an exact formal expression for the xc kernel that arises from a given orbital-functional for the xc potential, $v_{\text{xc}}[\{\phi_i]\}(r, t)$. The frequency dependences coming from various orbital functionals are analyzed.

We do however make one assumption in this section: we perturb around orbitals that can be considered to be stationary, i.e. we will evaluate derivatives around orbitals that satisfy a time-independent Schrödinger equation. This means, for example, that all response-type
functions can be written in a form that involves only the time-difference.

Taking the density functional derivative of the xc potential we have xc kernel as

\[ f_{xc}(r; r') = \frac{\delta v_{xc}(rt)}{\delta n(r')} \]

\[ = \sum_j \int dr_1 dr_2 dt_1 dt_2 \left( \frac{\delta v_{xc}(rt)}{\delta \varphi_j(r_1t_1)} \frac{\delta \varphi_j(r_1t_1)}{\delta v_s(r_2t_2)} + \frac{\delta v_{xc}(rt)}{\delta \varphi^*_j(r_1t_1)} \frac{\delta \varphi^*_j(r_1t_1)}{\delta v_s(r_2t_2)} \right) \frac{\delta v_s(r_2t_2)}{\delta n(r')} \]  \quad (6.1)

Now we define the following notations to shorten our derivation.

\[ \lambda_j(rt; r_1t_1) = \frac{\delta v_{xc}(rt)}{\delta \varphi_j(r_1t_1)} = \left[ \frac{\delta v_{xc}(rt)}{\delta \varphi^*_j(r_1t_1)} \right]^* \]  \quad (6.2)

\[ \frac{\delta \varphi_j(r_1t_1)}{\delta v_s(r_2t_2)} = \frac{\delta \varphi^*_j(r_1t_1)}{\delta v_s(r_2t_2)} \]

\[ \frac{\delta v_s(r_2t_2)}{\delta n(r')} = \chi^{-1}_s(r_2, r', t_2 - t') \]  \quad (6.3)

\[ G_0(r_1, r_2, t_1 - t_2) = (-i)\theta(t_1 - t_2) \sum_k \varphi_k(r_1) \varphi_k(r_2) e^{-i\epsilon_k(t_1 - t_2)} \]

and \( \chi^{-1}_s \) is the non-interacting inverse response function both are functions only of the time-difference when evaluated around stationary states. We get \( f_{xc}(r; r') \) as:

\[ \sum_j \int dr_1 dr_2 dt_1 dt_2 \left( \lambda_j(rt; r_1t_1)G_0(r_1, r_2, t_1 - t_2)\varphi_j(r_2)e^{-i\epsilon_j t_2} + c.c. \right) \chi^{-1}_s(r_2, r', t_2 - t_1). \]  \quad (6.5)

We will want to express xc kernel in frequency-space and we know that around stationary states that \( f_{xc} \) on the left of Eq. 6.5 depends only on \( t - t' \) so that the RHS of this equation must also depend only on \( t - t' \). But the individual functions \( \lambda \) and the orbital phase that go into this expression do not just depend on time-differences although the Green function \( G_0 \) and density-response function \( \chi_s \) do. So we make a combination of the terms to define functions that do just depend on the time-differences in order to make taking the Fourier transform easier later on. That is we should be able to write \( \lambda_j(xt; x_1t_1)\varphi_j(r_2)e^{-i\epsilon_j t_2} \) as a function of \( t - t_1 \) and \( t - t_2 \) given that the LHS is a function of only time-differences and the
other terms on the right also. We note that the $G_0$ depends on only $t - t_1$ so aim to couple
the $(t - t_1)$-dependence of $\lambda_j(rt; r_1, t_1)\varphi_j(r_2)e^{-i\omega_0 t_2}$ with that of $G_0$. To this end we divide and
multiply by $\varphi_j^*(r_1 t_1) = \varphi_j^*(r_1)e^{i\omega_0 t_1}$ defining (dividing by this):
\[
\Lambda_j(rt; r_1 t_1) = \frac{1}{\varphi_j^*(r_1 t_1)} \lambda_j(rt; r_1 t_1) \quad (6.6)
\]
and its conjugate $\Lambda_j^*(rt; r't') = \lambda_j^*(rt; r't')/\varphi_j(r't')$ and defining (multiplying)
\[
\tilde{G}_0^j(r_1, r_2, t_1 - t_2) = \varphi_j^*(r_1 t_1)G_0(r_1, r_2, t_1 - t_2)\varphi_j(r_2)e^{-i\omega_0 t_2} \\
= \varphi_j^*(r_1)G_0(r_1, r_2, t_1 - t_2)\varphi_j(r_2)e^{-i\omega_0 (t_2 - t_1)}. \quad (6.8)
\]
Note that
\[
\tilde{G}_0^j(r_1, r_2, t_1 - t_2) = -i\theta(t_1 - t_2)\varphi_j^*(r_1)\varphi_j(r_2)\sum_k \varphi_k(r_1)\varphi_k(r_2)e^{-i(\epsilon_k - \epsilon_j)(t_1 - t_2)} \quad (6.9)
\]
We therefore can re-write Eq. (6.5) for the exact xc kernel in the time-domain equivalently as
\[
f_{xc}(r, r', t - t') = \sum_j \int dr_1 dr_2 dt_1 dt_2 \left( \Lambda_j(rt; r_1 t_1)\tilde{G}_0^j(r_1, r_2, t_1 - t_2) + \text{c.c.} \right) \chi_0^{-1}(r_2, r', t_2 - t') \quad (6.10)
\]
Now we are ready to Fourier transform with the help of the convolution theorem. We define
\[
\Lambda_j(r, r_1, \omega) = \int d\tau e^{i\omega\tau} \Lambda_j(r, r_1, \tau) \quad (6.11)
\]
and their complex conjugate counterparts
\[
\Lambda_j^*(r, r_1, \omega) = \int d\tau e^{i\omega\tau} \Lambda_j^*(r, r_1, \tau) \quad (6.12)
\]
\(\tilde{G}_0^j\) is constructed such that it’s phase-invariant and therefore it’s straightforward to obtain
the fourier transform as below.
\[
\tilde{G}_0^j(r, r', \omega) = \int d\tau \tilde{G}_0^j(r, r', \tau)e^{i\omega\tau} = \sum_k \frac{\varphi_j^*(r)\varphi_j(r')\varphi_k(r)\varphi_k^*(r')}{\omega - \omega_{kj} + i\eta} \quad (6.13)
\]
\[ \omega_{kj} = \epsilon_k - \epsilon_j. \] Its counterpart is

\[ \Gamma_{ij}(r, r', \omega) = \langle \tilde{G}_{ij}^0(r, r', -\omega) \rangle^* \] (6.14)

The common inverse response function is

\[ \chi^{-1}_s(r_2, r', \omega''') = \int \frac{d\tau e^{i\omega''\tau}}{2\pi} \chi^{-1}_s(r_2, r', \tau). \] (6.15)

and xc-kernel as

\[ f_{XC}(r, r', \tau) = \int \frac{d\omega}{2\pi} e^{-i\omega\tau} f_{XC}(r, r', \omega). \] (6.16)

Hence the exact expression for the xc kernel \( f_{XC}(r, r', \omega) \) is written as

\[ \sum_j \int dr_1 dr_2 \left[ \Lambda_j(r_1, r_2, \omega) \Gamma_{ij}^0(r_1, r_2, \omega) + \Lambda_j^*(r_1, r_2, \omega) \tilde{\Gamma}_{ij}^* \right] \chi^{-1}_s(r_2, r', \omega) \] (6.17)

We note that

\[ \chi_s(r_1, r_2, \omega) = \sum_{jk} \left( f_j - f_k \right) \frac{\varphi_j^*(r_1)\varphi_k(r_1)\varphi_j(r_2)\varphi_k^*(r_2)}{\omega - \omega_{kj} + i0^+} \] (6.18)

\[ = \sum_j f_j \left( \tilde{G}_{ij}^0(r_1, r_2, \omega) + \tilde{\Gamma}_{ij}^* \right) \chi_s^{-1}(r_2, r', \omega) \] (6.19)

where the \( f_j \) are occupation numbers. We categorize different forms for the orbital functional \( \Lambda_j(x, x', \omega) \) with a view to understanding the relation between frequency-(in)dependent orbital functionals and frequency-(in)dependent density-functionals.

- The simplest case is when \( \Lambda_j(x, x', \omega) = \Lambda_j^* = f_j \Lambda(x, x', \omega) \) i.e. non-zero only for occupied orbitals, and real, and the same for all the occupied orbital derivatives, then from Eq. (6.17) and Eq. (6.19), we see directly that

\[ f_{XC}(x, x', \omega) = \Lambda(x, x', \omega) \] (6.20)

This is the case for any pure density-functional, i.e. any xc potential that can be written directly as \( v_{XC}(n) \). In particular, for LSDA, where \( \Lambda_j(x, x', \omega) = \frac{d\nu_{xc}}{dn} |n_0(x) \delta(x - x') \)
for all occupied orbitals and zero for others. It is also true for EXX for two electrons, but is not true for EXX for more than two electrons.

So, for any pure density-functional, any frequency-dependence in the xc kernel obtained from writing it as an orbital functional then follows from that of the density functional, which is as expected; one cannot “create” frequency-dependence just by writing it as an orbital functional.

\[ \Lambda_j = f_j \Lambda_{\text{occ}}(x, x', \omega) + (1 - f_j)\Lambda_{\text{unocc}}(x, x', \omega) \] where \( \Lambda_{\text{(un)occ}} \) is real, i.e. where now the xc potential depends also on the unoccupied orbitals (or some limited number of them), with the property that the orbital derivative is the same for all occupied orbitals, and also the same for the unoccupied orbitals but a different function. Then

\[ f_{\text{xc}}(x, x', \omega) = \Lambda_{\text{occ}}(x, x', \omega) + \int dx_1 dx_2 \Lambda_{\text{unocc}}(x, x_1, \omega) \sum_j (1 - f_{j'}) \left[ \tilde{G}_0^j(x_1, x_2, \omega) + \tilde{G}_0^{j'}(x_1, x_2, \omega) \right] \chi^{-1}(x_2, x', \omega) \] (6.21)

(the prime on the sum just takes care of functionals that only depend on some unoccupied orbitals so that it means that the sum goes over the unocc orbitals that appear in the xc potential).

For functionals with this property, even if \( \Lambda_{\text{(un)occ}}(x, x', \omega) = \Lambda_{\text{(un)occ}}(x, x') \) are frequency-independent, the second term might yield a frequency-dependence.

- \( \Lambda_j \) not uniform in \( j \), then XC kernel is frequency dependent in general.

Introducing a frequency dependent kernel via an orbital functional might lessen the violation of the exact condition, which is worth exploring for the future work. The categorization indicates that the direction is to include unoccupied orbitals.
Chapter 7

Conclusions and Outlook

In this thesis, I have discussed the theoretical framework of DFT and TDDFT. In particular, available approximations in TDDFT are adiabatic which leads to a frequency independent linear response xc kernel.

We have presented a decomposition of the exact time-dependent xc potential into kinetic and potential components, similar to the corresponding decomposition in the ground-state which has proven useful for understanding features of the ground-state xc potential\cite{9,32,33,35}. We have made the first studies of these components for three different non-perturbative dynamical situations and compared them to their adiabatically-exact counterparts. Step structures in the ground-state are associated with strong deviation from a SSD, but we found that the relationship between the time-dependent NOONs and the dynamical step is not so simple. There may be strong static correlation in the system, while there is no step, and the step may be large even when the system is weakly correlated. Rather, we found that the oscillations of the dynamical step size are associated with oscillations in the time-dependent NOONs, interestingly, and further explorations of the trends and dependences in different cases can be carried out.

The examples studied suggest that one may get away with an adiabatic approximation for
$v_{C}^{\text{hole}}$, while the error from an adiabatic approximation to $v_{C}^{W}$ and particularly $v_{C}^{T}$ would be much larger. Still, the importance of each of these terms in influencing the dynamics has yet to be studied. A point of future study would be to self-consistently propagate separately under the three components mentioned to gauge their relative importance on the resulting dynamics. To disentangle the effect of the adiabatic approximation itself and the choice of the ground-state approximation, a self-consistent propagation under the AE approximation would be enlightening, and is an important avenue for future work.

We have also investigated the step structures in the linear response regime. The step structures appear in the xc potential, which is a non-linear phenomenon, which justifies that the nonadiabatic nonlocal step feature that was generically found there in the time-dependent correlation potential is a feature of nonlinear dynamics and is related to having appreciable population in excited states. It also explains why the adiabatic approximation gives good spectra while these approximations may, in many case, yield inaccurate dynamics.

An exact condition for xc kernel is formulated, which helps illustrates the time-dependent spectra recently observed. It shows that the time-dependence of the spectra obtained in adiabatic TDDFT might be caused by the spuriousness of ATDDFT, which should not be simply entangled with effects of moving ions. One possible fix is to correct the $f_{XC}$ as the calculation flows. Also, orbital functional including KS memory should be able to yield a frequency dependent xc kernel, which might decrease the degree of the violation. Further explorations are necessary to justify these expectations.
Bibliography


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[51] M Levy. Universal variational functionals of electron densities, first-order density
matrices, and natural spin-orbitals and solution of the v-representability problem.


[68] M. Ruggenthaler and D. Bauer. Rabi oscillations and few-level approximations in


[77] M. Thiele and Stephan Kummel. Photoabsorption spectra from adiabatically exact


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