

Fall 2014

# Theory of density functionals

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**GRADUATE SCHOOL**  
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By Martín Mosquera-Tabares

Entitled THEORY OF DENSITY FUNCTIONALS

For the degree of Doctor of Philosophy

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11/19/2014

Head of the Graduate Program

Date



# THEORY OF DENSITY FUNCTIONALS

A Dissertation

Submitted to the Faculty

of

Purdue University

by

Martín A. Mosquera-Tabares

In Partial Fulfillment of the

Requirements for the Degree

of

Doctor of Philosophy

December 2014

Purdue University

West Lafayette, Indiana

To Laura, Miriam, Mauricio, and José.

## ACKNOWLEDGMENTS

I am very grateful to all those who, in many ways, helped me thrive as an amateur scientist and person. The following list is non-exclusive, with no particular order in mind, nor educational degree: Michael Mack, Jean Pierre Pinto, Edwin Antillon, Ross Hohen, Rougang Tang, Daniel Whitenack, Carlos Borca, Ferney Rivera, Daniel Jensen, and Jonathan Nafziger.

I am very thankful to the following faculty members of Purdue University and other universities: Sabre Kais, Lyudmila Slipchenko, Dor Ben-Amotz, Kieron Burke, Neepta Maitra, and Eberhard Gross.

I am very proud of having had the honor of serving the group of Density Functional Theory at Purdue University, “the Suspenders”, commanded by Adam Wasserman. I thank Prof. Wasserman for his support and trust in me, also for helping me achieve scientific preciseness, sharpness, rigor, patience, and clarity.

Finally, my family, whose combined effort made this journey possible: Miriam Tabares (Mother), José Jaír Mosquera (Father), Mauricio Andrés Mosquera (Brother), and my wife, Laura Arango, my infinite source of energy.

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## ABSTRACT

Mosquera-Tabares, Martín A. Ph.D., Purdue University, December 2014. Theory of Density Functionals. Major Professor: Adam Wasserman.

Density functional theory is an alternative quantum mechanical theory that offers simple ways of performing calculations of the electronic properties of matter. Many different methods derive from density functional theory. The most appealing for its simplicity and rigor is the theory of Kohn and Sham. In this thesis I propose new methods in density-functional theory that are helpful to address some important problems in the application of the local-density approximation within Kohn-Sham DFT to the analysis of ground-states and dynamical properties of electronic systems.

## 1. INTRODUCTION

The main topic concerning this thesis, as that of many others, is a challenge: The electronic properties of molecules. Many technical aspects can be outlined pointing to the difficulties of calculating the state of molecules, but after extensive and exhausting readings about the topic I reach the conclusion: “solving the non-relativistic electronic ground-state of a molecule in the Born-Oppenheimer picture is impossible, but a reliable estimation has to be possible”. I must, however, specify what I mean by solving the ground-state. Avoiding refined concepts of quantum mechanics, solving is providing the answer to a question that is posed as a critic and obscure equation, i.e., the non-relativistic time-independent Schrödinger equation (TISE), often seen as  $H$  times  $\Psi$  equals  $E$  times  $\Psi$ .

Gazing for a while at  $H\Psi = E\Psi$  leads me to ask myself questions like: what is a solution? how can I solve this problem with finite precision numbers ( $H\Psi = E\Psi$  is defined over an Archimedean field, the real numbers) do we really ever find a solution?. We can ask these questions even for a simple mathematical problem. For example, the initial value problem  $y'(t) = -y(t)$ . One would accept a solution of the form  $y(t) = \exp(-t)$ . What is  $y(\pi)$ ?. We know it is a real number. But, then what is the meaning of  $\exp(-\pi)$ ? The symbol  $\exp$  is only a label for a function that has certain properties. More specifically, that function is  $\exp(-t) = \sum_n (-1)^n t^n / n!$ . This is an infinite expansion that requires an infinite number of operations to calculate a number with infinite precision. These simple observations are trivial, and involve a simple function, the exponential. Unless one can simplify the infinite series, one has to employ some numerical method to approximate  $\exp(-\pi)$ , and, of course, the

number  $\pi$ . It seems that only in few cases we produce an exact answer to the solution of a differential equation that is expressed as a series of numbers.

The calculation of the number  $\exp(-\pi)$  cannot be performed with infinite precision as of the year 2014, and the mathematical theory of numbers and functions still grows. The problem  $y'(t) = -y(t)$  is apparently a simple one. Yet, it is quite involved. Most laws of nature, e.g., electromagnetism, gravitation, quantum mechanics (and its many variations), are expressed using differential equations whose domains are the real numbers. These are often overlooked in applied science. The real numbers are useful for theories, but problematic for calculations. The machinery of integral and differential calculus offers a method to express laws of nature in simplistic and subjectively beautiful forms. However, these laws are computationally quite demanding because operations between real numbers require infinite number of operations. We, humans, might conceive the existence of maps involving infinite number of calculations; we can only perform a finite number of them. Thus, modifications of the idealized formulas of physics is often required, leading to truncated, subjectively ugly, versions of the laws.

Truncated forms of our fundamental equations, i.e., theories of approximation, are usually sought by scientists to perform calculations that aid the interpretation and understanding of experiments. An approximated theory often embodies assumptions that are applied to the strict formal theory to obtain modified equations that ease the computational calculations. The penalty of using approximated equations and finite precision numbers is errors, deviations from the experimental values (which also are prone to different sorts of errors). Minimizing such errors is the job of theoreticians. Proposing an approximated theory is easier than finding the error because the former only needs assumptions based on a posteriori knowledge that derives from formal observation of the strict theory, or from reliable experiments. Error estimation is quite more difficult because one needs to resort to the exact theory and its intricacies.

The development of quantum mechanics relies on experimental measurements. It has been through experiments that the fundamental equations were refined until a

satisfactory theory of atoms was proposed; there is, of course, still doubt about the relativistic form of the laws for multi-electronic systems. The development of quantum mechanics is based on human intuition and experimental observation. Quantum mechanics is empirical. The quantum problem can be formulated in such a way that one needs only few parameters such as the mass, charge, spin moment, speed of light, permittivity, and the Planck and Boltzmann constants. The resulting equations (for example  $H\Psi = E\Psi$ ) are difficult to solve, except for special cases like atoms and molecules with few electrons.

The complexity of the quantum mechanical equations is due to correlation: All the electrons' degrees of freedom are interdependent: One degree of freedom changes all the others in a complex form<sup>1</sup> (a degree of freedom is a spin-spatial coordinate pair). In light atoms, the nuclear charge exerts a stronger force to the electrons than that they exert on one another. If we assign a high importance to the electron-nucleus interaction, then one can construct a wave function being just a product of the orbitals representing each electron. The antisymmetry principle demands that the wave function is a Slater determinant (this introduces some correlation because two degrees of freedom cannot be assigned the same orbital). A space of Slater determinants is defined and the energy wave-functional is minimized over such space. This procedure leads to the Hartree-Fock (HF) equations, which display correlation between the degrees of freedom. The way the orbitals are correlated in the HF formalism is not enough to yield the right energies.

Post-Hartree-Fock methods are too expensive and intricate because of the complexity of the Hamiltonian matrix that is to be diagonalized. The Hamiltonian contains transition amplitudes between all possible states of the system. The problem is that the more electrons are included in the analysis the more possible transitions between electronic state arise. The number of possible combinations grows very fast as a function of the number of electrons. This problem can be solved by introducing

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<sup>1</sup>Note that what we mean here by correlation is not the conventional definition in quantum chemistry, which is usually used to express a the deviation from Hartree-Fock theory in quantum chemistry.

a method that eliminates the plethora of combinations. Density-functional Theory (DFT) offers many ways to eliminate the exponential growth of combinations. In this theory, a map is shown to exist between the ground-state wave-function of the system and its ground-state density. This map can then be used to show that every ground-state observable of the system is a density-functional. The philosophy of this theory is to approximate the energy functional instead of the wave-function, leading to alternative and productive methods to model molecular systems.

There are many ways, as I show in this thesis, to approximate the energy density-functional. The Kohn-Sham (KS) formulation is, perhaps, the most widely used. In this formulation the system of real electrons is mapped into a system of fictitious ones, where they do not interact but are subject to an effective external potential whose job is to force these electrons to yield the true density of the system. The energy is then expressed in terms of the kinetic energy of the fictitious electrons, their attraction energy with the nuclei, and the exchange-correlation (XC) energy, which is the quantity needed to match the true energy of the system. An explicit expression in terms of the electronic density is the primordial objective. The XC energy functional can be used to obtain the XC potential, which is part of the effective potential that the fictitious electrons are subject to in order to yield the ground-state density of the molecule.

In the author’s opinion one may say that the electrons in KS-DFT interact through a local potential. This interaction is neither a mean-field interaction nor a purely Coulombic one. It is only by means of the XC potential that such interaction is determined. The advantage of a local potential representing the density is an apparently low computational cost. DFT allows us to reformulate the ground-state problem using an appealing and convenient picture, such as the non-interacting electrons, but introduces an unknown term. The way of introducing formalisms in DFT usually works as follows: Let  $F$  be our target functional, and let  $G$  be some functional that is close to  $F$ . Then, write  $F = G + X$ , where  $X$  is exact and it is defined as  $X = F - G$ . One can thus state that  $X$  is the missing piece and approximations to it allows us to



approximate  $F$  as  $G + X^{\text{appr}}$ . In some cases, however,  $X^{\text{appr}}$  can be very accurate. Because one can define an infinite number of different  $G$ s, there is an infinite number of DFT formulations. Nevertheless, many formulations are discarded by defining  $G$  and  $X$  by demanding that they are accurate, or exact, in some limit.

This thesis is about formulations of DFT that lead to analytical forms that are exact in some limit. Specifically, we will discuss some formal properties of KS-DFT, Generalized-KS-DFT, and partition DFT. A common statement between these theories is: “This  $G$ -DFT formulation is exact in principle, but  $X$  is the missing piece” (as explained in the previous paragraph). An important feature of  $X$  is that it can be explored in some limit; then, one expresses it as a density-functional and extends it to another regime. Another way of performing approximations to  $X$  is by introducing a set of experimental quantities, fit a suitable form of  $X$ , and then extrapolate. This methodology, is referred to as empiricism by those who approximate  $X$  based in some limit. In the author’s point of view, these two methods are empirical: In both cases one observes some behavior and then extrapolates it to other regimes, and there is no guarantee for success. The author believes that useful approximations should be based on formal limits, experimental measurements, and experimental validation. This should be performed in a consistent and methodical way such that the use of DFT approximations is more transparent.

This thesis is organized as follows: chapter 2 provides a compact mathematical background. In chapter 3 I discuss non-analytic functionals, which are required to describe the dissociation limit of molecules. Chapter 4 presents recent developments on partition DFT, a formulation to study molecular dissociation. Useful functionals for time-dependent Density-functional Theory (TDDFT) are introduced in chapter 5. These functionals avoid the causality paradox dilemma: a perturbation in the density in the future affects the potential in the past. The dynamics of fragments with fixed number electrons that are subject to electromagnetic-fields is presented in chapter 6. A formalism to study fragments with variable number of electrons is shown in Chapter 7. Finally, I conclude with a short remark.

The majority of the developments shown in this thesis are reported in the literature. Section 3.3 is reported in *Physical Review A* [1]. Chapter 4 (excluding sections 4.5 and 4.6, which are in preparation along with Section 3.2 [2]) is published in *Molecular Physics* [3]. Chapter 5 can be found in *Physical Review A* Ref. [4]. Chapter 6 is an invited article to a special issue celebrating forty years of the Hohenberg-Kohn theorem by *the Journal of Chemical Physics* [6]; this paper is also an extension of our previous work published in *Physical Review Letters* [5]. And, Chapter 7 is material in preparation [7]. The published articles are attached at the end of this thesis. I also attached an invited “new views” article [8] for *Molecular Physics* (this paper is related to the material presented in chapter 3).

Finally, below there is a list of the schools and conferences I attended with the work presented.

1. Midwest Theoretical Chemistry Conference, Northwestern University, Chicago IL (2014), talk: “*Fragment-based Time-dependent Density-functional Theory with Variable Occupation Numbers*”.
2. APS March Meeting, Denver CO (2014), talk: “*Recovering the Integer Discontinuity of Density-functional Theory*”.
3. Centre Européen de Calcul Atomique et Moléculaire, Lusanne, Switzerland (2014), talk: “*Recovering the Integer Discontinuity of Density-functional Theory*”.
4. 6th Time-dependent Density-functional Theory, Benasque, Spain (2014), poster: “*Partitioning the Current-density in Time-dependent Current-density-functional Theory*”,
5. International Conference of Density-functional Theory, Durham University, United Kingdom (2013), poster: “*Partition Density-Functional Theory: Some Formal Results*”.

6. Semiclassical Origins of Density Functional Approximations, University of California at Los Angeles (2013), poster: “*Partition Spin Density Functional Theory*”.
7. Midwest Theoretical Chemistry Conference, University of Illinois, Urbana IL (2013), poster: “*Partition Current-density-functional Theory*”.
8. Midwest Theoretical Chemistry Conference, University of Wisconsin, Madison WI (2012), poster: “*Partition Spin Density Functional Theory*”.
9. 1st Colombian School of Theory and Computation in the Molecular Sciences, Cali, Colombia (2012), talk: “*Time-dependent Partition Density Functional Theory*”.
10. APS March Meeting, Boston MA (2012), poster: “*Time-dependent Partition Density Functional Theory*”.
11. Panamerican Advanced Studies Institute, Cartagena Colombia (2011), poster: “*Derivative Discontinuities in Density Functional Theory: A Simple Illustration*”.

### 1.1 References

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## 2. BACKGROUND

### 2.1 Definitions

In this chapter, the background required for the following sections is introduced. Here we only discuss the basic formal framework of TD and ground-state DFT. The mathematics in this thesis is presented almost entirely in Dirac's notation.

#### 2.1.1 Quantum Mechanics

Let  $H_N = \wedge^N L^2(\mathbb{R}^{3N}, \mathbb{C}^{2N})$  be a space of antisymmetric wave functions. The basic composite unit of the space  $H_N$  is the spin-orbital:

$$\chi(\mathbf{r}, \mathbf{z}) = \phi(\mathbf{r})\mathbf{z} , \quad (2.1)$$

where  $\phi \in L^2(\mathbb{R}^3)$ ,  $\mathbf{z} \in \mathbb{C}^2$ , and  $\mathbf{r} = (r_1, r_2, r_3)$  is the position vector in Cartesian coordinates.  $\mathbf{z}$  has two components, and we write  $\mathbf{z} = (z_0, z_1)^T$ . Both  $\phi$  and  $\mathbf{z}$  are normalized, i.e.,  $\int |\phi|^2 = 1$  and  $z_0^2 + z_1^2 = 1$ . The natural basis for  $\mathbb{C}^2$  is  $\{\mathbf{z}_\uparrow, \mathbf{z}_\downarrow\}$ , where  $\mathbf{z}_\uparrow = (1, 0)^T$  and  $\mathbf{z}_\downarrow = (0, 1)^T$ . In this representation the spin-measurement operators are simply matrices in  $\mathbb{C}^{2 \times 2}$ , for example:

$$\mathbf{S}_3 = \frac{1}{2}\sigma_3 = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.2)$$

is the  $z$ -component of the spin operator. Therefore  $\mathbf{S}_3\mathbf{z}_\uparrow = 1/2\mathbf{z}_\uparrow$  and  $\mathbf{S}_3\mathbf{z}_\downarrow = -1/2\mathbf{z}_\downarrow$ . Although a wave-function in  $H_N$  is an acceptable object, we must also need to impose that it vanishes in the asymptotics. This requirement avoids inconsistencies with functions like shrinking combs.

Throughout this work Dirac notation will be used. We assume that the wavefunctions of  $H_N$  are represented by kets in an abstract Hilbert space  $\mathcal{H}_N$ . Thus we say that  $\psi \in H_N$  is represented by  $|\psi\rangle$ , and the dual  $\langle\phi| \in \mathcal{H}_N^*$  is such that:

$$\langle\phi|\psi\rangle = \int \phi^* \psi . \quad (2.3)$$

Operators acting on  $\mathcal{H}_N$  are denoted with a hat.  $D(\hat{O})$  is the domain of the operator  $\hat{O}$ . We define:

$$\langle\phi|\hat{O}|\psi\rangle = \langle\phi|(\hat{O}|\psi\rangle) . \quad (2.4)$$

If  $|\phi\rangle \in D(\hat{O}^\dagger)$ , then we can write the above equation as  $(\hat{O}^\dagger|\phi\rangle)^\dagger|\psi\rangle$ .

Great part of this work concerns states with variable number of electrons. For this reason we introduce the Fock space  $\mathcal{F}$ :

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \dots , \quad (2.5)$$

and also the Liouville space,  $\mathcal{L}$ , of density matrices of the form

$$\hat{\Gamma} = \sum_{M,\mathbf{k}} w_{M,\mathbf{k}} |\psi_{M,\mathbf{k}}\rangle \langle\psi_{M,\mathbf{k}}| . \quad (2.6)$$

This sum is performed over energy levels ( $\mathbf{k}$ ) and particle number ( $M$ ) of a given system. One can define an energy operator  $\hat{H}_N$  that operates on  $\mathcal{H}_N$ . In coordinate representation this operator can be written as:

$$\hat{H}_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M) = -\frac{1}{2} \sum_j \nabla_{\mathbf{r}_j}^2 + \sum_{i>j} V(\mathbf{r}_i - \mathbf{r}_j) + \sum_j v(\mathbf{r}_j) , \quad (2.7)$$

$\nabla_{\mathbf{r}_j}^2$  is the laplacian operator with respect to variable  $\mathbf{r}_j$ ,  $V$  is the Coulombic repulsion potential:

$$V(\mathbf{r}_1 - \mathbf{r}_2) = \frac{-1}{|\mathbf{r}_1 - \mathbf{r}_2|} , \quad (2.8)$$

and  $v$  is the 1-body external potential.

The energy operator in the Fock space is:

$$\hat{H} = \bigoplus_{M \in \mathbb{N}} \hat{H}_M . \quad (2.9)$$

This operator can be expressed in terms of creation ( $\hat{\psi}^\dagger(\mathbf{r})$ ) and annihilation ( $\hat{\psi}(\mathbf{r})$ ) operators, which satisfy  $\{\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')\} = \delta(\mathbf{x} - \mathbf{x}')$ . Using these operators we can write:

$$\hat{H}[v] = \int d^3\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \bar{h}[v](\mathbf{r}) \hat{\psi}(\mathbf{r}) , \quad (2.10)$$

here

$$\bar{h}[v](\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + \hat{v}_H(\mathbf{r}) + v(\mathbf{r}) , \quad (2.11)$$

and

$$\hat{v}_H(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\hat{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \quad (2.12)$$

The energy operator  $\hat{H}$  is a function of the 1-body external potential  $v$ , this observation is essential for the development of density-functional theory.

The operator  $\hat{n}(\mathbf{r})$  corresponds to the density operator, which is defined as:

$$\hat{n}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) . \quad (2.13)$$

The particle-number operator is  $\hat{N} = \int \hat{n}$ . The operator  $\hat{H}[v]$  is particle-conserving,  $[\hat{H}[v], \hat{N}] = 0$ . This means that a measurement of an energy of the system conserves the number of particles, an observation that does not hold at high energies.

### 2.1.2 Functional Derivatives

It is customary to introduce a space of functions before defining functionals, which are the central objects of this work. Let  $G$  be a Banach space. A functional  $f$  is typically defined as a map  $f : G \rightarrow \mathbb{R}$ . However, we will refer to anything that takes values on a space of functions as a functional.

Suppose  $n, m \in G$  are given, the variation of  $f$  at  $n$  in the  $m$  direction is:

$$\delta_m f[n] = \lim_{\epsilon \rightarrow 0} \frac{f(n + \epsilon m) - f(n)}{\epsilon} . \quad (2.14)$$

We say  $f$  is differentiable if there is a linear functional  $\delta f / \delta n$  such that

$$\delta_m f[n] = \left\langle \frac{\delta f}{\delta n}[n], m \right\rangle \quad (2.15)$$

for any  $m \in G$ . For example, in  $L^2(\mathbb{R}^3)$  we have that:

$$\left\langle \frac{\delta f}{\delta n}[n], m \right\rangle = \int d^3\mathbf{x} \frac{\delta f}{\delta n(\mathbf{x})}[n] m(\mathbf{x}) . \quad (2.16)$$

The function  $\delta f / \delta n(\mathbf{x})$  is called the *functional derivative*.

## 2.2 Energy Functionals

The ground-state energy of a system of electrons under a 1-body external potential  $v$  is:

$$E(M; [v]) = \inf \{ \langle \psi_M | \hat{H}[v] | \psi_M \rangle \mid |\psi\rangle \in \mathcal{H}_M, M \in \mathbb{N} \} . \quad (2.17)$$

To calculate the above quantity one needs the number of particles and the 1-body external potential; although, the energy of a system of electrons is in fact a function of many variables: masses, charges, spin, etc. The electron-electron interaction potential is another parameter needed to determine the energy. The ground-state problem would be easy to solve if the electron-electron interaction were negligible, because we would only need a Slater-determinant to describe the energy; consequently, excited states would be easy to estimate as well.

For the development of density-functionals it is convenient to analyze the different components of the energy operator. We thus define the following operator

$$\hat{H}_\lambda[v; \hat{W}] = \hat{H}_\lambda^0[\hat{W}] + \int d^3\mathbf{r} v(\mathbf{r}) \hat{n}(\mathbf{r}) , \quad (2.18)$$

where

$$\hat{H}_\lambda^0[\hat{W}] = \hat{T} + \lambda \hat{W} , \quad (2.19)$$

here  $\hat{W}$  is an electron-electron interaction operator. We will assume that  $\hat{W}$  is given, but it must bear mind that different choices are allowed. For example, screened, electron-electron repulsion.

From the minimization of Eq. (2.17) the following physical theorem emerges, due to Hohenberg and Kohn:

**Theorem 1.** Assume a Hamiltonian  $\hat{H}_\lambda$ , and two potentials  $v$  and  $v'$  that differ by more than a constant are given. Two non-degenerate ground-state kets  $|\psi\rangle$  and



$|\psi'\rangle$  corresponding to  $v$  and  $v'$ , respectively, cannot give rise to the same density,  $\langle\psi|\hat{n}(\mathbf{x})|\psi\rangle \neq \langle\psi'|\hat{n}(\mathbf{x})|\psi'\rangle$ .

A corollary of the above theorem, often overlooked in the literature, is that the potential *and* number of particles determine the density, and vice versa. This correspondence requires a proper mathematical map.

One can extract a non-degenerate ket from Eq. (2.17) as follows:

$$|\Upsilon_M[v]\rangle = \arg \inf_{|\phi\rangle \in \mathcal{H}_M} \langle\phi|\hat{H}[v]|\phi\rangle . \quad (2.20)$$

Suppose  $\mathcal{V}$  is a space of potentials and  $\mathcal{D}_M$  is a space of the densities generated by the non-degenerate kets coming from  $\mathcal{V}$ ; this space of kets can be expressed as  $|\Upsilon_M[\mathcal{V}]\rangle$ . Theorem 1 implies that there is a map between the spaces  $\mathcal{D}_M$  and  $\mathcal{V}$ . Let us define the map  $\Lambda_M : \mathcal{V} \rightarrow \mathcal{D}_M$ . Hence, for a given number of particles  $M$  and potential  $v \in \mathcal{V}$  we obtain the density by setting  $\Lambda_M[v]$ . Using  $\Lambda_M$  we can define a *density-functional*  $|\tilde{\Upsilon}[n]\rangle = |\Upsilon \circ \Lambda_M^{-1}[n]\rangle$ . This last observation allows us to define an energy functional via the relation  $E_{\text{HK}}[n; v] = \langle\tilde{\Upsilon}[n]|\hat{H}[\hat{W}, v]|\tilde{\Upsilon}[n]\rangle$ . An interesting observation, also made by Hohenberg and Kohn, is that  $E_{\text{HK}}$ , for a given external potential  $v$  and number of particles  $M$ , can be minimized over the set  $\mathcal{D}_M$  to give the ground-state of the system corresponding to the potential  $v$ . Note that the definition of the energy functional  $E_{\text{HK}}$  involves *only* densities with integer number of electrons.

The second theorem also due to Hohenberg and Kohn is:

Theorem 2. For a given potential  $v \in \mathcal{V}$  and number of electrons  $M$ , the ground-state energy of the system is

$$\inf_{n \in \mathcal{D}_M} E_{\text{HK}}[n; v] . \quad (2.21)$$

The construction of *computable* density-functionals is the challenge in ground-state quantum chemistry. As we will discuss in the next section, a density-functional approach has proven useful as an alternative to the strict formulation of quantum mechanics. Nevertheless,  $E_{\text{HK}}$  is defined within the space  $\mathcal{D}_M$ , which is a space that is restricted to densities that come from a ground-state.

### 2.3 Kohn-Sham Theory

A useful functional extending the domain of that of Hohenberg and Kohn is:

$$E_v^\lambda[n] = \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}) + \min_{|\psi\rangle \rightarrow n} \langle \psi | \hat{H}_\lambda^0[\hat{W}] | \psi \rangle . \quad (2.22)$$

Kohn and Sham defined an auxiliary system of non-interacting electrons that are subject to an effective external potential such that a preset density is recovered. The kinetic energy of this system of electrons is defined as:

$$T_s[n] = \inf \{ \langle \Phi | \hat{T} | \Phi \rangle | \langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle = n(\mathbf{r}) \} , \quad (2.23)$$

where the search for the minimum is performed strictly over Slater determinants. The energy is then split into three components:  $T_s$ ,  $\int v n$ , and the Hartree-exchange correlation part, which is defined as follows:

$$E_{\text{HXC}}[n] = E_v^1[n] - E_v^0[n] . \quad (2.24)$$

This quantity is the change of energy associated to connecting the system of fictitious electrons ( $\lambda = 0$ ) with that of fully interacting electrons. The HXC energy is further split into the Hartree energy and the XC energy, where we define the XC energy as:

$$E_{\text{HXC}}[n] = \int d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[n] . \quad (2.25)$$

The density is obtained from the orbitals that are solution of the KS equations, these read  $(-1/2\nabla_{\mathbf{r}}^2 + v_{\text{HXC}}(\mathbf{r}) + v(\mathbf{r}))\phi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}(\mathbf{r})$ , where  $v_{\text{HXC}}(\mathbf{r}) = \delta E_{\text{HXC}}/\delta n(\mathbf{r})$ . By occupying the KS orbitals of system we obtain the electronic density  $n(\mathbf{r}) = \sum_{\mathbf{k}} f_{\mathbf{k}} |\phi_{\mathbf{k}}|^2$ . The occupation numbers are obtained from a proper electron-distribution; for example, Fermi-Dirac.

### 2.4 Time-dependent Density-functional Theory

The dynamical properties of the molecular system are obtained from the TD Schrödinger Eq.:

$$i\partial_t |\Psi_\lambda[u](t)\rangle = \hat{H}_\lambda[u(t)] |\Psi_\lambda[v](t)\rangle . \quad (2.26)$$

For full interactions ( $\lambda = 1$ ), the solution of the above equation would provide us the TD wave function to calculate the dynamical observables of the system. It is quite difficult, however, to solve this problem even for a system with few electrons.

Assume that  $u^1$  is the TD external potential driving the molecule of fully-interacting electrons. In TDDFT, one searches for an effective potential  $v^0$  such that:

$$\langle \Psi_0[v^0](t) | \hat{n}(\mathbf{r}) | \Psi_0[v^0](t) \rangle = n[u^1](\mathbf{r}, t) . \quad (2.27)$$

In this equation  $n[u^1]$  is the density of the system of fully interacting electrons under potential  $u^1$ . If we denote the solution of the above equation as  $u^0$ , then we can define the HXC TD potential as follows:

$$u_{\text{HXC}}(\mathbf{r}, t) = u^0(\mathbf{r}, t) - u^1(\mathbf{r}, t) . \quad (2.28)$$

In analogy with ground-state DFT a one-to-one map between potentials and densities exists, this result is known as the Runge-Gross theorem. The information about the evolution of the system is calculated from the TD KS. The orbitals satisfy the equation  $(-1/2\nabla_{\mathbf{r}}^2 + u^0(\mathbf{r}, t))\phi_{\mathbf{k}}(\mathbf{r}, t) = i\partial_t\phi_{\mathbf{k}}(\mathbf{r}, t)$ . Because the function  $u^1$  is set by the user, the TD HXC potential is sufficient to determine the evolution of the system. Finally, the density of the system is  $n(\mathbf{r}, t) = \sum_{\mathbf{k}} f_{\mathbf{k}} |\varphi_{\mathbf{k}}(\mathbf{r}, t)|^2$ . From the evolution of the density we obtain the excitation frequencies of the molecule via the linear response formalism.

### 3. NON-ANALYTIC DENSITY FUNCTIONALS

In this chapter I show how to derive density-functionals with derivative discontinuities, essential features to describe molecular dissociation correctly.

#### 3.1 Introduction

When the distance between two atoms in a diatomic molecule is very large, their charges are predicted to be fractional numbers by the local-density approximation [1,2]. This is caused by an extra flexibility of the energy functional for densities that integrate to non-integer numbers [3]. The KS equations are single-particle equations. For a single orbital in KS theory, the molecule can be thought of as a set of wells that the electrons wander about; moreover, the integral of an orbital density around an atom is the probability of finding a KS electron in such atom. There is only one constraint on the total density: It must integrate to the total number of electrons in the molecule. A free electron is more likely to be found around the most favorable well, usually the deepest one. Unfortunately, the local-density approximation only provides wells to the KS electrons, and no matter how far atoms are (ground-state quantum mechanics involves no dynamics), the lack of constraints allow the KS electrons to wander free, giving rise to fractional charges, or non-physical spins, in the separated atoms. The KS potential should display a barrier between the atoms to force the likelihood of finding a KS electron in an atom to be consistent with ground-state quantum mechanics. However, no functional to date can display such barrier. The grids used in most codes are atom-centered. The barriers are present in

regions between the atoms; thus, if the bond distance is increased, the shells used for integration do not overlap anymore, missing the barriers.

Perdew et al. [4] (PPLB) showed that the problem mentioned above has its roots on the lack of derivative discontinuity of density functional approximations: To address static correlation, one expresses the wave function as a linear combination of wave functions describing the possible products of the dissociation, if the stretching is performed adiabatically one would obtain pure states and a desired spin symmetry. If one considers a system of well separated atoms close to their ground-states, X and Y, there is a wave function for XY, and there is one for the state  $X^+Y^-$ , each state is weighted by a probability amplitude. When the energy is measured, it is the sum of the energies of the states, weighted by their respective probabilities. PPLB showed that the energy minimizes non-analytically with a derivative discontinuity with respect to the average amount of charge transferred between the atoms. At dissociation, many density-functional approximations (DFAs), on the other hand, lead to a non-linear minimization where the energy derivative with respect to the amount of charge transfer is continuous, giving rise to a spurious state with fractional charges.

The DD of the XC energy functional and the linear dependency between discrete intervals is required to improve the physics of density functionals. The missing integer discontinuity causes problems in the estimation of ground-state properties like binding energies [1] and reaction barriers [5]. In TDDFT, the missing integer discontinuity is also required to improve the accuracy of density-functional approximations [6–11], especially to describe bond-stretching processes. In general, most approximations in DFT are unable to describe bond stretching without recurring to spin-polarized DFT, in which the symmetry is broken. The non-linearity with respect to the number of electrons is pervasive and affects all calculations that use continuously differentiable XC energy functionals such as the local density approximation (LDA) [2]. These known problems point to the need to develop new functionals with the correct piecewise linearity, capable of describing bond-stretching without resorting to symmetry breaking.

The problem of fractional charges is usually addressed by splitting the Coulomb-repulsion potential into a short-range (SR) and long-range (LR) part [12, 13]. For the SR regime, a local exchange energy-functional is used, and for the LR regime, exact exchange is employed. This procedure improves the description of dissociation, but it does not completely yield neutral charges at infinite separation. Non-long range-corrected Hybrid functionals, by using non-local exchange energy, also offer improvements but not a complete solution to the problem. A usual problem with most approximate methods is that they, as mentioned earlier, break spin-symmetry and the orbitals employed are not, strictly speaking, Kohn-Sham orbitals, but orbitals closer to those of Hartree-Fock theory.

In this chapter I show how to solve the problem of fractional charges with a density-functional, herein defined, that is exact in the molecular dissociation limit, where it displays the desired non-analiticity. This functional allows us to divide the *space of molecular configurations* into two domains, a SR, and a long-range LR one. For the long-range domain, the energy is obtained from the functional with the correct derivative discontinuity, and in the short range domain the regular density-functional approximation is used. Both regimes are then connected employing a kernel smoother. This procedure eliminates the problem of fractional charges, allows for the use of van der Waals functionals, and also offers simple ways to eliminate the self-interaction error.

### 3.2 Density-functional Theory for Molecular Dissociation

In this work we use 1-body density operators of the form

$$\hat{\gamma} = \int d^3\mathbf{r} d^3\mathbf{r}' \gamma(\mathbf{r}, \mathbf{r}') \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) , \quad (3.1)$$

where  $\gamma(\mathbf{r}, \mathbf{r}')$  is the coordinate representation of  $\hat{\gamma}$ :

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_n f_n \phi_n^*(\mathbf{r}) \phi_n(\mathbf{r}') , \quad (3.2)$$

$\phi_n$  is the orbital of level  $n$ , and  $\{f_n\}$  is the set of occupation numbers. Let us define the 1-body Hamiltonian operator:

$$\hat{h}_v = \int d^3\mathbf{r} \left[ \hat{t}(\mathbf{r}) + v(\mathbf{r})\hat{n}(\mathbf{r}) \right] . \quad (3.3)$$

where  $\hat{t}(\mathbf{r}) = 1/2(\nabla\hat{\psi}^\dagger(\mathbf{r})) \cdot (\nabla\hat{\psi}(\mathbf{r}))$ . In KS-DFT, the energy as a density functional is:

$$E_v[n] = \min_{\hat{\gamma} \rightarrow n} \mathcal{E}_v[\hat{\gamma}] , \quad (3.4)$$

where  $\mathcal{E}_v$  is the energy-functional:

$$\mathcal{E}_v[\hat{\gamma}] = \text{tr}\{\hat{h}_v\hat{\gamma}\} + E_{\text{HXC}}[n] . \quad (3.5)$$

Here,  $n(\mathbf{r}) = \text{tr}\{\hat{n}(\mathbf{r})\hat{\gamma}\}$ , and  $E_{\text{HXC}}[n] = E_{\text{H}}[n] + E_{\text{XC}}[n]$ .

$$E_{\text{H}}[n] = \int d^3\mathbf{r} d^3\mathbf{r}' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| \quad (3.6)$$

is the Hartree energy. The ground-state energy of the system is then obtained by minimizing  $E_v[n]$  for a given integer number of electrons,  $M$ . The ground-state energy is thus

$$E_v^0(M) = \min_{n \rightarrow M} E_v[n] . \quad (3.7)$$

The minimization in Eq. (3.4) is carried out over 1-body density matrices (1BDMs) of the form shown in Eq. (3.2). Hence, the orbitals are obtained from self-consistent solution of the KS equations:

$$\left( -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{HXC}}[n](\mathbf{r}) + v(\mathbf{r}) \right) \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}) . \quad (3.8)$$

The orbitals  $\{\varphi_k\}$  are functionals of the external potential  $v$ . By the Hohenberg-Kohn theorem there is an invertible map,  $u^{-1}$ , that assigns  $v$  a unique density. Let  $\{\varphi_k[n]\}$  be the KS orbitals expressed as density-functionals, where these are solutions of the KS equations with potential  $u[n]$ .

We assign each fragment a 1-body density operator representing the fragment with a given integer number of electrons,  $M_\alpha$ :

$$\gamma_{\alpha, M_\alpha}(\mathbf{r}, \mathbf{r}') = \sum_k f_{\alpha, k} \phi_{\alpha, k}^*(\mathbf{r}) \phi_{\alpha, k}(\mathbf{r}) . \quad (3.9)$$

The occupation numbers satisfy  $\sum_k f_{\alpha, k} = M_{\alpha, k}$ .

In section 3.3 I show that the XC energy functional for states with fractional number of electrons includes a relaxation kinetic energy that current DFAs miss. This problem is avoided in partition DFT by assigning discrete number of electrons to each fragment in the molecule and then averaging over an ensemble of different discrete configurations. The density operator describing a configuration is

$$\hat{\gamma}_{\mathbf{f}, \mathbf{M}} = \bigoplus_{\alpha} \hat{\gamma}_{\alpha, M_\alpha} , \quad (3.10)$$

where  $\mathbf{M} = \{M_\alpha\}$ . An ensemble of such molecules is represented by the density matrix:

$$\hat{\gamma}_{\mathbf{f}} = \sum_{\mathbf{M}} w_{\mathbf{M}} \hat{\gamma}_{\mathbf{f}, \mathbf{M}} , \quad (3.11)$$

where  $w_{\mathbf{M}} \geq 0$  and  $\sum_{\mathbf{M}} w_{\mathbf{M}} = 1$ . The use of direct sums allows us to express the 1-body energy in the form  $\text{tr}\{\hat{h}_v \hat{\gamma}_{\mathbf{f}, \mathbf{M}}\} = \sum_{\alpha} \text{tr}\{\hat{h}_v \hat{\gamma}_{\alpha, M_\alpha}\}$ . The energy of the localized electrons with classical electrostatic interactions is defined as:

$$\mathcal{G}_v[\hat{\gamma}_{\mathbf{f}, \mathbf{M}}] = \text{tr}\{\hat{h}_v \hat{\gamma}_{\mathbf{f}, \mathbf{M}}\} + E_{\text{HXC}}[n_{\mathbf{M}}^+] , \quad (3.12)$$

where  $n_{\mathbf{M}}^+(\mathbf{r}) = \text{tr}\{\hat{n}(\mathbf{r}) \hat{\gamma}_{\mathbf{f}, \mathbf{M}}\}$ .

Now introduce the functional:

$$\mathcal{G}_v[\hat{\gamma}_{\mathbf{f}}] = \sum_{\mathbf{M}} w_{\mathbf{M}} \mathcal{G}_v[\hat{\gamma}_{\mathbf{f}, \mathbf{M}}] . \quad (3.13)$$

The energy of an auxiliary molecular configuration is:

$$G_v(\mathbf{N}) = \inf_{\hat{\gamma}_{\mathbf{f}} \rightarrow \mathbf{N}} \mathcal{G}_v[\hat{\gamma}_{\mathbf{f}}] , \quad (3.14)$$



where  $\mathbf{N} = \{N_\alpha\}$  are fractional numbers. Finally the auxiliary ground-state is obtained by minimizing over electron-occupation of the fragments, we denote this energy as  $G_v^0$  and is given by:

$$G_v^0(M) = \inf_{\mathbf{N} \rightarrow M} G_v(\mathbf{N}) . \quad (3.15)$$

The function  $G$  displays derivative discontinuities when the fragments have integer number of electrons, it is exact in the atomization limit, when all fragments are at infinite separation, and it also reveals where the avoided crossing point is located.

The total 1-body external potential of the system is a sum of fragment 1-body potentials,  $v = \sum_\alpha v_\alpha$ .  $v_\alpha$  is the potential representing the interaction between an electron and the nuclei in fragment  $\alpha$ . In partition density functional theory (PDFT) [14], a given electronic density  $n$ , can be decomposed into localized fragment-densities by solving the minimization problem:

$$\min \left\{ \sum_\alpha E_{v_\alpha}[n_\alpha] \mid \sum_\alpha n_\alpha = n \right\} . \quad (3.16)$$

This requires the introduction of an auxiliary Lagrange multiplier, the partition potential, that represents  $n$ . The densities that solve the above problem are density-functionals and are denoted as  $\{\tilde{n}_\alpha\}$ . The density of a fragment is given by a sum of KS orbital-densities:  $\tilde{n}_\alpha = \sum_k f_{\alpha,k} |\varphi_{\alpha,k}|^2$ .  $\varphi_{\alpha,k}$  satisfies the equation:

$$\left( -\frac{1}{2} \nabla^2 + v_{\text{HXC}}[n_\alpha](\mathbf{r}) + v_\alpha(\mathbf{r}) + v_p(\mathbf{r}) \right) \varphi_{\alpha,k}(\mathbf{r}) = \epsilon_{\alpha,k} \varphi_{\alpha,k}(\mathbf{r}) , \quad (3.17)$$

where  $v_p$  is the partition potential, a Lagrange-multiplier used to satisfy the constraint shown in Eq. (3.16). The partition potential can be expressed as a density-functional; for each density there is a corresponding partition potential, and vice versa. Using these orbitals we introduce the 1BDM  $\hat{\gamma}_{\alpha,M_\alpha}^p[n](\mathbf{r}, \mathbf{r}') = \sum_\alpha f_{\alpha,M_\alpha} \varphi_{\alpha,k}^*(\mathbf{r}) \varphi_{\alpha,k}(\mathbf{r}')$ . Where these orbitals are density-functionals as well. Now, the energy functional is expressed as:

$$E_v[n] = \mathcal{G}_v[\hat{\gamma}^p[n]] + E_p^k[n] , \quad (3.18)$$

where  $\hat{\gamma}^p = \sum_{\mathbf{M}} w_{\mathbf{M}}^p \hat{\gamma}_{\mathbf{M}}^p$ , and  $E_p^k[n] = \text{tr}\{\hat{t}(\hat{\gamma}[n] - \hat{\gamma}^p[n])\}$ ; in section 4.5 I show a method to approximate  $E_p^k$ . If the functional  $E_p$  were known, then minimization

of  $E_v[n]$  could be carried out over a complete basis set representing the orbitals of a fragment. And, solution of the partition KS equations would yield the localized fragment densities. Fortunately, basis sets for orbital expansion are constructed using atom-localized basis-functions. Thus we restrict the fragment 1BDM to be of the form

$$\gamma_{\alpha, M_\alpha}^L(\mathbf{r}, \mathbf{r}') = \sum_{\mu\nu} P_{\mu\nu}^\alpha(M_\alpha) \phi_{\alpha, \mu}^*(\mathbf{r}) \phi_{\alpha, \nu}(\mathbf{r}') , \quad (3.19)$$

where  $\{\phi_{\alpha, \mu}\}$  are contracted, atomic basis-functions, and

$$P_{\mu\nu}^\alpha(M_\alpha) = \sum_{\mathbf{k}} f_{\mathbf{k}}(M_\alpha) (C_{\mu, M_\alpha}^\alpha)^* C_{\nu, M_\alpha}^\alpha . \quad (3.20)$$

We denote the space of 1BDM of the form  $\sum_{\mathbf{M}} w_{\mathbf{M}} \hat{\gamma}_{\mathbf{M}}^L$ , where  $\hat{\gamma}_{\mathbf{M}}^L = \oplus_{\alpha} \hat{\gamma}_{\alpha, M_\alpha}^L$ , as  $\mathcal{L}_{\mathbf{f}}$ .

Let  $\hat{\gamma}_{\mathbf{f}, 0} = \arg \inf \{\mathcal{G}_v[\hat{\gamma}_{\mathbf{f}}] \mid \hat{\gamma}_{\mathbf{f}} \in \mathcal{L}_{\mathbf{f}}\}$  be an optimal density matrix of the fragmented molecule. The calculation of  $\hat{\gamma}_{\mathbf{f}, 0}$  consists in the following: Set the fragment occupation numbers  $\mathbf{M}$ . Suppose  $n_{\mathbf{M}}$  is the total density of the fragments in the  $\mathbf{M}$  electronic configuration. Define the matrix

$$F_{\mu\nu}^\alpha[n_{\mathbf{M}}] = \int d^3\mathbf{r} \phi_{\alpha, \mu}^*(\mathbf{r}) \hat{f}[n_{\mathbf{M}}](\mathbf{r}) \phi_{\alpha, \nu}(\mathbf{r}) , \quad (3.21)$$

where  $\hat{f}[n_{\mathbf{M}}](\mathbf{r}) = -1/2\nabla^2 + v_{\text{HXC}}[n_{\mathbf{M}}](\mathbf{r}) + v(\mathbf{r})$ . Also, let  $S_{\mu\nu}^\alpha = \int d^3\mathbf{r} \phi_{\alpha, \mu}^*(\mathbf{r}) \phi_{\alpha, \nu}(\mathbf{r})$ . The coefficients determining the optimal density matrix of a fragment are obtained from self-consistent solution of  $\mathbf{F}^\alpha \mathbf{C}_{M_\alpha}^\alpha = \epsilon^\alpha \mathbf{S}^\alpha \mathbf{C}_{M_\alpha}^\alpha$ . Once the coefficients are determined we can construct the optimal density matrix. The functional  $\mathcal{G}_v$  does not couple the statistical weights  $w_{\mathbf{M}}$ ; therefore, in a diatomic molecule,  $\hat{\gamma}_{\mathbf{f}, 0}$  represents states with complete charge transfer.

Define the electronic density:

$$n_0^+(\mathbf{r}) = \text{tr}\{\hat{n}(\mathbf{r}) \hat{\gamma}_{\mathbf{f}, 0}\} . \quad (3.22)$$

We use  $n_0^+$  to generate a biased XC local scalar field for the KS electrons. The biased orbitals of the system satisfy the Kohn-Sham equations:

$$\left( -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{H}}[n](\mathbf{r}) + v_{\text{XC}}[n_0^+](\mathbf{r}) + v(\mathbf{r}) \right) \varphi_n^0(\mathbf{r}) = \epsilon_n^0 \varphi_n^0(\mathbf{r}) , \quad (3.23)$$

where  $n(\mathbf{r}) = \sum_n f_n |\varphi_n^0(\mathbf{r})|^2$ . Hence, the 1-body KS density matrix of the complete molecule is  $\gamma_0(\mathbf{r}, \mathbf{r}') = \sum_n f_n (\varphi_n^0(\mathbf{r}))^* \varphi_n^0(\mathbf{r}')$ . By means of this quantity we calculate the biased ground-state energy:

$$E_v^0 = \text{tr}\{\hat{h}_v \hat{\gamma}_0\} + E_{\text{HXC}}[n_0] , \quad (3.24)$$

where  $n_0(\mathbf{r}) = \text{tr}\{\hat{n}(\mathbf{r}) \hat{\gamma}_0\}$ . Because  $n_0$  differs from the exact ground-state density of the system, we have the inequality:

$$E_v^0(M) \geq E_v(M) . \quad (3.25)$$

This inequality holds even if a DFA is used for the XC energy.

The methodology shown above assumes that the positions of the nuclei are fixed. We now denote  $\hat{\gamma}_0(\mathbf{X})$  and  $\hat{\gamma}_f(\mathbf{X})$  as the optimal 1-body density operators corresponding to a nuclear configuration represented by  $\mathbf{X}$ , a tuple of all nuclear coordinates. The function  $\mathcal{G}_f[\hat{\gamma}_0(\mathbf{X})]$  is correct at very large distances between the atoms. When these are brought together, the function  $\mathcal{G}_f[\hat{\gamma}_0(\mathbf{X})]$  overbinds the molecule because each atom is only subject to the electrostatic and XC forces due to the other atoms, increasing the interaction energy, while keeping the kinetic energy below its true value. The function  $\mathcal{G}_f[\hat{\gamma}_0(\mathbf{X})]$  cannot account for electron hopping between atoms properly, a variable quantifying the domain of application of  $\mathcal{G}_f$  is:

$$\eta(\mathbf{X}) = \left| \frac{\text{tr}\{\hat{h}_v(\hat{\gamma}_f^0(\mathbf{X}) - \hat{\gamma}_f^\infty)\}}{\delta_E} \right| , \quad (3.26)$$

where  $\hat{\gamma}_f^\infty$  is the 1BDM of the system at the complete fragmentation limit, i.e. when all the fragments are at infinite distance.  $\delta_E$  is a characteristic energy deviation. Let us partition the space of nuclear coordinates into LR and SR regions:

$$\Omega = \Omega_{\text{sr}} \cup \Omega_{\text{lr}} , \quad (3.27)$$

where

$$\Omega_{\text{lr}} = \{\mathbf{X} \in \Omega \mid \eta(\mathbf{X}) < \eta^{\text{ref}}\} . \quad (3.28)$$

Here,  $\eta^{\text{ref}}$  is the level of deviation tolerance with respect to  $\delta_E$ . The short range space is obviously the complement of the long range one.

Given a function of the nuclear coordinates  $f$ , we define its long range part as follows  $f_{\text{lr}}$ :

$$f_{\text{lr}}(\mathbf{X}) = \begin{cases} f(\mathbf{X}) & \text{if } \mathbf{X} \in \Omega_{\text{lr}} \\ 0 & \text{otherwise .} \end{cases} \quad (3.29)$$

If  $f$  is an observable, in general, its long range part, defined as above, will display discontinuities. Since observables are continuous, a smooth function can be obtained by an integral transformation of  $f_{\text{lr}}$ . If  $K_\theta(\mathbf{X}, \mathbf{X}')$  is a smoothing kernel, with  $\theta$  being a smoothing parameter, the filtered LR function reads:

$$\begin{aligned} \tilde{f}_{\text{lr}}(\mathbf{X}) &= \hat{K}_\theta(\mathbf{X}) * f_{\text{lr}} \\ &= \int d^{N_e} \mathbf{X}' K_\theta(\mathbf{X}, \mathbf{X}') f_{\text{lr}}(\mathbf{X}') \quad \forall \mathbf{X}' \in \Omega . \end{aligned} \quad (3.30)$$

For example, to correct the energy of a regular DFA, we first define  $\varepsilon_{v,\text{lr}}(\mathbf{X}) = \mathcal{G}_{\text{f}}[\hat{\gamma}_{\text{f}}^0(\mathbf{X})] - \mathcal{E}_v[\hat{\gamma}_0(\mathbf{X})]$ . The correction to the energy is thus:

$$\tilde{\varepsilon}_{v,\text{lr}}(\mathbf{X}) = \hat{K}_\theta(\mathbf{X}) * \varepsilon_{v,\text{lr}} . \quad (3.31)$$

Finally the ground-state energy estimation reads:

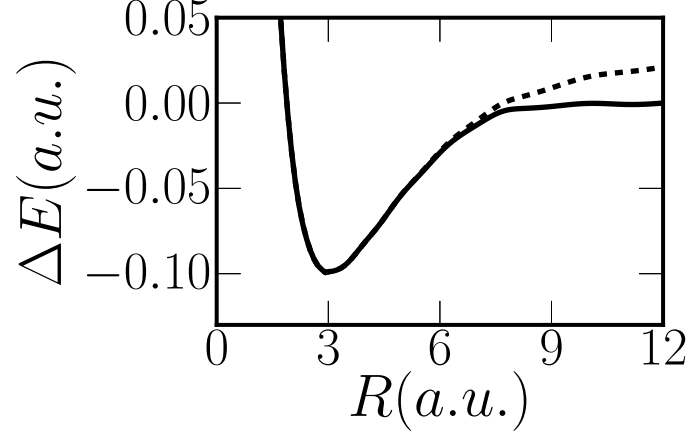
$$E_v^{\text{gs}}(\mathbf{X}) = \mathcal{E}_v[\hat{\gamma}_0(\mathbf{X})] + \tilde{\varepsilon}_{v,\text{lr}}(\mathbf{X}) . \quad (3.32)$$

An obvious advantage of the separation is that it allows for the use of van der Waals potentials in the LR region, avoiding the problem of charge penetration, i.e., large negative energies at equilibrium distances.

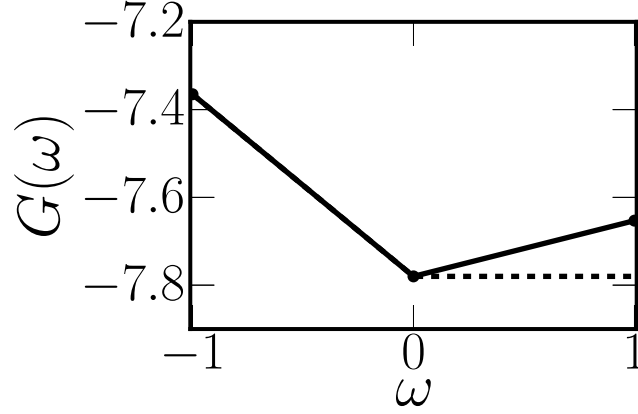
The calculations for our example were carried out using a script that I developed based on the quantum chemistry package PyQuante. The algorithm consists in generating the density matrices for the individual atoms and the molecule, then the Fock matrix is partitioned into two blocks, one for atom A and another for atom B (we restrict our discussion to diatomic molecules). The XC matrix is obtained using the usual multi-center grid suggested by Becke [15]. For each block the eigenvalues are obtained and then new densities are generated, the DIIS [16] algorithm

is employed for each fragment as well (the 6-311++G\*\* basis set was used [17–19]). Once the procedure has converged, an XC potential is generated for the molecule using the atomic densities. For this potential, the KS equations are solved, only the Hartree potential is updated. Once the calculations are performed for each nuclear configuration, the LR and SR regions are defined using  $\eta$ . A Gaussian kernel,  $K_\sigma(\mathbf{X}, \mathbf{X}') = \exp\left(-|\mathbf{X} - \mathbf{X}'|/2\sigma^2\right)$ , was used to connect the two regions ( $\sigma = 1.5$ ). The VWN LDA form for correlation was employed [22].

Now we apply the functional  $G_v$  to a simple system, lithium hydride; the original system employed by PPLB to illustrate the problem of the derivative discontinuities!. Let  $\omega$  be the average amount of electronic charge transferred between Li and H; a given value of  $\omega \in [-1, 1]$  corresponds to the lowest-energy configuration  $\text{Li}^\omega \cdots \text{H}^{-\omega}$ . If  $\mathbf{N} = (N_{\text{Li}}, N_{\text{H}})$ , then we define the average energy as a function of  $\omega$  is  $G(\omega) = G_v(J_{\text{Li}} + \omega, J_{\text{H}} - \omega)$ . Note that  $G(\omega) = E_{\text{Li}}^{\text{ens}}(J_{\text{Li}} + \omega) + E_{\text{H}}^{\text{ens}}(J_{\text{H}} - \omega)$ , where  $E_{\text{X}}^{\text{ens}}$  is the ensemble average at 0K of atom  $\text{X} = \text{Li}$  or  $\text{H}$  (see next section). The avoided crossing point is predicted by the function  $E_\omega$  to be  $R_c = 7.9$  with LDA. At distances less than  $R_c$  the auxiliary atoms are in the charge-transfer state of lowest energy,  $\text{Li}^+ \cdots \text{H}^-$ . At  $R_c$ , the configurations  $\text{Li}^+ \cdots \text{H}^-$ , and  $\text{Li} \cdots \text{H}$ , are equivalent in energy,  $G(1.0) = G(0.0)$ , so does any combination of those two configurations. In Fig. 4.1.a we show the dissociation curve of LiH with the LDA approximation and its correction. At complete dissociation, the charges predicted by LDA are approximately  $-0.3$  at hydrogen and  $+0.3$  on lithium. The functional  $G(\omega)$ , on the other hand, predicts neutral charges on each atom, and the derivative discontinuity (Fig. 4.1.b).



(a)



(b)

Figure 3.1. a) Dissociation energy curve of LiH. Solid line: Present method, dashed line: KS-LDA. b) Energy as a function of the charge transfer amount  $\omega$ . The dashed line is the energy at the avoided crossing point.

### 3.3 Density-functional Theory of Ensembles

The PPLB density functional is defined as:  $E_v[n] = F[n] + \int d^3\mathbf{r} n(\mathbf{r})v(\mathbf{r})$ , where  $F[n]$  is the constrained-search functional:

$$F[n] = \inf_{\hat{\Gamma} \rightarrow n} \text{tr}\{(\hat{T} + \hat{W})\hat{\Gamma}\}. \quad (3.33)$$

$\hat{T}$  is the kinetic energy operator,  $\hat{W}$  is the electron-electron repulsion operator, and  $\hat{\Gamma}$  is the density matrix operator in Fock space. The notation “ $\hat{\Gamma} \rightarrow n$ ” indicates

that the search for the infimum is performed over all density matrices satisfying  $\text{tr}\{\hat{\Gamma}\hat{n}(\mathbf{r})\} = n(\mathbf{r})$ . In order to carry out an equivalent search without requiring this density constraint, we introduce the Lagrange multiplier  $u[n]$  as indicated below. The generalized energy  $\mathcal{E}_N[u]$ , now a functional of  $u[n]$ , involves a search over all density matrices corresponding to  $N$  electrons ( $N$  is in general non-integer):

$$\mathcal{E}_N[u] = \inf_{\hat{\Gamma} \rightarrow N} \text{tr}\{(\hat{T} + \hat{W} + \int d^3\mathbf{r} u(\mathbf{r})\hat{n}(\mathbf{r}))\hat{\Gamma}\} . \quad (3.34)$$

Here,  $N$  is a real number between  $J$  and  $J + 1$ , where  $J$  is a positive integer. If the convexity assumption holds, i.e.  $\mathcal{E}_{J-1}[u] - \mathcal{E}_J[u] \geq \mathcal{E}_J[u] - \mathcal{E}_{J+1}[u]$  for any  $J$ , then  $\mathcal{E}_N[u] = (1 - \omega)\mathcal{E}_J[u] + \omega\mathcal{E}_{J+1}[u]$ , where  $\omega[n] = \int d^3\mathbf{r} n(\mathbf{r}) - J$ . We assume that  $0 < \omega < 1$ . The search for the infimum in Eq. (3.34) yields a density matrix  $\hat{\Gamma}[n]$  that is also a linear interpolation of integer-number density matrices,  $\hat{\Gamma}_J$  and  $\hat{\Gamma}_{J+1}$ . For example, if the bordering systems are pure ground states then  $\hat{\Gamma}_M = |\psi_M\rangle\langle\psi_M|$ ,  $M = J, J + 1$ . The densities of the pure states, that is  $n_M[u](\mathbf{r}) = \text{tr}\{\hat{\Gamma}_M[u]\hat{n}(\mathbf{r})\}$ ,  $M = J, J + 1$ , satisfy the restriction:

$$n(\mathbf{r}) = (1 - \omega)n_J[u](\mathbf{r}) + \omega n_{J+1}[u](\mathbf{r}) . \quad (3.35)$$

Because  $u$  is a functional of the density, so are the densities  $n_J$  and  $n_{J+1}$ . Inserting the minimizing density matrix  $\hat{\Gamma}[n]$  into  $F[n]$  we find that

$$F[n] = (1 - \omega[n])F[n_J] + \omega[n]F[n_{J+1}] . \quad (3.36)$$

For notational convenience, we introduce the average function:

$$y(x) = \begin{cases} 1 & x = 0 , \\ 1 - x & 0 < x < 1 , \\ 1 + x & -1 < x < 0 , \\ 0 & \text{otherwise} , \end{cases} \quad (3.37)$$

which allows us to express  $F$  (as well as the energy, density, etc.) as:

$$F[n] = \sum_M y(N - M)F[n_M] , \quad (3.38)$$

where  $N = \int n$  is of course a density-functional as well, and  $M$  runs over non-negative integer numbers. The functional  $F[n]$  is split in the usual Kohn-Sham manner:

$$F[n] = T_s[n] + E_{\text{HXC}}[n] , \quad (3.39)$$

where

$$T_s[n] = \inf \{ \text{tr}[\hat{T}\hat{\Gamma}_s] | \hat{\Gamma}_s \rightarrow n \} , \quad (3.40)$$

and  $E_{\text{HXC}}[n] = E_{\text{H}}[n] + E_{\text{XC}}[n]$ , the Hartree and exchange-correlation energy functionals.

The ground-state energy for the auxiliary system of non-interacting electrons,  $\mathcal{E}_{s,N}$  can be thought of as a functional of  $u_s(\mathbf{r})$ , an analog of  $u(\mathbf{r})$  introduced to carry out the non-interacting search version of Eq. (3.34):

$$\mathcal{E}_{s,N}[u_s] = \inf_{\hat{\Gamma}_s \rightarrow N} \text{tr} \{ (\hat{T} + \int d^3\mathbf{r} u_s(\mathbf{r}) \hat{n}(\mathbf{r})) \hat{\Gamma}_s \} . \quad (3.41)$$

As in the case of  $F[n]$ , the minimization performed to obtain  $T_s[n]$  returns two densities  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  that, when added together with the weight factor  $y(N - M)$ , yield the density  $n(\mathbf{r})$  of the interacting system. In what follows, we will refer to  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  as the non-interacting bordering-integer densities. We emphasize that even employing the *exact* exchange-correlation functional, the non-interacting integer density  $n_{s,M}(\mathbf{r})$  is *not* equal to the  $M$ -electron density of the interacting system (see Fig. 2.a for a model system we describe later on). Rather than being the ground-state density of  $M$  interacting electrons in  $v(\mathbf{r})$  (or  $M$  non-interacting electrons in  $v_s(\mathbf{r})$ ), it is the ground-state density of  $M$  non-interacting electrons in  $u_s(\mathbf{r})$ , a potential that differs from  $v_s(\mathbf{r})$  for non-integer  $M$ , as illustrated in Fig. 2.b. For example,  $n_{s,J}(\mathbf{r}) = \sum_{i=1}^J |\phi_i(\mathbf{r})|^2$ , and  $n_{s,J+1}(\mathbf{r}) = n_{s,J}(\mathbf{r}) + |\phi_{J+1}(\mathbf{r})|^2$ , where  $\{\phi_i\}(\mathbf{r})$  are single-particle orbitals that satisfy

$$\left( \hat{T} + \int d^3\mathbf{r} u_s(\mathbf{r}) \hat{n}(\mathbf{r}) \right) |\phi_i\rangle = \epsilon_i |\phi_i\rangle , \quad (3.42)$$

and by definition  $\sum_M y(N - M) n_{s,M}(\mathbf{r}) = n(\mathbf{r})$ . The non-interacting bordering-integer densities  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  are density functionals as well. Inserting Eq.



(3.39) on both sides of Eq. (3.38) and expanding  $T_s[n]$  as  $\sum_M y(N-M)T_s[n_{s,M}]$ , we obtain:

$$E_{\text{HXC}}[n] = \sum_M y(N-M) \left\{ (T_s[n_M] - T_s[n_{s,M}]) + E_{\text{HXC}}[n_M] \right\}, \quad (3.43)$$

an exact relation for  $E_{\text{HXC}}[n]$  in terms of quantities that describe pure quantum states, with  $T_s$  evaluated at both, the interacting and non-interacting bordering-integer densities. The form of the above equation follows from conjectures by Casida [20] and Harbola [21]. Here, we prove this formula from the assumption that the energy is a convex function of the number of electrons, and that the densities are ensemble- $v$ , interacting and non-interacting. Eq. (3.43) is trivially true when  $n(\mathbf{r})$  integrates to an integer number, but it is a useful identity when  $J < N < J + 1$  in the context of *approximate* DFT, as we show next.

In order to perform an ensemble-ground-state calculation, the external potential and non-integer number of electrons are required, one then needs to average two ground-state energies corresponding to states with integer numbers of electrons, provided the convexity assumption holds. These pure ground-state densities are combined to produce the ensemble density and, through a density-inversion procedure (as illustrated in the next section), one obtains ensemble KS potentials, which formally also come from Eq. (3.43) by means of functional differentiation. By approaching an integer number of electrons from above, one then observes the discontinuity in the XC potential. An alternative way of performing the calculation is by employing a suitable approximation to the functionals appearing on the right-hand-side of Eq. (3.43) and estimating the KS ensemble potential through the optimized effective potential method or variations of it (see, for example, Ref. [23]).

Let us denote as  $E_{\text{HXC}}^{\text{app}}[n_M]$  an approximation for  $M = 1, 2, \dots$ . Inserting this functional into Eq. (3.43) yields  $E_{\text{HXC}}^{\text{app}}[n]$ , a useful approximation to the ensemble

functional. The densities  $\{n_M\}$  can in principle be obtained from the search in  $F[n]$ , a functional we do not know. But we can circumvent the use of  $F[n]$  by defining

$$G_s[n] = \inf_{\{\tilde{n}_M\} \rightarrow n} \sum_M y(N-M) G_s[\tilde{n}_M] , \quad (3.44)$$

where

$$G_s[\tilde{n}_M] = \inf_{\hat{\Gamma}_s \rightarrow \tilde{n}_M} \text{tr} \{ (\hat{T} + \int d^3\mathbf{r} v_{\text{HXC}}^{\text{app}}[\tilde{n}_M](\mathbf{r}) \hat{n}(\mathbf{r})) \hat{\Gamma}_s \} . \quad (3.45)$$

By  $\{\tilde{n}_M\} \rightarrow n$  we refer to the constraint  $\sum_M y(N-M) \tilde{n}_M(\mathbf{r}) = n(\mathbf{r})$ . If  $J < N < J+1$ , the optimal densities  $\{n_M\}$  that minimize the right hand side of Eq. (3.44) are obtained from solving two sets of KS equations self-consistently: one with KS potential  $\tilde{v}_s[\tilde{n}_J] = v_{\text{HXC}}^{\text{app}}[\tilde{n}_J] + \tilde{u}$  and another with  $\tilde{v}_s[\tilde{n}_{J+1}] = v_{\text{HXC}}^{\text{app}}[\tilde{n}_{J+1}] + \tilde{u}$ . The orbitals arising from the KS equations with  $\tilde{v}_s[\tilde{n}_J]$  and  $\tilde{v}_s[\tilde{n}_{J+1}]$  are complex-squared and added together to yield the densities  $\tilde{n}_J$  and  $\tilde{n}_{J+1}$ . The external potential  $\tilde{u}$  is a Lagrange multiplier arising from the constraint  $\{\tilde{n}_M\} \rightarrow n$  and is to be varied until the constraint is satisfied. If  $\tilde{u}$  is set as the external potential of the system,  $v$ , then one obtains an approximation to the ensemble ground-state density. The functional in Eq. (3.44) reformulates the non-interacting  $v$ -representability problem for an approximate XC potential. When the *exact* XC potential is used, then setting  $\tilde{u} = v$  and solving the two sets of KS equations produces the orbitals needed to build the exact ground-state densities  $n_J$  and  $n_{J+1}$ .

The total energy of the system is

$$E_v^{\text{app}}[n] = \sum_M y(N-M) \left( T_s[n_M] + E_{\text{HXC}}^{\text{app}}[n_M] + \int d^3\mathbf{r} v(\mathbf{r}) n_M(\mathbf{r}) \right) . \quad (3.46)$$

The approximated ground state energy is found by setting  $E_N^{\text{app}}[v] = \inf_{n \rightarrow N} E_v^{\text{app}}[n]$ .

If the convexity assumption holds for our system of interest then

$$E_N^{\text{app}}[v] = \sum_M y(N-M) E_M^{\text{app}}[v] , \quad (3.47)$$

where

$$E_M^{\text{app}}[v] = \inf_{n_M} T_{s,M}[n_M] + E_{\text{HXC},M}^{\text{app}}[n_M] + \int d^3\mathbf{r} v(\mathbf{r}) n_M(\mathbf{r}) . \quad (3.48)$$

Eq. (3.47) shows that it is possible to recover the piecewise linear dependence of the approximated energy. Using the analog of Eq. (3.35) for  $J - 1 < N < J$  and the KS equations, it can be shown that:

$$\begin{aligned} \frac{\delta E_{\text{HXC}}^{\text{app}}}{\delta n(\mathbf{r})} &= E_J^{\text{app}} - E_{J-1}^{\text{app}} - \epsilon_J^{\text{app}} + v_{\text{HXC}}^{\text{app}}(\mathbf{r}) \\ &\quad + \sum_M y(N - M) \int d^3\mathbf{r}' \left( \frac{\delta E_{v,M}^{\text{app}}}{\delta n_M(\mathbf{r}')} \right) \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})} . \end{aligned} \quad (3.49)$$

The proof is as follows: Eq. (3.43) is equivalent to:

$$E_{\text{HXC}}[n] = -T_s[n] + \sum_M y(N - M)(T_s[n_M] + E_{\text{HXC}}[n_M]) . \quad (3.50)$$

Set  $v = u[n]$  as fixed. We can add  $-\int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}) + \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r})$  to the right hand side of the above equation to yield

$$E_{\text{HXC}}[n] = -T_s[n] - \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}) + \sum_M y(N - M)E_v[n_M] . \quad (3.51)$$

Suppose  $J - 1 < N < J$ , and note that  $\delta T_s / \delta n(\mathbf{r}) = \epsilon_J - u_s[n](\mathbf{r})$  [3], where  $u_s[n] = v_{\text{HXC}}[n] + u[n]$ . Using the chain and product rules we get the equation leading to Eq. (3.49):

$$\begin{aligned} \frac{\delta E_{\text{HXC}}}{\delta n(\mathbf{r})} &= -\epsilon_J + u_s[n](\mathbf{r}) - v(\mathbf{r}) + \sum_M \left\{ \frac{\delta N}{\delta n(\mathbf{r})} \frac{\partial y}{\partial x} (N - M) E_v[n_M] \right. \\ &\quad \left. + y(N - M) \int d^3\mathbf{r}' \frac{\delta E_v[n_M]}{\delta n_M(\mathbf{r}')} \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})} \right\} . \end{aligned} \quad (3.52)$$

Where

$$\frac{\partial y}{\partial x} = \begin{cases} \text{sgn}(-x) & -1 < x < 1 \\ 0 & \text{otherwise} , \end{cases} \quad (3.53)$$

and  $\delta N / \delta n(\mathbf{r}) = 1$ .

The term  $\delta E_{v,M}^{\text{app}} / \delta n_M(\mathbf{r}')$  is a constant at the minimum and  $\int d^3\mathbf{r}' \delta n_M(\mathbf{r}') / \delta n(\mathbf{r}) = 0$ , which leads to (dropping the Hartree contribution):

$$\frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} = -I^{\text{app}} - \epsilon_J^{\text{app}} + v_{\text{XC}}^{\text{app}}(\mathbf{r}) . \quad (3.54)$$

Since  $v_{\text{XC}}^{\text{app}} = \delta E_{\text{XC}}^{\text{app}} / \delta n$ , by definition, we obtain the Janak's theorem [24]  $\epsilon_J^{\text{app}} = -I^{\text{app}}$ , where  $I^{\text{app}} = E_{J-1}^{\text{app}}[u] - E_J^{\text{app}}[u]$  is the ionization energy of the system, and  $J-1 < N < J$ . We can also write Eq. (3.54) as:

$$\frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} = -I^{\text{app}} - \frac{\delta T_{\text{s}}}{\delta n(\mathbf{r})} - u(\mathbf{r}) . \quad (3.55)$$

This result allows us to calculate the XC DD as:

$$\begin{aligned} \Delta_{\text{XC}} &= \lim_{\Delta N \rightarrow 0^+} \left. \frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} \right|_{J+\Delta N} - \left. \frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} \right|_{J-\Delta N} \\ &= I^{\text{app}} - A^{\text{app}} - (\epsilon_{\text{L}}^{\text{app}} - \epsilon_{\text{H}}^{\text{app}}) , \end{aligned} \quad (3.56)$$

where  $A^{\text{app}} = E_J^{\text{app}}[u] - E_{J+1}^{\text{app}}[u]$  is the electron affinity of the  $J$ -electron system and  $\epsilon_{\text{H}}^{\text{app}}$  and  $\epsilon_{\text{L}}^{\text{app}}$  are the HOMO and LUMO orbital energies of the  $J$ -electron system. The XC DD turns out to be the difference between the fundamental gap of the real system and the KS gap. However, the approximated XC DD serves the same purpose: correct the KS particle band gap.

For an ensemble DFA the Janak's theorem is valid but the ionization theorem is not, in general. For example, for a system with *strictly*  $J$  electrons it is known that the LDA HOMO energy does not match the ionization predicted by LDA, i.e. when  $N = J$ ,  $\epsilon_J^{\text{LDA}} \neq -I^{\text{LDA}}$ . To satisfy the Janak's theorem, a constant must be added to the approximate XC potential to replace the HOMO orbital by the DFA ionization. When  $J-1 < N < J$ , this constant is  $-I - \epsilon_{\text{H}}(N = J)$ . At  $N = J$ , however, there is no need for such correction since the functional derivative with respect to the density at this point is not defined uniquely. On the other hand, using the XC energy functional, the ionization theorem for Coulombic systems leads to the well-known expression for the DD of the XC energy functional:  $-A - \epsilon_{\text{L}}$ .

Eq. (3.43) indicates that the approximation  $\tilde{E}_{\text{XC}}^{\text{app}}[n] = (1 - \omega)E_{\text{XC}}^{\text{app}}[n_{\text{s}, J-1}] + \omega E_{\text{XC}}^{\text{app}}[n_{\text{s}, J}]$  misses the different KS kinetic energy contributions leading to the piecewise linear features of the energy; also observe that  $\tilde{E}_{\text{XC}}^{\text{app}}$  is an average using the densities  $n_{\text{s}, M}$  instead of  $n_M$ . (Note:  $\tilde{E}_{\text{XC}}^{\text{app}}$  does hold for the uniform electron gas where the level spacing is negligible. The discrete-state densities returned in that

case by the minimization of the kinetic energy are negligibly different from those returned by  $F$  when both are evaluated at the electron-gas density  $n$ , and  $N$  is not an integer). Employing the optimized effective potential method, Kraisler and Kronik [23] showed that the linear dependency on the number of electrons is almost restored using the functional  $\tilde{E}_{\text{XC}}^{\text{app}}$ . With the kinetic energy and density contributions of Eq. (3.43), it is *completely* restored.

### 3.4 Numerical Example

To illustrate our findings, let us consider the example of a system of contact-interacting fermions [25, 26] described by the energy functional

$$E_v[n_M] = T_s[n_M] + E_H[n_M] + E_x[n_M] + \int dx v(x) n_M(x) , \quad (3.57)$$

where  $E_H[n_M] = 1/2 \int dx n_M^2(x)$  and  $E_x[n_M] = -1/4 \int dx n_M^2(x)$ . Suppose that

$$n_N^{\text{ref}}(x) = (Na/\pi) \text{sech}(ax) \quad (3.58)$$

is a density of interest with  $N = 2.5$  and  $a = 2$ . To find the potential  $u[n]$ , we minimize the error functional:

$$e_N^2[u] = \|\sqrt{n_N}[u] - \sqrt{n_N^{\text{ref}}}\|_2^2 . \quad (3.59)$$

The preset density is recovered by solving the KS equations for  $N = 2$  and  $N = 3$  and setting  $n_{2.5}[u](x) = \frac{1}{2}n_2[u](x) + \frac{1}{2}n_3[u](x)$ . Note that the self-consistent procedure has to be applied twice, once for  $v_x[n_2] = -\frac{1}{2}n_2(x)$  and once for  $v_x[n_3] = -\frac{1}{2}n_3(x)$ ; in both cases, the same estimation of  $u$  is used. The finite differences method was employed to solve the Kohn-Sham equations. We represent  $u$  in a spline basis set and  $e_N^2[u]$  is minimized with the Levenberg-Marquardt algorithm [27, 28]. This procedure yields the optimal potential  $u[n_{2.5}]$  shown in Fig. 4.1.a. Now we set that potential as fixed  $v(x) = u(x)$  and calculate the ensemble energy as a function of the number of electrons. Fig. 4.1.b shows the results. The solid line represents the piecewise ensemble interpolation and the dashed lines result from setting  $E_x[n_N] = -1/4 \int dx n_N^2(x)$

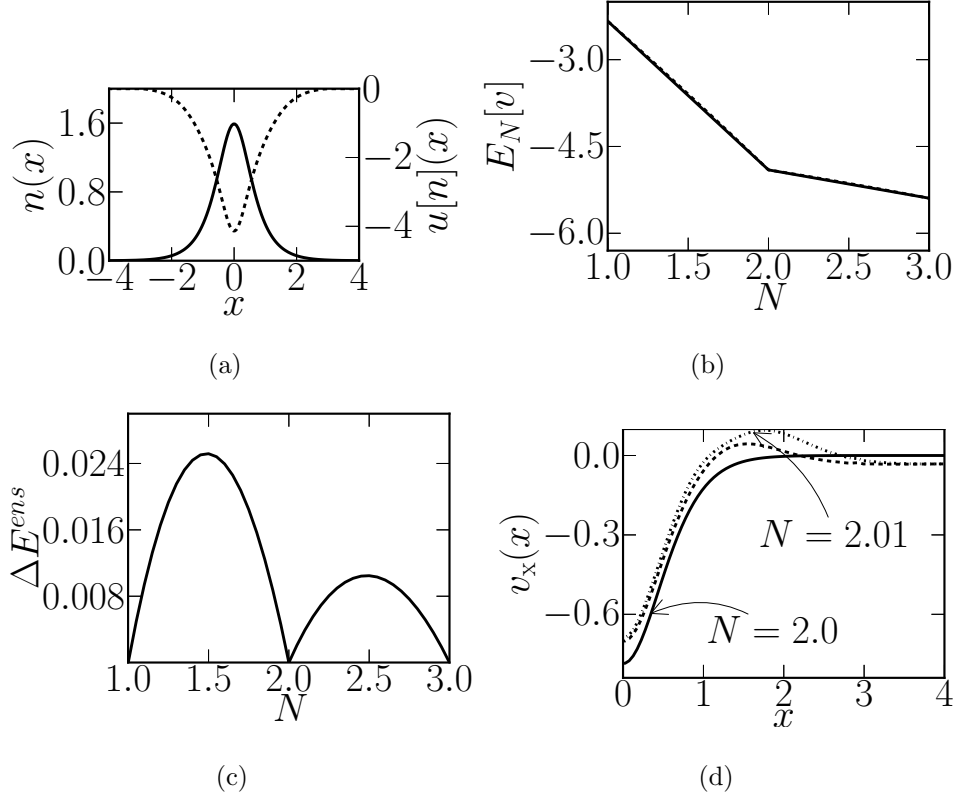


Figure 3.2. a) Preset ensemble density for  $N = 2.5$  (solid line), external potential (dashed line). b) Energy as a function of  $N$  (solid line), approximated energy (dashed line). c) Difference between Eq. (3.47) and the energy calculated using  $E_x[n_N] = -\lambda/4 \int n_N^2$  for any  $N$ . d) Ensemble exchange potential for  $N = 2.0$  (solid line),  $N = 2.15$  (dashed line), and  $N = 2.01$  (dashed-dotted line).

(which lacks the DD) to calculate the energy for any number of electrons. The solid and dashed lines look to the eye very close to each other, but their differences are made clear in Fig. 4.1.c. This difference is small for the functional chosen. The deviation is more severe for the 3D LDA functional [1].

In Fig. 3.2.d we show the estimation of the DD that results from inverting the KS equations for a non-integer number of electrons close to  $N = 2$ . To impose the Janak's theorem we minimize the error functional:

$$\tilde{e}_N^2[u_s] = \|\sqrt{n_N}[u_s] - \sqrt{n_N^{\text{ref}}}\|_2^2 + (\epsilon_{H,N}[u_s] - \epsilon_H^{\text{ref}})^2, \quad (3.60)$$

where  $n_N^{\text{ref}}$  is the target “exact” ensemble density that corresponds to the external potential shown in Fig. 3.2.a and electron number  $N$ .  $\epsilon_H^{\text{ref}}$  is the HOMO eigenvalue of the system with  $N = 3$ , obtained from solving the KS eqs. with  $v_x = -1/2n_3$  and external potential  $v$ .  $\tilde{e}_N^2$  is minimized using the conjugate-gradient method [29]. Because the ionization theorem is not satisfied, the potential satisfying  $v_x \rightarrow 0$  as  $x \rightarrow \pm\infty$  must be shifted by the constant  $-A - \epsilon_H(N = 3)$ . In accordance with Eq. (3.56), the ensemble exchange potential displays its corresponding derivative discontinuity. In Fig. 1d, the difference between the curves for  $N = 2.01$  and  $N = 2.0$  is  $-A[v] - \epsilon_L(N = 2.0)$ . If we shifted the solid curve by  $-I[v] - \epsilon_H(N = 2.0)$  ( $I[v] = E_1[v] - E_2[v]$ ) and compared the shifted curve (which is  $\lim_{N \rightarrow 2^-} v_x$ ) with the curve for  $N = 2.01$ , we would observe the discontinuity shown in Eq. (3.56) around the center of the 1d atom. On the other hand, the KS potential far from the center is given by  $u_s(x) \rightarrow \text{Const.} + 1/(2\phi_2)d^2\phi_2/dx^2$ . When the number of electrons is slightly increased above  $N = 2$ , we are adding a density  $\delta n = \epsilon n_3$  with a slower asymptotic decay than that of the system with 2 electrons, causing the discontinuity in Fig. 1.d because  $\delta n(x)$  only affects the potential at distances that are far from the center.

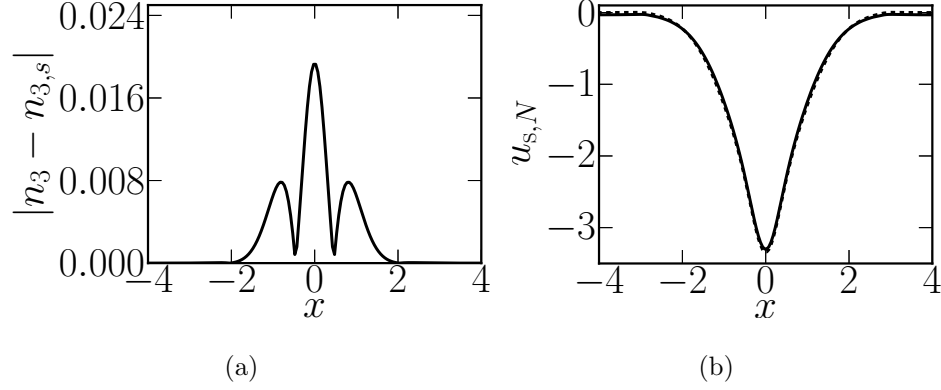


Figure 3.3. a) Difference between  $n_M$  and  $n_{s,M}$  for  $M = 3$ ; these densities are required to yield the density in Fig. 1.a. b) Kohn-Sham potentials corresponding to  $N = 2.5$  (solid line) and  $N = 2.0$  (dashed line).

A functional approximation for discrete states is sufficient to determine, through Eq. (3.43), an approximation to the XC functional that is also applicable to ensembles. However, solving the linearity problem in DFAs is not enough to solve the problem of molecular dissociation, which is caused by incorrect electron delocalization. A possible solution is to induce localization by partitioning a molecule into subsystems or a system-bath complex [30]. In such case, a functional with the correct DD is required since the theory of ensembles provides a rigorous framework for defining energy functionals of open systems. This idea follows the main argument of Ref. [4] pointing to the importance of the XC DD, which was the case of adiabatic electron transfer between two different atoms separated at certain large distance.

### 3.5 Conclusions

The construction of energy density-functionals, applicable to both molecular dissociation and the ensemble case, featuring derivative discontinuities has been shown in this work. These functionals can be used, within partition density functional theory, to recover the right atom (or fragment) electric charges without having to introduce



modifications to the local density approximation, and resort to non-local potential operators, which solve the problem partially.

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## 4. PARTITION DENSITY FUNCTIONALS

Partition density-functional theory (PDFT) is a set of tools and principles to treat molecules as composed of molecular fragments for computational purposes. In this chapter I present an extension of PDFT to also include spin-densities, approximate the partition potential, and consider molecular fragments under static electromagnetic fields.

### 4.1 Introduction

The practice of chemical sciences relies on the concept of molecular fragment. This can be from a single atom or ion, or groups of several atoms. The paradigm of dividing molecules into fragments has been useful to understand chemical reactivity and to identify the components of molecules that are present in a given sample. For this reason this concept needs to be formalized in terms of quantum mechanics and density functional theory (DFT). Bader [1] introduced a definition of atoms in molecules in terms of the gradient of the density. He suggested that an atom in a molecule is enclosed by the surface over which the gradient of the density is zero. This definition depends on the density, which is the key variable in DFT. Other definitions like those of Voroni [2] and Hirschfeld [3] also link the molecular electronic density to the definition of a fragment in a molecule. This motivates using DFT and spin-density functional theory (SDFT) as tools to further advance the quantum mechanics of molecules as composed of fragments joined together.

The scaling of the computational cost tends to be a limiting issue in quantum-chemical simulations; even an approximate DFT calculation may be expensive for

systems with hundreds of atoms. Several theories of molecular fragmentation have been proposed, whose purpose is to allow for a divide-and-conquer approach (for example, see Ref. [4]); this also establishes a qualitative way to study molecules because it permits to assign electrostatic charges to individual fragments [3]. The key is the division of a large molecular system into simpler and smaller subsystems for which arbitrarily accurate calculations are feasible. The division of a molecule into its atomic fragments is one of the most natural choices, and DFT offers several appealing ways to define “atoms in molecules” [5–8]. The basic idea is to take advantage of the fact that the external potential is the sum of nuclear attractive potentials. An energy functional can then be defined for an electron density associated with each individual nucleus; such energy functional only depends on a localized density which corresponds to that fragment and (ideally) tends to localize around the fragment’s nucleus. Two constraints are imposed: (i) the total number of electrons must be conserved, and (ii), the sum of localized densities must coincide with the total molecular density. The first constraint gives rise to the well-known chemical potential, and the second one yields a Lagrange multiplier which is a function of the position [7].

A mathematical formulation of the above ideas within DFT was then proposed in a series of papers by Cohen and collaborators [9–11]. The culmination of their work is Ref. [11], in which they introduced an energy functional  $E_f$ , defined as the minimum sum of the energies of the isolated fragments under the constraint that the sum of the fragments’ electronic densities add up to the total molecular density. In order to match  $E_f$  with the true energy functional, a residual functional needs to be introduced, the ‘partition energy’,  $E_p$ . Its associated potential, the *partition potential*, is a global potential. This means that every fragment is influenced by this scalar potential. The theory of Elliot et al. [11], named partition density functional theory (PDFT), is an exact reformulation of the ground state problem that provides solid footing to the ideas of Parr and co-workers [5–8]. There are other approaches that are closely related to partition theory and the philosophy it is based upon. One of these is the embedding theory, whose primary purpose is to treat a particular region within

a large system [12–14]. This theory is focused on the particular system-surrounding interaction, and offers the possibility to treat the system and surroundings with different levels of theory. Another partitioning scheme is frozen DFT, in which the density of the surroundings is fixed, then the total density of the system is divided into fragment densities and partitioning is applied to the KS equations [15, 16]. Additionally, a method called Self-consistent atomic deformation has been proposed, in which it is possible to partition the KS kinetic functional in terms of more tractable kinetic energy functionals, these depend on localized atom-centered densities. These densities are obtained from KS-type equations in which each fragment comes from a definite external potential that depends on the fragment kinetic energy functionals, exchange correlation, and external potentials [17–20]. In my opinion, this theory is quite close to PDFT, but the former is focused on the kinetic energy partition, while PDFT partitions the energy functional itself, and thus the deformation theory may be regarded as a special case of PDFT.

In this chapter I propose a simple extension of PDFT to derive computable approximations. Based on this extension, I formulate Partition *Spin*-density Functional Theory (PSDFT). First, the basic formalism is derived for a non-relativistic Hamiltonian which is free of static electric and magnetic fields. This requires partitioning the external potential in the usual way, and assigning spin-up and spin-down densities to each fragment. The associated partition potentials, which depend on the spin, are derived. This formalism is then extended to include electric and magnetic fields. We present two simple examples to illustrate how to apply the theory: An electron in a symmetric double-cosh potential, and a asymmetric double-cosh potential with three contact-interacting electrons. Finally, I propose a method that bridges SDFT and DFT, and eliminates the problem of symmetry breaking in approximated SDFT.

## 4.2 PDFT

We begin reviewing the basic formulation of PDFT. This theory offers a new way to minimize the energy density functional [11]:  $E_v[n] = F[n] + \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r})$  where  $F$  is the conventional Levy functional:  $F[n] = \min_{\hat{\Gamma} \rightarrow n} \text{tr}\{\hat{\Gamma}(\hat{T} + \hat{W})\}$  Here  $\hat{\Gamma}$  is the zero-temperature density matrix of the molecular system. This allows us to introduce variations in total number of electrons within a physical context.

Suppose we partition the external potential into  $N_f$  fragment potentials:

$$v(\mathbf{r}) = \sum_{\alpha=1}^{N_f} v_{\alpha}(\mathbf{r}) . \quad (4.1)$$

In principle this potential can be partitioned in many ways, depending on the physics of the system. For example, for a molecule with  $N_f$  nuclei, the external field of the electron is:

$$v(\mathbf{r}) = \sum_{\alpha=1}^{N_f} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} , \quad (4.2)$$

where  $Z_{\alpha}$  and  $\mathbf{R}_{\alpha}$  are the charge and position of the nucleus, respectively. A simple and natural way to partition the above external potential is by defining

$$v_{\alpha}(\mathbf{r}) = \sum_{I \in \text{frag}, \alpha} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|} , \quad (4.3)$$

where the sum runs over the nuclei of the fragment. Now partition the total electronic density as follows

$$n(\mathbf{r}) = \sum_{\alpha=1}^{N_f} n_{\alpha}(\mathbf{r}) . \quad (4.4)$$

Here the density  $n_{\alpha}$  is assigned to the potential  $v_{\alpha}$ . An intuitive energy functional can be defined for the molecule divided into fragments. If we imagine that the fragments are non-interacting then the energy of the system would be simply the sum over the isolated fragments' energies. However, such quantity would not be a density functional because it depends on each fragment's electronic density. This can be fixed by forcing



the sum of energies to be a minimum under the constraint that the sum of fragment's densities is the total molecular density. Hence, this energy functional is [11]:

$$E_f[n] = \min_{\{n_\alpha\} \rightarrow n} \sum_{\alpha} E_{v_\alpha}[n_\alpha] . \quad (4.5)$$

In order to relate this quantity with the true energy, the following density-functional, called partition energy, is introduced:

$$E_p[n] = E_v[n] - E_f[n] . \quad (4.6)$$

This functional is the difference of energies coming from two states: The true state of the molecule, which is given by  $E_v$ , and the state in which the molecule is partitioned. To obtain the ground state of the molecule one needs to minimize  $E_v[n]$ . If the minimization were carried out only in terms of the density, then the motion equation for the energy would be  $\delta E_v / \delta n(\mathbf{r}) = \mu$ , where the Lagrange multiplier  $\mu$  arises from the restriction that the total number of electrons is conserved. A similar and well known Lagrange multiplier is used in thermodynamics to minimize the free energy, this is termed chemical potential. Because  $\mu$  plays the same role as that used in thermodynamics, then it is also called chemical potential.

In order to minimize  $E_v$  within PDFT, Elliot et al. [11], in light of Equation (4.4), assume that the energy functional  $E_v$  can be expressed in the form  $E_v[n_1, n_2, \dots, n_{N_f}]$  because  $n = \sum_{\alpha} n_{\alpha}$ . Thus, around the minimum density, any perturbation to the total density that comes from a perturbation in a fragment's density will yield a higher value for the energy. This can be expressed by the Euler-Lagrange equation:

$$\frac{\delta E_v}{\delta n_{\alpha}(\mathbf{r})} = \mu . \quad (4.7)$$

On the other hand if we minimize  $E_f$  around the density  $n(\mathbf{r})$  which minimizes the energy  $E_v[n]$  we would obtain the motion equations (see Elliot et al. [11]):

$$\frac{\delta E_{v_{\alpha}}}{\delta n_{\alpha}(\mathbf{r})} + v_p(\mathbf{r}) = \mu , \quad (4.8)$$

where  $v_p(\mathbf{r})$  is a Lagrange multiplier which enforces that the sum of the densities,  $\{n_\alpha\}$ , add up to the total density  $n(\mathbf{r})$ . If we substitute Equation (4.18) into Equation (4.7) and compare with Equation (4.8) we get

$$v_p(\mathbf{r}) = \frac{\delta E_p}{\delta n_\alpha(\mathbf{r})} . \quad (4.9)$$

This equation shows that the potential  $v_p$  is similar to the chemical potential because it is the functional derivative of  $E_p$  with respect to any fragment's density. This methodology is valid in principle, however, it does not employ the total density as the main variable.

In Kohn-Sham DFT and its generalization, the density is used as an intrinsic parameter, for example, the exchange correlation potential is:

$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})} . \quad (4.10)$$

This definition of the exchange-correlation potential shows that variations of the total density are still employed even though the calculations use the Kohn-Sham orbitals. We can recover a similar expression for the  $v_p$  potential by noting that the derivative shown in Equation (4.9) is indeed a partial derivative and that  $n = \sum_\alpha n_\alpha$ , thus Equation (4.9) should be written as

$$v_p(\mathbf{r}) = \frac{\delta E_p[n = \sum_\beta n_\beta]}{\delta n_\alpha(\mathbf{r})} , \quad (4.11)$$

if we employ the chain rule as follows then we obtain:

$$v_p(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\delta E_p}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta n_\alpha(\mathbf{r})} = \frac{\delta E_p}{\delta n(\mathbf{r})} . \quad (4.12)$$

Because of this expression, we propose to minimize the functional  $E_v$  over the total density rather than over the fragments' densities. Moreover, the fragmentation energy  $E_f$  can be assumed to depend on each individual fragment's density  $n_\alpha(\mathbf{r})$ . And, the density-conservation rule can be introduced by means of the following Lagrange functional:

$$\begin{aligned} \mathcal{L}[\{n_\alpha\}, n] = & E_f[\{n_\alpha\}] + E_p[n] + \int d^3\mathbf{r} v_p(\mathbf{r}) \times \\ & \left[ \sum_\beta n_\beta(\mathbf{r}) - n(\mathbf{r}) \right] + \mu \left[ N - \int d^3\mathbf{r} \sum_\beta n_\beta(\mathbf{r}) \right] . \end{aligned} \quad (4.13)$$

This functional guarantees particle-number conservation and leads to the Euler-Lagrange equations expressed by Equation (4.8). Additionally, it leads to the previous result for the partition potential, that is:

$$v_p(\mathbf{r}) = \frac{\delta E_p}{\delta n(\mathbf{r})} . \quad (4.14)$$

This approach minimizes the energy along a single path in the space of electronic fragment densities. Thus, we assume that the fragments' electronic densities are functional of the total density. On the other hand, the approach of Elliot et al. [11] minimizes in multiple directions, this means that a variation in the density is caused by a variation in a fragment density. In our method, a variation of the density induces a variation in the electronic fragment densities. In the following section we will show how this alternative formulation of the minimizing procedure can be used to obtain practical approximations for the partition potential and the total energy  $E_v$ .

#### 4.3 Partition Spin Density Functional Theory for Scalar, External Potentials

Under the SDFT variational principle we need to minimize the following functional in order to obtain the ground state energy and spin-densities:

$$E_v[n_\uparrow, n_\downarrow] = F[n_\uparrow, n_\downarrow] + \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}) , \quad (4.15)$$

where  $F$  is, in analogy with the previous section:

$$F[n_\uparrow, n_\downarrow] = \min_{\hat{\Gamma} \rightarrow n_\uparrow, n_\downarrow} \text{tr}\{\hat{\Gamma}(\hat{T} + \hat{W})\} . \quad (4.16)$$

The potential is again partitioned as shown in Equation (4.1). Now, each fragment has two spin-densities associated to it. We identify the electronic density of fragment  $\alpha$  as  $n_\alpha(\mathbf{r}) = n_{\uparrow\alpha}(\mathbf{r}) + n_{\downarrow\alpha}(\mathbf{r})$ . Hence, the total spin-density  $n_\sigma$  is expressed as follows:

$$n_\sigma(\mathbf{r}) = \sum_{\alpha} n_{\sigma\alpha}(\mathbf{r}) . \quad (4.17)$$

Now, let us define the partition functional as

$$E_p[n_\uparrow, n_\downarrow] = E_v[n_\uparrow, n_\downarrow] - E_f[n_\uparrow, n_\downarrow] , \quad (4.18)$$

where

$$E_f[n_\uparrow, n_\downarrow] = \min_{\{n_{\sigma\alpha}\} \rightarrow n_\sigma} \sum_{\alpha} E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] . \quad (4.19)$$

As in the previous case, we need to introduce the following Lagrangian functional to minimize the ground state energy:

$$\begin{aligned} \mathcal{L}[\{n_{\sigma\alpha}\}, \{n_\sigma\}] = & E_f[\{n_{\sigma\alpha}\}] + E_p[\{n_\sigma\}] + \sum_{\sigma} \left\{ \int d^3\mathbf{r} v_{p,\sigma}(\mathbf{r}) \times \right. \\ & \left. \left[ \sum_{\beta} n_{\sigma\beta}(\mathbf{r}) - n_\sigma(\mathbf{r}) \right] \right\} + \mu \left[ N - \int d^3\mathbf{r} \sum_{\sigma\beta} n_{\sigma\beta}(\mathbf{r}) \right] . \end{aligned} \quad (4.20)$$

Minimization of this functional with respect to the densities yield the following motion Equation:

$$\frac{\delta E_{v_\alpha}}{\delta n_{\sigma\alpha}(\mathbf{r})} + v_{p,\sigma}(\mathbf{r}) = \mu , \quad (4.21)$$

$$v_{p,\sigma}(\mathbf{r}) = \frac{\delta E_p}{\delta n_\sigma(\mathbf{r})} . \quad (4.22)$$

This shows that each fragment must have the same chemical and partition potentials. If we partitioned into nuclear fragments, the polarized partition potential would repel or attract the electrons into the fragments to ensure that the total density corresponds to the ground state density. In general, the characteristics of the polarized partition potentials depend on how the fragments' energies ( $E_{v_\alpha}$ ) are defined. Besides, for computer simulations, the partition potentials for positions close to certain fragments might be assumed to depend only on nearest-neighbours densities. Now, to calculate the functionals  $\{E_{v_\alpha}\}$  we introduce fragment KS systems. Define the kinetic energy functional of a fragment with non-interacting electrons as follows:

$$T_{s,\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = \min_{\{\phi_{\sigma\alpha}\} \rightarrow n_{\sigma\alpha}} \sum_{i\sigma} f_{i\sigma\alpha} \langle \phi_{i\sigma\alpha} | \hat{t} | \phi_{i\sigma\alpha} \rangle . \quad (4.23)$$

This definition introduces KS spin-orbitals with occupation numbers for each fragment, there are denoted as  $\{f_{i\sigma\alpha}\}$ , these numbers are chosen following the theory of Perdew et al. [21]. Consequently, the localized spin-densities are expressed by means of the equation:

$$n_{\sigma\alpha}(\mathbf{r}) = \sum_i f_{i\sigma\alpha} |\phi_{i\sigma\alpha}(\mathbf{r})|^2 . \quad (4.24)$$

The total number of orbitals in our formulation is approximately the same as that in standard SDFT. For example, suppose we have a molecule with three spin-up electrons and a partition with two fragments has been chosen such that there are 1.5 electrons on each fragment. In SDFT we would need three spin-up orbitals to describe these electrons, while in PSDFT 4 orbitals are required. Hence, in terms of number of orbitals, the amount of computation does not increase significantly.

If the fragment spin-densities are non-interacting  $v$  representable, then these can be obtained from the KS equations:

$$\left[ -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{s,\sigma\alpha}(\mathbf{r}) \right] \phi_{i\sigma\alpha}(\mathbf{r}) = \epsilon_{i\sigma\alpha} \phi_{i\sigma\alpha}(\mathbf{r}) , \quad (4.25)$$

where we can set  $\frac{\delta T_{s,\alpha}}{\delta n_{\sigma\alpha}(\mathbf{r})} + v_{s,\sigma\alpha}(\mathbf{r}) = \mu$  Now, let us define:

$$E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = F[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} v_\alpha(\mathbf{r}) n_\alpha(\mathbf{r}) . \quad (4.26)$$

This energy can be split as follows

$$\begin{aligned} E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] &= T_{s,\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + E_H[n_{\uparrow\alpha}, n_{\downarrow\alpha}] \\ &\quad + E_{XC}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} v_\alpha(\mathbf{r}) n_\alpha(\mathbf{r}) . \end{aligned} \quad (4.27)$$

If we differentiate this functional with respect to the polarized fragment density  $n_{\sigma\alpha}$  and compare with the first Euler-Lagrange equation and Equation (4.23) we obtain

$$v_{s,\sigma\alpha}(\mathbf{r}) = v_H[n_\alpha](\mathbf{r}) + v_\alpha(\mathbf{r}) + v_{XC,\sigma}[n_{\uparrow\alpha}, n_{\downarrow\alpha}](\mathbf{r}) + v_{p,\sigma}(\mathbf{r}) . \quad (4.28)$$

Thus,  $v_{s,\sigma\alpha}$  differs from the usual definition only by the polarized partition potential. These effective potentials are input into the corresponding KS equations of each fragment which can be solved self-consistently: First, a reasonable approximation to the KS orbitals  $\{\phi_{i\sigma\alpha}\}$  is required, this can be employed to extract all the relevant densities which allow us to make the first estimation of the KS potentials, these potentials are then used to generate a new approximation to the densities and the KS potentials as well. If a tolerance in the spin-densities estimation has not been achieved then the procedure is repeated.

### 4.3.1 Practical Aspects of PSDFT

When the functional  $E_f$  is minimized for some spin-density pair  $n_\uparrow, n_\downarrow$  we obtain a set of electronic fragment-densities. Let us denote such set as  $\{\bar{n}_{\sigma\alpha}\}$ . Each one of these densities is a functional of the total spin-densities. In order to investigate the mutual influence of fragments, define the “Q” function:

$$Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) = \frac{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} . \quad (4.29)$$

The function  $Q$  satisfies the rule:

$$\sum_{\alpha} Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) = \delta_{\sigma,\sigma'} \delta(\mathbf{r} - \mathbf{r}') . \quad (4.30)$$

In order to take advantage of the  $Q$  functions we may need to employ an approximations. Suppose there is an idealized system in which a perturbation of the form  $\delta n_\sigma(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{z}) n_\sigma(\mathbf{r})$  induces a similar response in the spin-fragment  $\sigma\alpha$  as  $\delta \bar{n}_{\sigma\alpha}(\mathbf{r}') = \delta(\mathbf{r}' - \mathbf{z}) \bar{n}_{\sigma\alpha}(\mathbf{r}')$ , given that  $\delta \bar{n}_{\sigma\alpha}(\mathbf{r}') = \int d^3\mathbf{r} Q_{\sigma\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \delta n_\sigma(\mathbf{r})$  then we obtain the crude approximation to  $Q$ :

$$Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \approx \delta_{\sigma\sigma'} \delta(\mathbf{r}' - \mathbf{r}) \frac{\bar{n}_{\sigma'\alpha}(\mathbf{r}')}{n_\sigma(\mathbf{r})} . \quad (4.31)$$

This equation illustrates that the “ $Q$ ” function plays the role of that of a weighing factor, and it is analogous to a molar fraction. Also note that this approximation is consistent with the rule shown in Equation (4.30). To avoid confusion and for convenience we refer to the above Equation as the local- $Q$  approximation.

Let  $A$  be a functional that can be written as an explicit functional  $A[\{\bar{n}_{\sigma\alpha}[n_\uparrow, n_\downarrow]\}]$ , we can invoke the chain rule to obtain:

$$\frac{\delta A}{\delta n_\sigma(\mathbf{r})} = \sum_{\sigma'\alpha} \int d^3\mathbf{r}' \frac{\delta A}{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r}')} Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) . \quad (4.32)$$

For example let us apply this formula to the polarized partition potential:

$$v_{p,\sigma}(\mathbf{r}) = \sum_{\sigma'\alpha} \int d^3\mathbf{r}' v_{P,\sigma'\alpha}(\mathbf{r}') Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) , \quad (4.33)$$

where the spin-fragment partition potential is:

$$v_{p,\sigma\alpha}(\mathbf{r}) = \frac{\delta E_p}{\delta \bar{n}_{\sigma\alpha}(\mathbf{r})} . \quad (4.34)$$

Because  $n_\sigma = \sum_\alpha \bar{n}_\alpha$ , again, by the chain rule we obtain that:

$$v_{p,\sigma\alpha}(\mathbf{r}) = v_{p,\sigma\beta}(\mathbf{r}) . \quad (4.35)$$

Equation (4.32) is not useful for  $E_p$  because of the above result. Nonetheless, it can be applied to calculate the functional derivative of some functional  $E_p^*$  that approximates  $E_p$  and that does not satisfy the above equation. Because the partition KS equations are solved self-consistently then the fragment densities used during the iterative procedure are not the same as  $\{\bar{n}_{\sigma\alpha}\}$ . In other words, during the iterations, the partition potentials are assumed to be of the form shown in Equation (4.33), where they depend on the electronic fragment densities instead of the total density. We define such partition potential as follows:

$$u_{p,\sigma}[\{n_{\sigma\alpha}\}](\mathbf{r}) = \sum_{\sigma'\alpha} \int d^3\mathbf{r}' \frac{\delta E_p}{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r}')} \bigg|_{\bar{n}_{\mu\beta}=n_{\mu\beta}} Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \bigg|_{\bar{n}_{\mu\beta}=n_{\mu\beta}} , \quad (4.36)$$

and

$$u_{p,\sigma\alpha} = \frac{\delta E_p}{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r}')} \bigg|_{\bar{n}_{\mu\beta}=n_{\mu\beta}} . \quad (4.37)$$

For example, under the local-Q approximation we get:

$$u_{p,\sigma}[\{n_{\sigma\alpha}\}](\mathbf{r}) = \sum_\alpha u_{p,\sigma\alpha}(\mathbf{r}) \frac{\bar{n}_{\sigma\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})} . \quad (4.38)$$

Once the self-consistency has been achieved, all the fragment partition potentials for the channel  $\sigma$  become the same ( $u_{p,\sigma} \rightarrow v_{p,\sigma}$ ) (see section for more details). Now introduce the spin-fragment average:

$$\langle f_{\sigma',\alpha} \rangle_{sf}(\mathbf{r}) = \sum_{\sigma'\alpha} \int d^3\mathbf{r}' f_{\sigma',\alpha}(\mathbf{r}') Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) . \quad (4.39)$$

Therefore  $v_{p,\sigma}(\mathbf{r}) = \langle v_{p,\sigma'\alpha} \rangle_{sf}(\mathbf{r})$ , i.e. the polarized partition potential is an average over fragments and spins, and the  $Q$  function plays the role of weighing factor. It is plausible to conceive a fragment-localized approximation in which the spin-fragment partition potential is averaged only over its closest neighbours. This might be used to save computing time in practical calculations.

To obtain approximations to the partition potential it may be convenient to start from the partition functional. We can write Equation (4.18) as follows:

$$E_p[n_\uparrow, n_\downarrow] = E_k^p[n_\uparrow, n_\downarrow] + E_{\text{HXC}}^p[n_\uparrow, n_\downarrow] + E_{\text{ext}}^p[n_\uparrow, n_\downarrow] , \quad (4.40)$$

where the partition functional can be interpreted as the change of energy associated to the release of the electrons from the fragments. This gives origin to the kinetic ( $E_k^p$ ), Hartree-XC ( $E_{\text{HXC}}^p$ ), and external interaction ( $E_{\text{ext}}^p$ ) partition functionals that are associated to this change of state. The associated polarized partition potential for the self-consistent calculation is  $u_{p,\sigma} = u_{k,\sigma}^p + u_{\text{HXC},\sigma}^p + u_{\text{ext},\sigma}^p$ , where  $u_{X,\sigma}^p(\mathbf{r}) = \delta E_X^p / \delta n_\sigma(\mathbf{r})$  ( $X = k, \text{HXC}, \text{ext}$ ). The kinetic energy partition functional is given by the expression

$$E_k^p[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] - \sum_{\sigma\alpha} T[\bar{n}_{\uparrow\alpha}, \bar{n}_{\downarrow\alpha}] , \quad (4.41)$$

in this equation, and for the remaining partition terms, the polarized fragment densities are functionals of the total spin-densities. In principle the form of this functional is known because we could regard the orbitals as functionals of the total spin-densities. However, such approach is cumbersome because it might increase the computational demands, which would go against the practical purpose of PSDFT.

A simple approximation to the kinetic relaxation functional can be obtained by employing the von Weizsäcker kinetic energy functional:

$$T^{\text{vW}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = \frac{1}{2} \sum_{\sigma} \int d^3\mathbf{r} (\nabla \sqrt{n_{\sigma\alpha}(\mathbf{r})})^2 , \quad (4.42)$$

using the local-Q approximation, the partition kinetic potential  $u_{k,\sigma}^p$  is:

$$u_{k,\sigma}^p(\mathbf{r}) = -\frac{1}{2\sqrt{n_\sigma(\mathbf{r})}} \nabla^2 \sqrt{n_\sigma(\mathbf{r})} + \frac{1}{2} \sum_{\alpha} \frac{n_{\sigma\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})} \frac{1}{\sqrt{n_{\sigma\alpha}(\mathbf{r})}} \nabla^2 \sqrt{n_{\sigma\alpha}(\mathbf{r})} . \quad (4.43)$$

Even though the von Weizsäcker functional is convenient because of its simplicity, it is only exact for systems with one electron or less; alternative approximations to the kinetic energy functionals are required.

The contribution from the Hartree and XC energies is simply

$$E_{\text{HXC}}^p[n_\uparrow, n_\downarrow] = E_{\text{HXC}}[n_\uparrow, n_\downarrow] - \sum_{\sigma\alpha} E_{\text{HXC}}[\bar{n}_{\uparrow\alpha}, \bar{n}_{\downarrow\alpha}] , \quad (4.44)$$



under the local-Q approximation the contribution to the potential is

$$u_{\text{HXC},\sigma}^{\text{p}}(\mathbf{r}) = \frac{\delta E_{\text{HXC}}^{\text{p}}}{\delta n_{\sigma}(\mathbf{r})} - \sum_{\alpha} \frac{n_{\sigma\alpha}(\mathbf{r})}{n_{\sigma}(\mathbf{r})} \frac{\delta E_{\text{HXC},\alpha}^{\text{p}}}{\delta n_{\sigma\alpha}(\mathbf{r})} . \quad (4.45)$$

This equation can be used to approximate the HXC contribution to the partition potential. The analysis of this expression may lead to new approximations to the exchange-correlation potential because the partition potential has to yield the correct dissociation limit in molecules.

The last term of Equation (4.40) is:

$$E_{\text{ext}}^{\text{p}} = \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}) - \sum_{\alpha} \int d^3\mathbf{r} v_{\alpha}(\mathbf{r})\bar{n}_{\alpha}(\mathbf{r}) , \quad (4.46)$$

this external-field partition energy is approximated as:

$$u_{\text{ext},\sigma}^{\text{p}}(\mathbf{r}) \approx v(\mathbf{r}) - \sum_{\alpha} \frac{n_{\sigma\alpha}(\mathbf{r})}{n_{\sigma}(\mathbf{r})} v_{\alpha}(\mathbf{r}) . \quad (4.47)$$

As we will show in the next section, this term may not be negligible for the calculation of the density.

The approximations shown here for  $v_{\text{p},\sigma}$  and the density-density response function  $Q$  are entirely analogous for the spin-unpolarized case. We only need to drop the spin indices to the functions used. For example,

$$Q_{\alpha}(\mathbf{r}', \mathbf{r}) = \frac{\delta \bar{n}_{\alpha}(\mathbf{r}')}{\delta n(\mathbf{r})} \approx \delta(\mathbf{r} - \mathbf{r}') \frac{\bar{n}_{\alpha}(\mathbf{r}')}{n(\mathbf{r})} . \quad (4.48)$$

In Section 4.7 we show how to apply this formula for a simple system.

The physical insight in this formalism permits us to develop approximations that might help to decrease the computing time even below common approximate DFT calculations. Moreover, the method shown here is, in principle, exact and offers new ways to find approximations for a broad field of applications. For example, if a molecule were simulated with the local spin-density approximation (LSDA) we could reproduce the calculations by partitioning the molecule and introducing the partition potential that enforces that the sum of fragment densities add up to the LSDA density. Other functionals can be employed for this purpose as well, see [22]. Another

advantage of the partition method is that the SIE can be treated locally by selecting those fragments for which the SIE is relevant, like atoms with few electrons. Also, note that different levels of theory can also be employed for each fragment, for example, some fragments could be treated with the generalized gradient approximation while others with LSDA or exact-exchange, local derivative discontinuities can also be introduced.

The definitions of partition potential and fragmentation functional are general. There is an infinite number of partition functionals because one can define infinite  $E_f$  functionals. Moreover, this theory follows the philosophy of the generalized KS method [23], and it extends the non-interacting KS system such that an alternative fictitious system with interactions can be included. In principle any type of interaction can be introduced in the fictitious system, e.g. one may include a system defined as a Hartree-Fock system, where the electron-electron interactions are defined by Coulomb and exchange operators. Other example is a system of fictitious electrons interacting via screened Coulomb potential. To impose the restriction that the sum of squared modulus of each orbital yield the density, one needs a local multiplicative potential. In analogy with the partition potential, the residual potential of Seidl et al. [23] turns out to be the functional derivative of a residual functional with respect to the electronic density. If the energy of the fictitious system is closed enough to the actual energy, then the residual potential should have a small contribution to the ground state energy.

The chemical potential equalization defines the electronic occupation numbers for those fragments for which their energy functionals are differentiable with respect to their corresponding spin-densities. If the energy of a fragment is defined by means of the PPLB functional, then its energy is not differentiable when the number of electrons is an integer because the fragment does not have a definite chemical potential. To overcome this difficulty the energy has to be minimized with respect to the occupation numbers of the fragments without resorting to the chemical potential equalization.

This requires a derivative-free algorithm to minimize the energy. Despite this, the fragment KS equations remain valid.

#### 4.4 Inclusion of Static Electric and Magnetic Fields

It might not be convenient to partition an external field of the form  $v_{\mathcal{E}}(\mathbf{r}) = -\mu(\mathbf{r}) \cdot \mathcal{E}(\mathbf{r})$  as shown in Equation (4.1) because it would introduce spatial discontinuities that can be non-physical. A simpler and more physical alternative is to allow each fragment (which is defined by means of Equation (4.1)) to interact with the external field. Thus, the electrons in fragment  $\alpha$  now are subject to the external field:

$$\bar{v}_{\alpha}(\mathbf{r}) = v_{\alpha}(\mathbf{r}) + v_{\mathcal{E}}(\mathbf{r}) . \quad (4.49)$$

Note that Equation (4.1) does not hold for this type of partitioning because of the global character of the electric field.

The energy of a fragment now reads

$$E_{\bar{v}_{\alpha}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = F[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} \bar{v}_{\alpha}(\mathbf{r}) n_{\alpha}(\mathbf{r}) , \quad (4.50)$$

given that this potential is global as well, then the partition energy functional, which is a difference of the energy and the fragmentation energy, does not depend on the electric field explicitly. The spin-polarized KS potentials turn into

$$v_{s,\sigma\alpha}(\mathbf{r}) = v_H[n_{\alpha}](\mathbf{r}) + v_{\alpha}(\mathbf{r}) + v_{\mathcal{E}}(\mathbf{r}) + v_{\text{XC},\sigma}[n_{\uparrow\alpha}, n_{\downarrow\alpha}](\mathbf{r}) + v_{p,\sigma}(\mathbf{r}) . \quad (4.51)$$

This scheme enables one to calculate the polarizability of the ground state. A simple approximated approach is to calculate the ground state and find the partition potential, then it can be fixed and the density of the system can be estimated by solving the KS equations under the influence of the electric field.

The inclusion of magnetic fields is somewhat more involved than the previous case. For example, consider the Hamiltonian:

$$\hat{H}_{v,\mathbf{B}} = \hat{T} + \hat{W} + \int d^3\mathbf{r} \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) + \int d^3\mathbf{r} \hat{n}(\mathbf{r}) , v(\mathbf{r}) \quad (4.52)$$

where  $\hat{\mathbf{m}}$  and  $\mathbf{B}$  are the local magnetization and magnetic field, respectively. It is known that there is no a one-to-one correspondence between  $v$ ,  $\mathbf{B}$  and the local magnetization-density pair [24]. Capelle and Vignale [25] showed that if  $|\psi\rangle$  satisfies  $\hat{H}_{v,\mathbf{B}}|\psi\rangle = E|\psi\rangle$ , then it is possible to find perturbations  $\Delta v(\mathbf{r})$  and  $\Delta\mathbf{B}(\mathbf{r})$  such that:

$$\int d^3\mathbf{r} (\hat{n}(\mathbf{r})\Delta v(\mathbf{r}) + \hat{\mathbf{m}}(\mathbf{r}) \cdot \Delta\mathbf{B}(\mathbf{r}))|\psi\rangle = \Delta E|\psi\rangle . \quad (4.53)$$

This is valid as long as there is no level crossing induced by the magnetic field. The result of Capelle and Vignale poses a difficulty in applying our formalism to the Kohn Sham formalism of von Barth and Hedin [24] and Rajagopal and Callaway [26]. A simple solution is to regard the magnetic field as a fixed variable [27], thus the energy

$$E_{v,\mathbf{B}}[n_\uparrow, n_\downarrow] = G_{\mathbf{B}}[n_\uparrow, n_\downarrow] + \int d^3\mathbf{r} n(\mathbf{r})v(\mathbf{r}) , \quad (4.54)$$

is a functional of the spin-densities. The functional  $G$  is defined in the above Equation as follows:

$$G_{\mathbf{B}}[n_\uparrow, n_\downarrow] = \min_{\psi \rightarrow n_{\uparrow\alpha}, n_{\downarrow\alpha}} \langle \psi | \hat{T} + \hat{W} + \int d^3\mathbf{r} \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) | \psi \rangle . \quad (4.55)$$

Our partitioning approach is easily applicable to the functional given by Equation (4.54). If the energy of a fragment is defined as

$$E_{\bar{v}_\alpha, \mathbf{B}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = G_{\mathbf{B}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} n(\mathbf{r})\bar{v}_\alpha(\mathbf{r}) . \quad (4.56)$$

One may define a fragmentation energy as the sum of all fragments energies, where each energy is defined by the above equation. And the partition energy functional can be defined as the difference between the true energy functional and the fragmentation energy functional. The partition energy functional can thus be expanded as expressed in Equation (4.40), but a partition term must be added due to the magnetic field presence. This procedure avoids the non-uniqueness problems. However, it introduces more complexity to the energy functional because the magnetic field is treated as a inherent property of the system, just like the electron-electron interaction.

#### 4.5 Elimination of Spin-symmetry Breaking

The spin-polarized KS equations are quite successful because they break symmetry with the LSDA and can be used to eliminate the static correlation error of the LDA (no spin). Use of the unpolarized LDA misses the decomposition of the exchange energy into spin-channels. Curiously, the LDA allows us to construct Slater determinant with our desired spin-symmetry, but it does not perform well with energetics. I now show a way to avoid the symmetry breaking problem.

Let us express the Levy functional as:

$$F[n] = \min_{\{n_\uparrow, n_\downarrow\} \rightarrow n} F[n_\uparrow, n_\downarrow] . \quad (4.57)$$

Denote  $\tilde{n}_\uparrow, \tilde{n}_\downarrow$  as a pair of spin-densities that solve the above minimization problem. Suppose a given explicit form of the spin-polarized XC energy functional is given,  $E'_{\text{XC}}$ . Now express the XC density-functional as  $E_{\text{XC}}[n] = E'_{\text{XC}}[\tilde{n}_\uparrow, \tilde{n}_\downarrow]$ ; the spin-densities  $\{\tilde{n}_\sigma\}$  are functionals of the total density.

Using the chain rule we obtain:

$$v_{\text{XC}}(\mathbf{r}) = \sum_{\sigma} \int d^3\mathbf{r}' Q_{\sigma}(\mathbf{r}, \mathbf{r}') v_{\text{XC},\sigma}(\mathbf{r}') , \quad (4.58)$$

where  $Q_{\sigma}(\mathbf{r}, \mathbf{r}') = \delta\tilde{n}_{\sigma}(\mathbf{r}')/\delta n(\mathbf{r})$ , and  $v_{\text{XC},\sigma} = \delta E'_{\text{XC}}/\delta n_{\sigma}$ . Application of the local-Q approximation to the above formula gives:

$$v_{\text{XC}}^{\text{LQ}}(\mathbf{r}) = \sum_{\sigma} \frac{\tilde{n}_{\sigma}(\mathbf{r})}{n(\mathbf{r})} v_{\text{XC},\sigma}(\mathbf{r}) . \quad (4.59)$$

For practical approximations, the ratio of densities in the local-Q approximation can make difficult the calculations of the corresponding Fock matrix because the matrix elements, electrostatic integrals, would have to be calculated numerically. The need for numerical integrals could be eliminated by expanding the  $Q$  functions in terms of a Gaussian basis set. On the other hand, in the homogeneous electron gas, the polarized, approximated  $Q$  function is simply  $N_{\sigma}/N$ . For systems with large number of electrons, the spin channels are almost, equally populated. Therefore we arrive at the simple, practical approximation:

$$v_{\text{XC}}^{\text{hLQ}}(\mathbf{r}) = \frac{1}{2} v_{\text{XC},\uparrow}(\mathbf{r}) + \frac{1}{2} v_{\text{XC},\downarrow}(\mathbf{r}) . \quad (4.60)$$

Obviously, the formula is exact in the spin-unpolarized case because both spin channels are determined by the same polarized XC potential.

The prescription to connect approximations in SDFT with KS-DFT does not solve the static correlation problem, but allows us to better quantify exchange and correlation. However, if this solution of the symmetry breaking problem is combined with the non-analytic density functionals of chapter 3, the static correlation problem can be solved.

#### 4.6 Estimation of Partition Functionals

For an approximation in PDFPT to be computable and efficient, one needs to express each component of the partition energy as an explicit function of the electron-fragment densities. Suppose  $X \in (T, E_{\text{HXC}}, E_{\text{ext}})$  is some component of the energy, and let

$$X^{\text{P}}[n] = X[n] - \sum_{\alpha} X_{\alpha}[\tilde{n}_{\alpha}] . \quad (4.61)$$

Now divide the system into a fragment and its complement. Let  $\beta$  be our fragment of interest. Define  $\tilde{n}_{\beta}^{\text{c}} = n - \sum_{\alpha \neq \beta} \tilde{n}_{\alpha}$ . The total density of the system is that of fragment  $\beta$  plus the complementary density  $\tilde{n}_{\beta}^{\text{c}}$ . Now, assume that  $X[\tilde{n}_{\beta} + \tilde{n}_{\beta}^{\text{c}}]$  is a differentiable function of the density. If we further assume that  $\tilde{n}_{\beta}^{\text{c}}$  is a perturbation to the density  $\tilde{n}_{\beta}$  then:

$$X[\tilde{n}_{\beta} + \tilde{n}_{\beta}^{\text{c}}] \rightarrow X[\tilde{n}_{\beta}] + \int d^3\mathbf{r} \left. \frac{\delta X}{\delta n(\mathbf{r})} \right|_{n=\tilde{n}_{\beta}} \tilde{n}_{\beta}^{\text{c}}(\mathbf{r}) . \quad (4.62)$$

In this construction we omitted the other remaining fragments. A better estimation is thus:

$$X[n] \rightarrow \sum_{\alpha} \left( X[n_{\alpha}] + c_{\alpha} \int d^3\mathbf{r} \left. \frac{\delta X}{\delta n(\mathbf{r})} \right|_{n=n_{\alpha}} n_{\alpha}^{\text{c}}(\mathbf{r}) \right) . \quad (4.63)$$

Here,  $c_{\alpha}$ , the coupling strength, is a penalty parameter due to neglecting higher-order terms. The parameter  $c_{\alpha}$  is dependent on the fragments (or atoms) that surround the fragment (or atom)  $\alpha$ .

The form of the last equation leads us to identify the estimation to the  $X$  component of the partition energy as:

$$X^{\text{P}}[n] = \sum_{\alpha} c_{\alpha} \int d^3\mathbf{r} \left. \frac{\delta X}{\delta n(\mathbf{r})} \right|_{n=n_{\alpha}} \tilde{n}_{\alpha}^c(\mathbf{r}) . \quad (4.64)$$

A critical component of the partition energy, is the single-particle kinetic energy,  $X = T_{\text{s}}$ . Despite much effort is invested in finding approximations to the XC energy, the kinetic energy functional is an important contribution to the total energy. The explicit form of the LDA XC energy functional, and its interpretation, leads to a very practical use of the KS equations where the kinetic energy functional is not needed. Nonetheless, expressing  $T_{\text{s}}[n]$  as an explicit functional of the density is quite difficult because the definition of  $T_{\text{s}}$  is a constrained minimization problem: Given a density, we search for the best orbitals that yield  $n$  and minimize the kinetic energy. In few words, the formula defining  $T_{\text{s}}[n]$  is an algorithm.

An explicit functional form of  $T_{\text{s}}$  for multi-electron systems is unknown. Here I present a method to approximate the partition kinetic energy functional for applications in molecular dissociation: A simple approximation to  $T_{\text{s}}$  functional is the Thomas-Fermi (TF),  $T[n] = C_{\text{TF}} \int n^{7/3}$ ;  $C_{\text{TF}} = (6\pi^2/5)(3/8\pi)^{2/3}$ . This functional, however, is only suitable for the homogeneous, semi-classical, electron gas. For molecules, the TF functional does not bind atoms. Roughly speaking, the electrons gain too much momentum at “bonding” distances. For this reason, the coupling strengths should be less than the unity.

The single-particle kinetic energy component of the partition energy under the TF approximation is:

$$T_{\text{kin}}^{\text{P}}[n] = C'_{\text{TF}} \sum_{\alpha} c_{\alpha} \int d^3\mathbf{r} \tilde{n}_{\alpha}^{5/3}(\mathbf{r}) \tilde{n}^c(\mathbf{r}) , \quad (4.65)$$

where  $C'_{\text{TF}} = (7/3)C_{\text{TF}}$ . Finally, the partial partition potential corresponding to  $T_{\text{s}}$  is, ignoring the kinetic energy kernel:

$$v_{\text{kin},\alpha}^{\text{P}}(\mathbf{r}) = C'_{\text{TF}} \sum_{\beta \neq \alpha} c_{\beta} \tilde{n}_{\beta}^{5/3}(\mathbf{r}) . \quad (4.66)$$

The computation of this potential is fast, as well as its corresponding matrix elements over a basis set. Extending this functional to the spin-polarized only requires adding the spin-label to the quantities involve and summation over the spin-up and spin-down channels.

## 4.7 A Simple Illustration

### 4.7.1 An Electron in a Double-cosh Potential

Consider a one-dimensional electron under a double cosh potential (see Figure 4.1.a):

$$v(x) = V_0 \left( \frac{1}{\cosh^2((x + d/2)/a)} + \frac{1}{\cosh^2((x - d/2)/a)} \right), \quad (4.67)$$

where  $V_0 < 0$  is the depth of each well,  $d$  is the distance between the wells, and  $a$  is the width of each well. We can omit the spin subindex in the electronic densities because there is only one electron under the effect of the above potential. We want to find the ground state energy and density for this system. A partition scheme must be introduced to solve this problem. An intuitive choice is:

$$\begin{aligned} v_1(x) &= \frac{V_0}{\cosh^2((x + d/2)/a)} \\ v_2(x) &= \frac{V_0}{\cosh^2((x - d/2)/a)}. \end{aligned} \quad (4.68)$$

Given that this Equation represents a symmetric well and there is only one electron then we can set the occupation numbers as one half for each well.

Assume that  $\phi_1$  and  $\phi_2$  are the KS orbitals of fragments 1 and 2, respectively. Therefore the partition KS equations are:

$$\begin{aligned} \left[ -\frac{1}{2} \frac{d^2}{dx^2} + v_1(x) + u_p(x) \right] \phi_1(x) &= \epsilon_1 \phi_1(x) \\ \left[ -\frac{1}{2} \frac{d^2}{dx^2} + v_2(x) + u_p(x) \right] \phi_2(x) &= \epsilon_2 \phi_2(x), \end{aligned} \quad (4.69)$$



atomic units are used from now on. There is only two contributions to the partition potential. The first one comes from the kinetic energy relaxation. In this case we can use the von Weizsäcker functional and the local-Q approximation, thus

$$u_k^r(\mathbf{r}) = -\frac{1}{2\sqrt{n(x)}}\nabla^2\sqrt{n(x)} + \frac{1}{2}\frac{n_1(x)}{n(x)}\frac{1}{\sqrt{n_1(x)}}\nabla^2\sqrt{n_1(x)} + \frac{1}{2}\frac{n_2(x)}{n(x)}\frac{1}{\sqrt{n_2(x)}}\nabla^2\sqrt{n_2(x)}. \quad (4.70)$$

The second contribution comes from the relaxation with the external field

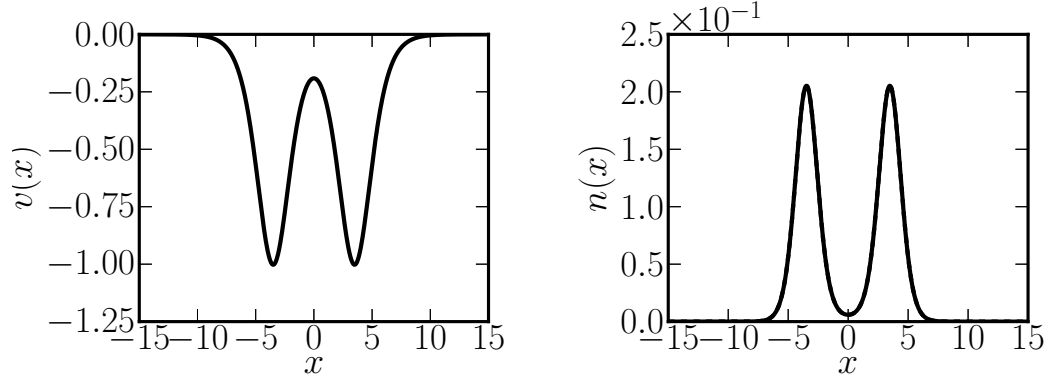
$$u_{\text{ext}}^r(x) = v(x) - \frac{n_1(x)}{n(x)}v_1(x) - \frac{n_2(x)}{n(x)}v_2(x), \quad (4.71)$$

the density of this system is obtained by means of

$$n(x) = n_1(x) + n_2(x) = \frac{1}{2}|\phi_1(x)|^2 + \frac{1}{2}|\phi_2(x)|^2. \quad (4.72)$$

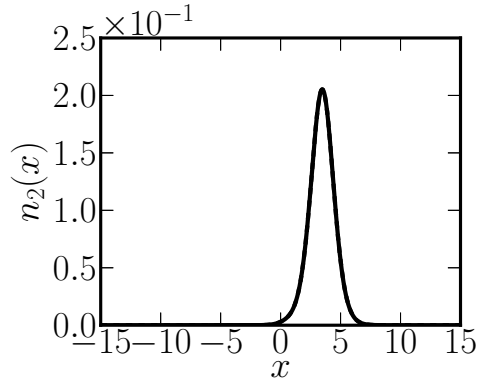
A reasonable initial estimation of the KS orbitals is necessary to solve these equations. The orbitals obtained by omitting the partition potential can be used initially, then the density is calculated and an estimation to the partition potential is obtained. If one solves the KS equations with such estimation one obtains a new set of spin-densities which can be used to obtain another approximation to the partition potential. This procedure is repeated until a desired convergence criterion is met.

To obtain the true density of the system we solve the Schrödinger equation with the finite difference method, and calculate the “exact” density of the system. A simple inversion algorithm was employed to obtain the exact partition potential: First, the partition potential is estimated by solving the fragment KS equations with the partition potential given by our local-Q approximation, then the KS equations are solved iteratively. The partition potential generated by this calculation is used as initial input to obtain a new approximation by means of the iterative scheme [28]:  $v_p^{(i+1)}(x) = v_p^{(i)}(x) + \gamma(n^{(i)}(x) - n(x))$  where  $n^0$  and  $n$  are the estimated and reference electronic density, respectively; and,  $\gamma$  is a positive constant. This procedure is performed until a convergence criterion is satisfied. Despite it performs well for our purposes, the formula shown above is rather slow, and might not be suitable for large scale inversion problems.

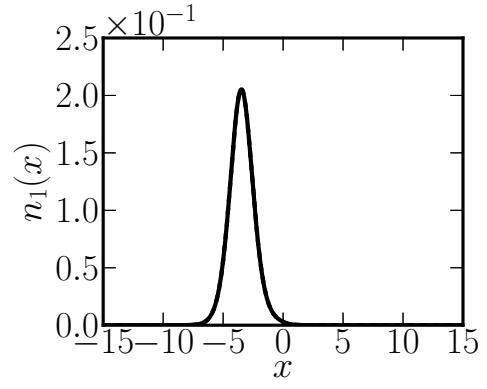


(a) Symmetric double-cosh potential

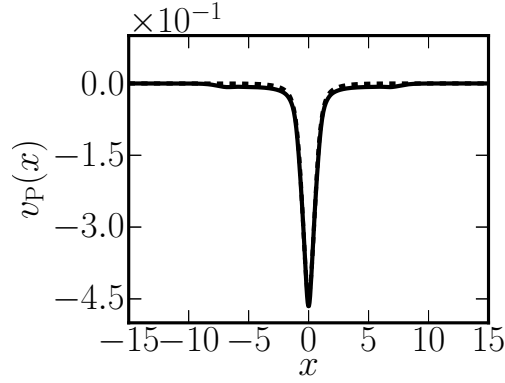
(b) Exact density



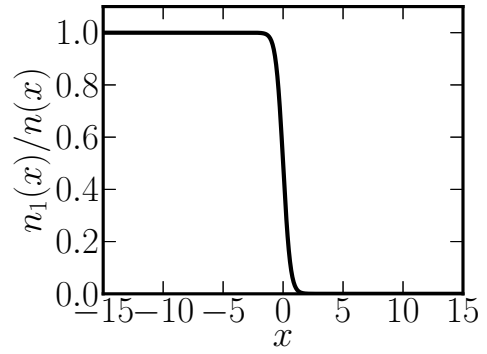
(c) Density of fragment 1



(d) Density of fragment 2



(e) Partition potential



(f) Integrated density-density response of fragment 1

Figure 4.1. Results for one electron in a double-cosh potential, parameter values:  $a = 2.0$ ,  $V_0 = 1.0$ , and  $d = 7.0$ . Dashed lines: approximation, solid line: exact.

Figure 4.1.a shows the potential employed to generate the densities, a box of length 30 a.u. was set for the simulation and a grid of size 600 was used to solve the KS equations. In Figure 4.1.b we show the electronic density of the system. The densities obtained by our approximation and the inversion method are quite close. The error in the density estimation is 0.01 % and in the energy is negligible, the Schrödinger and PDFT equations predict the ground state energy as -0.698 a.u. If we neglect the partition potential, which is equivalent to assume that the fragments do not interact, then the energy of the system would be -0.690 a.u. In this case the approximations work well because we are using exact functionals for the kinetic energy and the density is low in the intermediate region. This is also confirmed in Figure 4.1.c, which shows the partition potential. Qualitative agreement can be noted between the exact partition potential and the local-Q approximation. In this case we observe that the partition potential has a purely bonding character. The symmetry of the potential in this case offers an intuitive method to equalize the fragments' chemical potentials. By setting the occupation numbers on the left and right as 1/2, it is obtained equal eigenvalues on both sides.

Figures 4.1.d and 4.1.e illustrate the fragment densities. As expected, they are localized around their respective potential well. This relative localization of the densities might help to approach the ground state problem from a divide-and-conquer perspective. Finally, Figure 4.1.e shows the integrated response  $\int d^3\mathbf{r}' Q_1(\mathbf{r}, \mathbf{r}')$ , this function behaves like a step function. We note that the response of fragment 1 to perturbations in the density is negligible on the right hand side well. This is correct for positions that are far from the left hand side well. However, due to the local nature of the approximation employed, the response might be higher in the intermediate region. Thus non-local corrections are required to further improve the estimation of the partition potential. This simple example shows that it is possible to estimate the partition potential by means of intuitive approximations; improvement of these approximations will be subject for future works.

### 4.7.2 Application to 1d Contact-interacting Electrons

Now consider three electrons in an asymmetrical double cosh potential:

$$v(x) = \frac{V_{0,a}}{\cosh^2((x + d/2)/a)} + \frac{V_{0,b}}{\cosh^2((x - d/2)/a)} . \quad (4.73)$$

This potential is partitioned as in the previous case:

$$\begin{aligned} v_1(x) &= \frac{V_{0,a}}{\cosh^2((x + d/2)/a)} \\ v_2(x) &= \frac{V_{0,b}}{\cosh^2((x - d/2)/a)} . \end{aligned} \quad (4.74)$$

The Hamiltonian of this system is:

$$\hat{H} = \sum_{i=1}^3 -\frac{1}{2} \frac{\partial^2}{\partial x_i^2} + \lambda \sum_{i>j} \delta(x_i - x_j) + \sum_i v(x_i) . \quad (4.75)$$

For the sake of the discussion we ignore the correlation and only include the electron-exchange energy by means of the local approximation of Magyar and Burke [29]:

$$E_X[n, \zeta] = -\frac{\lambda}{4} \int dx \, n^2(x) [1 + \zeta^2(x)] . \quad (4.76)$$

The relaxation with the external field is approximated with Equation (4.47). The relaxation associated to the Hartree energy can be regarded as an electrostatic repulsion between the fragments. This term is

$$E_H^p = \int dx \, dx' \, n_1(x) v(x - x') n_2(x') , \quad (4.77)$$

where  $v(x - x') = \lambda \delta(x - x')$ . The above expression can also be obtained by employing its definition. Given that the fragment densities present a small overlapping, some exchange takes place in the bonding region. To account for this we used the definition shown in Equation (4.45) along with the Magyar-Burke functional. In the previous example we noted that the response of the fragments density might be higher than that obtained with the local-Q approximation. To improve this response we approximated the response function as  $Q_{\sigma'\alpha,\sigma} = \delta_{\sigma'\sigma} \delta(\mathbf{r}' - \mathbf{r})$ . This approximation does not satisfy the sum rule completely but it helps us to qualitatively predict the shape of the partition potential for the spin-up channel. For the all the other terms we

employed the local-Q approximation. Additionally, we neglected the kinetic partition functional because the von Weisäcker functional is valid for one electron or less, whereas the spin-up channel is populated by two electrons.

It is also possible to obtain the partition potentials that yield the “exact” densities. We emphasize that these partition potentials depend on the particular energy functional that we have chosen, i.e. contacting-interacting electrons with local exchange only in this case, and electronic correlation is ignored. These partition potentials can be obtained by a simple inversion procedure that is quite similar to that shown in the previous subsection. First we make an approximation to the partition potentials and KS orbitals, the potentials are fixed until self consistency is achieved, if the total density differs from the “exact” density then the following scheme is used to obtain a new estimate of the partition potentials [30]:

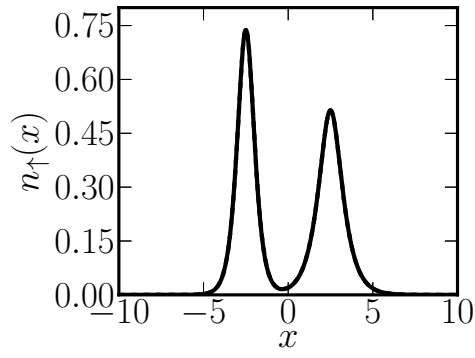
$$v_{p,\sigma}^{(i+1)}(x) = v_{p,\sigma}^{(i)}(x) + \gamma_{\sigma}(n_{\sigma}^{(i)}(x) - n_{\sigma}(x)) . \quad (4.78)$$

The procedure is repeated until the density converges. In this example we set the convergence tolerance as  $1.0 \times 10^{-5}$  for the estimation of the total density.

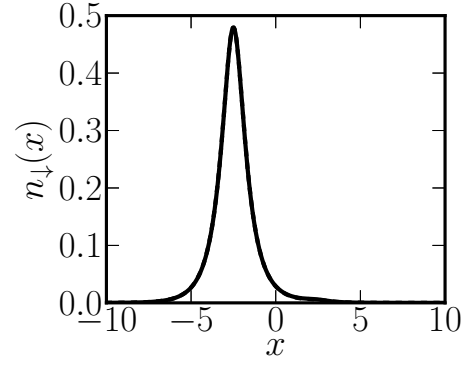
Table 4.1

Eigenvalues and energies of the pseudo HeH molecule. A box of length 30 a.u. and a grid of size 500 were employed. Dash lines: approximation, solid lines: exact. \* for the KS-SDFT results the fragment subindex refers to energy level instead of fragment.

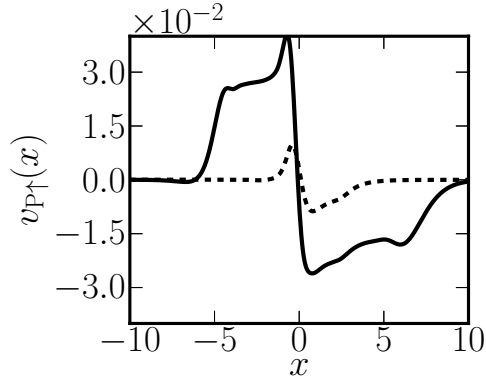
Method	$\epsilon_{\uparrow 1}$ (a.u.)	$\epsilon_{\uparrow 2}$ (a.u.)	$\epsilon_{\downarrow 1}$ (a.u.)	Energy (a.u.)	$E_P$ (a.u.)
Local Q	-0.9400	-0.3366	-0.1641	-1.6488	$-1.9 \times 10^{-3}$
PSDFT	-0.9127	-0.3531	-0.1635	-1.6473	$-7.5 \times 10^{-4}$
KS-DFT*	-0.9405	-0.3366	-0.1649	-1.6473	-



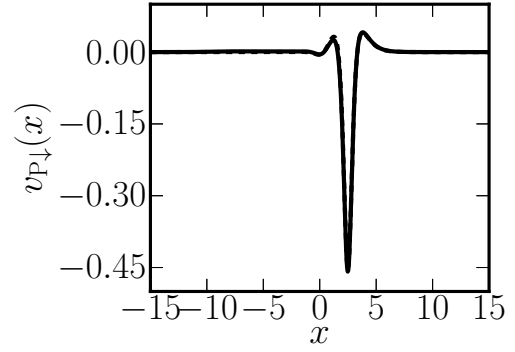
(a) Spin-up densities



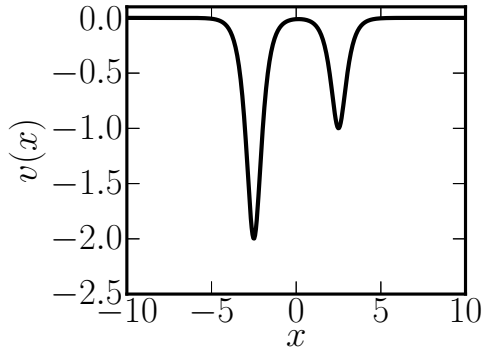
(b) Spin-down densities



(c) Spin-up partition potential



(d) Spin-down partition potential



(e) Potential

Figure 4.2. Results for three contact-interacting electrons in a double well potential; parameters:  $\lambda = 1.0$ ,  $a = 0.4$ ,  $d = 5.0$ ,  $V_{0,a} = 2$ ,  $V_{0,b} = 1$ . A box of length 30 with a grid of size 500 was used. Dashed lines: approximation, solid line: exact.

We found that there is essentially one spin-up electron on the left, one spin-up electron on the right, and one spin-down electron on the left. This is consistent with the physical picture obtained from applying the unrestricted Hartree-Fock method to the HeH molecule. Moreover, this integer-occupation phenomenon has been found to be persistent for fragments with large internuclear separation [31]. The numerical results are shown in Table 4.1. As expected the approximation used here tends to localize the densities around the corresponding potential wells. In Figures. 4.2.a and 4.2.b we show both the exact densities, and the densities obtained by our approximation. It may be observed that the partition theory predicts the spin-densities qualitatively. Moreover, the energies are close to one another, this suggests that it is possible to apply this theory to 3d Coulombic systems for which dissociation can be better described.

In Figures 4.2.c and 4.2.d the partition potentials are illustrated. The approximations work reasonably well. Nonetheless, the results with the approximation we used for the kinetic term suggests that contributions from the spin-densities of the whole molecule must be taken into account to improve the response function  $Q$ . The estimation of  $v_{p,\uparrow}$  might not be reliable enough in terms of accuracy but it predicts qualitatively the behavior of the “exact” partition potential obtained from the inversion in the bonding region. This potential shows a repulsive barrier for negative positions and an attractive well for positive positions. This basically shrinks the zero order spin-up density of the left fragment, and it spreads out the spin-up density of the right fragment. By zero order density I refer to that density obtained by neglecting the partition potentials while keeping fixed the occupation numbers. Therefore the local approximation employed for the  $Q$  function might be suitable as a first estimation in inversion procedure and on further refinements of the partition functional. Moreover, this simple example suggests that it is possible to determine in practice the partition potentials to obtain electron densities and energies than are size-consistent (see Ref. [22]).

Due to the non-differentiability of  $E_f$ , it is not possible to equalize the chemical potentials on both spin channels. This is reflected in the numerical values of the KS eigenvalues shown in Table 4.1. On the other hand, the partition energy was found to be small compared to the energy values. This is due to the particular choice of fragmentation energy, which includes the contributions from kinetic energy, electron-electron repulsion, and electron-nucleus interaction. Other type of fragmentation schemes may lead to higher values of partition energy, for example if we assume that the electrons do not repel each other then the partition energy should be higher because it would account for the electronic repulsion that takes place in the real system.

#### 4.8 Conclusions

In summary, a new approach to approximate the partition potential and also extended PDFT to include electronic spin-densities has been proposed. The introduction of the polarized partition functional guarantees the exactness of the theory as long as the spin-densities are “ $v_p$  representable”. The method presented here is a candidate to address the problems of regular KS-DFT related to molecular dissociation. It also offers flexibility to combine different XC energy functionals that are available, and include nearest-neighbor approximations to  $v_p$ . In the long term, these approximations may also be useful to speed up the computational simulations of large molecules. The cost and stability of these calculations will depend on the partitioning of the external potential, and the approximations to the XC and partition energy functionals.



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## 5. ACTION FUNCTIONALS

The Dirac-Frenkel principle of stationarity to find equations of motion that yield or approximate the time dependent Schrödinger equation is not applicable to time dependent density functional theory. Such incorrect application can lead to causality paradoxes in the interpretation of the Runge-Gross map. For example, a perturbation of the density in the future influences the external potential of the molecule in the past. In this chapter, I review and re-interpret recent solutions to this problem and propose an alternative formulation based on the space of Keldysh that restores the causality. I further show that conventional TD XC potentials can be obtained from this formalism, and how other TD XC potentials can be derived as well.

### 5.1 Introduction

To study the dynamics of molecules, algorithms based on time dependent density functional theory are quite used. Methods derived from TDDFT [1–3] are very flexible, improvable, and numerically efficient. The target objects to extract useful properties are the TD electronic density, and the density-density response functions. The methods of TDDFT are mainly used to study electronic excitation in the linear regime (i.e., analysing the density response to short perturbations), and the ground-state energy and density [4, 5].

The Runge-Gross (RG) [6] theorem is the pillar of TDDFT: Given the initial state of the system, the TD electronic density of the system is uniquely determined, up to a TD constant, by the TD external potential the system is subject to. This theorem was later extended by van Leeuwen [7], who showed that the

system of interacting electrons, whose equations of motion are extremely difficult to solve, can be represented by a system of free electrons that are subject to an effective TD potential, i.e., the KS equations. Some main challenges in TDDFT are solving accurately: Double excitations [8], van der Waals interactions, charge transfer excitations [9, 10], and electron-transfer rates of molecular junctions [11–13]. All the observables of the molecule can be interpreted as density-functionals because the wave function can be determined by a density-functional. The theorem of Runge and Gross, however, is limited to TD external potentials that are Taylor-expandable with respect to time. Eliminating such restriction is still ongoing research [?], as well as calculations of TD external potentials corresponding to a given TD density [15–17].

The ground-state exchange-correlation (XC) potential is the functional derivative of the XC energy in ground-state DFT. A similar relationship between the TD XC potential and a proper functional is difficult to find. [18] proposed a Dirac-Frenkel action functional with a variational principle for TDDFT. Following Ref. [18], Runge and Gross [6] expressed the TD XC potential as a functional derivative of a XC action functional with respect to the density. This assignment of XC potentials to actions led to a problem: a disturbance of the density in the future induces a potential-response in the past [19]. This implies that the inverse first order response functional violates causality.

Several approaches addressing the violations of causality are available. For example, an action functional based on the work of [20] in quantum field theory was proposed by Rajagopal [21]. However, in this formalism the density is not the main variable. A density-functional in the Keldysh contour obeying causality was introduced by van Leeuwen [22]. A pseudo-density in the Keldysh space that becomes the physical density upon a symmetry operation is the main variable in this case. The van Leeuwen formalism requires expansion and truncation, while that of Runge and Gross does not. [23] also resolved the causality violation by fixing a boundary condition in the Runge-Gross formulation.

In this chapter I present an alternative solution to the problem of causality by combining the formalisms of Vignale and Van Leeuwen, and does not require expansion nor display a dependency on the upper limit of the propagation. The method presented in this chapter also leads to a variational equation that relates the XC potential with a well-behaved XC action functional. I show that the ALDA and the optimized effective potential method are solutions of such variational equation.

## 5.2 Causality in TDDFT

Finding stationary values of the Dirac-Frenkel functional:

$$\mathcal{W}[|\psi\rangle; v] = \int_{t_0}^{t_1} dt \langle \psi(t) | i \frac{\partial}{\partial t} - \hat{H}[v](t) | \psi(t) \rangle , \quad (5.1)$$

not only allow us to derive the TDSE but also approximations to it. In this chapter we only consider non-relativistic Hamiltonians of the form:

$$\hat{H}[v](t) = \hat{T} + \hat{W} + \int d^3\mathbf{r} v(\mathbf{r}t) \hat{n}(\mathbf{r}) , \quad (5.2)$$

where  $\hat{T}$  and  $\hat{W}$  are the kinetic energy and electron-electron repulsion energy operators, respectively, and  $\hat{n}(\mathbf{r})$  is the density operator. The domain of the Dirac-Frenkel functional is the Hilbert space of antisymmetric wave-functions integrating to  $N$  electrons. The TDSE is a solution to the problem:  $\delta \mathcal{W}[|\psi\rangle; v] = 0$ . The boundary conditions are  $\delta|\psi(t_0)\rangle = \delta|\psi(t_1)\rangle = 0$ . The solution  $|\psi[v](t)\rangle$ , is a ket satisfying:  $i\partial_t|\psi[v](t)\rangle = \hat{H}[v](t)|\psi[v](t)\rangle$ . We say that  $|\psi[v](t)\rangle$  is a  $v$ -representable ket in real-time; its evolution is given by the unitary evolution operator applied to the initial state:

$$|\psi[v](t)\rangle = \hat{U}[v](t, t_0) |\psi(t_0)\rangle , \quad (5.3)$$

where

$$\hat{U}[v](t, t_0) = \hat{\mathcal{T}} \exp \left( -i \int_{t_0}^t ds \hat{H}[v](s) \right) . \quad (5.4)$$

$\hat{\mathcal{T}}$  is the time-ordering operator in real-time. The integral is taken over the interval  $[t_0, t]$ :

$$\int_{t_0}^t ds \hat{H}[v](s) := \lim_{\epsilon \rightarrow 0} \int_{t_0}^{t-|\epsilon|} ds \hat{H}[v](s) . \quad (5.5)$$

The above definition, when inserted into Eq. (5.4) and the result is applied to the initial state, determines the evolution of the system. The dependency on the potential of Eq. (5.4) is referred to as the *strict causality assumption*. This assumption is to be employed in the next section to simplify the formalism.

Our choice of integration is related to the question: Does a perturbation of the form  $\delta v_1(\mathbf{r}'t'; t) = c(\mathbf{r}')\delta(t - t')$  cause a response in any observable at time  $t$ , i.e., at the very moment when the perturbation occurs?. In this work I elect to postulate that the instantaneous perturbation  $\delta v_1$  does only affect the system strictly after it has occurred; enforcing the intuitive notion that the time delay between a cause and its effect has to be greater than zero. This choice on how the integration in time is taken excludes any response to  $\delta v_1(\mathbf{r}'t'; t)$  when  $t' \leq t$ .

From the strict causality assumption we can infer that  $\delta\hat{U}(t, t_0)/\delta v(\mathbf{r}'t') = 0$  if  $t = t'$  and that the ket  $|\psi[v](t)\rangle$  is a strictly causal functional of the potential: The potential  $v$  at times less than  $t$  determines  $|\psi[v](t)\rangle$ . Additionally, all observables of the form  $O[v](t) = \langle\psi(t_0)|\hat{U}^\dagger[v](t, t_0)\hat{O}\hat{U}[v](t, t_0)|\psi(t_0)\rangle$  are also strictly causal functionals of  $v$ , i.e.,

$$\frac{\delta O[v](t)}{\delta v(\mathbf{r}'t')} = 0 \quad t' \leq t. \quad (5.6)$$

For example, the density of the system,

$$n[v](\mathbf{r}t) = \langle\psi(t_0)|\hat{U}^\dagger[v](t, t_0)\hat{n}(\mathbf{r})\hat{U}[v](t, t_0)|\psi(t_0)\rangle, \quad (5.7)$$

is determined by the evolution of  $v$  in the interval  $[t_0, t)$  [3].

The potential  $v$  at times in  $[t_0, t)$  uniquely determines  $n$  in the interval  $[t_0, t)$ , and vice versa. If we denote as  $u[n]$  the external potential as a functional of the TD density, then a first order variation in  $u$  is given by a variation of  $n$  over the interval  $[t_0, t)$ :

$$\delta u[n](\mathbf{r}t) = \int_{t_0}^t dt' \int d^3\mathbf{r}' \chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t'), \quad (5.8)$$

where  $\chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') = \frac{\delta u(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}$ . Hence,  $\delta u(\mathbf{r}t)/\delta n(\mathbf{r}'t')$  for  $t \leq t'$  is not defined because it does not contribute to the integral of Eq. (5.8). For convenience we set:

$$\chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') = 0 \quad t \leq t'. \quad (5.9)$$

[23], however, employing the evolution equation of the current, showed that  $\delta u(\mathbf{r}t)/\delta n(\mathbf{r}'t')$  is related to  $\delta(t - t')$  and its first and second order time-derivatives when  $t = t'$ . This result is obtained under two assumptions different from ours: First,  $u(\mathbf{r}t)$  is determined by  $n(\mathbf{r}'t')$  for  $t' \leq t$ . And secondly, the functional derivative of the *stress* tensor with respect to the density vanishes at equal times. Our assumption avoids this singularity in  $\chi^{-1}$  and will be used to simplify our calculations in the Keldysh space.

Consider the RG action functional:

$$A_v[n] = \int_{t_0}^{t_1} dt \langle \psi[n](t) | i \frac{\partial}{\partial t} - \hat{H}[v](t) | \psi[n](t) \rangle , \quad (5.10)$$

where  $|\psi[n](t)\rangle = |\psi[u[n]](t)\rangle$ ,  $v$  is some TD external potential, and  $t_1 > t_0$ . Note that the ket  $|\psi[n](t)\rangle$  is causal, i.e., it is determined by  $n$  in the interval  $[t_0, t)$ . [6] imposed that  $\delta\psi(t_0) = \delta\psi(t_1) = 0$  and  $\delta A_v/\delta n(\mathbf{r}t) = 0$ , which leads to the following alternative form of the variational principle:

$$\frac{\delta B[n]}{\delta n(\mathbf{r}t)} - v(\mathbf{r}t) = 0 , \quad (5.11)$$

where  $B[n]$  is the action functional:  $B[n] = \int_{t_0}^{t_1} dt \langle \psi[n](t) | i \partial_t - \hat{T} - \hat{W} | \psi[n](t) \rangle$ . If Eq. (5.11) were valid then we could assert that [24]:  $u[n](\mathbf{r}t) = \delta B[n]/\delta n(\mathbf{r}t)$ . Unfortunately, when the above function is further differentiated with respect to  $n$ ,

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta^2 B[n]}{\delta n(\mathbf{r}'t') \delta n(\mathbf{r}t)} , \quad (5.12)$$

one finds an inconsistency because the above equation implies that  $\chi(\mathbf{r}t, \mathbf{r}'t') \neq 0$  for  $t < t'$ . This is known as the *causality paradox* [19]. The problem is the neglect of the  $v$ -representability of kets and the boundary condition  $\delta|\psi(t_0)\rangle = 0$ . We can only set  $\delta|\psi(t_0)\rangle = 0$  because a perturbation  $\delta n(\mathbf{r}t)$ , in general, will induce a response  $\delta\psi(t_1) \neq 0$  [23].

The solution of Vignale [23] is a direct implementation of the causality principle into the RG functional. For example, the internal action  $B[n]$ , using the TDSE, can be written as [3]:  $B[n] = \int_{t_0}^{t_1} dt u[n](\mathbf{r}t)n(\mathbf{r}t)$ . The density-functional  $u[n]$  is causal by



the RG theorem. If we differentiate the above functional with respect to the density and insert the result into the functional derivative of the RG action functional we obtain

$$\frac{\delta A_v}{\delta n(\mathbf{r}t)} = u[n](\mathbf{r}t) - v(\mathbf{r}t) + \int_t^{t_1} dt' \int d^3\mathbf{r}' \chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') n(\mathbf{r}'t') . \quad (5.13)$$

Now let  $n_v$  be the TD density corresponding to  $v$ , then:

$$\left. \frac{\delta A_v}{\delta n(\mathbf{r}t)} \right|_{n=n_v} = \int_t^{t_1} dt' \int d^3\mathbf{r}' \chi^{-1}[n_v](\mathbf{r}t, \mathbf{r}'t') n_v(\mathbf{r}'t') . \quad (5.14)$$

This last equation is an alternative form of the Vignale variational formulation that shows that  $n_v$  is not a stationary value of  $A_v[n]$ . This is a consequence of constraining the wave-functions of the RG functional to be density-functionals of the form  $\psi[u[n]]$ . [24] showed that not every TD wave-function can be associated with a TD external potential (or a TD density). Hence the domain of the RG functional is just a subset of the domain of the Dirac-Frenkel functional, explaining why the RG and the Dirac-Frenkel functionals lead to different results.

### 5.3 Action Formalism in the Keldysh Space

Let us add a super index  $+$  or  $-$  to the time variable  $t$ . The Keldysh contour,  $\mathcal{C}$ , is expressed as  $\mathcal{C} = \mathcal{C}^+ \cup \mathcal{C}^-$ , where  $\mathcal{C}^+ = [t_0^+, t_1^+]$  and  $\mathcal{C}^- = [t_0^-, t_1^-]$ . We denote  $z$  as a variable in the contour  $\mathcal{C}$ , and let  $z_i = t_0^+$  and  $z_f = t_1^-$ . The arrow of time in  $\mathcal{C}$  points from  $t_0^+$  to  $t_1^+$  and from  $t_1^-$  to  $t_0^-$  (see Fig. 4.1). Thus, any  $z \in \mathcal{C}^-$  is said to be later than any  $z' \in \mathcal{C}^+$ . If  $z, z' \in \mathcal{C}^-$  we say that  $z$  is later than  $z'$  if  $t(z) < t(z')$ , where  $t(z)$  is the real value of  $z$ . A ket in  $\mathcal{C}$  is denoted as  $|\psi_c[u_c](z)\rangle$ , where  $u_c(\mathbf{r}z)$  is some potential in  $\mathcal{C}$ . A physical potential in  $\mathcal{C}$  is denoted as  $\bar{u}_c$  and it satisfies  $\bar{u}_c(\mathbf{r}t^+) = \bar{u}_c(\mathbf{r}t^-)$ . Thus a potential in real-time is mapped to the Keldysh space when setting  $\bar{u}_c(\mathbf{r}t^\pm) = u(\mathbf{r}t)$  ( $t^\pm$  we denotes evaluation at  $\mathcal{C}^+$  or  $\mathcal{C}^-$ ).

We now extend the unitary propagator  $\hat{U}$  to the Keldysh space as follows:

$$\hat{U}_c[u_c](z, z_i) = \hat{\mathcal{T}}_c \exp \left[ -i \int_{z_i}^z dz' \hat{H}_c[u_c](z') \right] , \quad (5.15)$$

where  $\hat{\mathcal{T}}_{\mathcal{C}}$  is the path-ordering operator in  $\mathcal{C}$  (for example,  $\hat{\mathcal{T}}_{\mathcal{C}}[\hat{B}_c(z')\hat{A}_c(z)] = \hat{A}_c(z)\hat{B}_c(z')$  if  $z$  is later than  $z'$ ). The Hamiltonian in the Keldysh space now reads  $\hat{H}_c[u_c](z) = \hat{T} + \hat{W} + \int d^3\mathbf{r} u_c(\mathbf{r}z)\hat{n}(\mathbf{r})$ . The integration over the pseudo-time is defined as:

$$\int_{z_i}^z dz' f_c(z') := \lim_{\epsilon \rightarrow 0} \begin{cases} \int_{t_0}^{t-|\epsilon|} dt' f_c(t'^+), & z = t^+ \\ \int_{t_1}^{t_0} dt' f_c(t'^+) + \int_{t_1}^{t+|\epsilon|} dt' f_c(t'^-), & z = t^-. \end{cases} \quad (5.16)$$

The above expresses, in analogy with the real-time case, that the end point of the integral in Eq. (5.15) is not included by definition. This is the strict causality assumption in the Keldysh contour.

A  $v$ -representable ket in  $\mathcal{C}$  is thus expressed as  $|\psi_c[u_c](z)\rangle = \hat{U}_c[u_c](z, z_i)|\psi_c(z_i)\rangle$ , where  $|\psi_c(z_i)\rangle = |\psi(t_0)\rangle$  is the initial state of the system. Note that  $\psi_c(z)$  does not depend on the potential  $u_c$  at later times than  $z$ . We define the density in  $\mathcal{C}$  as [25]:

$$n_c[u_c](\mathbf{r}z) = \langle \hat{U}_c^\dagger[u_c](z, z_i)\hat{n}(\mathbf{r})\hat{U}_c[u_c](z, z_i) \rangle, \quad (5.17)$$

where  $\langle \cdot \rangle = \langle \psi_c(z_i) | \cdot | \psi_c(z_i) \rangle$ . To prove that there is a one-to-one mapping between  $n_c$  and  $u_c$ , it is sufficient to notice that  $\psi_c$  satisfies the Schrödinger equation in  $\mathcal{C}^+$ . Therefore, if the potential can be expressed as a power series around  $z_i$ , then the RG theorem and its extension [14] including non-analytic potentials apply in this case.

Let us examine the action functional proposed by van Leeuwen [22]:  $A_{\text{vL}}[u_c] = i \ln \langle \hat{U}_c[u_c](z_f, z_i) \rangle$ . The functional derivative of this functional with respect to the potential  $u_c$  yields the pseudo-density [22]:

$$n_{\text{vL}}(\mathbf{r}z) = \frac{\langle \hat{U}_c(z_f, z)\hat{n}(\mathbf{r})\hat{U}_c(z, z_i) \rangle}{\langle \hat{U}_c(z_f, z_i) \rangle}. \quad (5.18)$$

However, the above density is an average of the operator:  $\hat{n}_{\text{vL,H}}(\mathbf{r}) = \hat{U}_c(z_f, z)\hat{n}(\mathbf{r})\hat{U}_c(z, z_i)$ , which is not a Hermitian operator. Therefore  $\int d^3\mathbf{r} \hat{n}_{\text{vL,H}}(\mathbf{r}z) = \hat{N}\hat{U}_c(z_f, z_i)$ , where  $\hat{N}$  is the particle-number operator. This implies that  $n_{\text{vL}}$  does not integrate to  $N$ ; except when the potential  $u_c$  is physical [22]. The density  $n_c$ , on the other hand, integrates to  $N$  and is always positive.

It can be shown that the response function of the density in  $\mathcal{C}$  is given by:

$$\chi_c[u_c](\mathbf{r}z, \mathbf{r}'z') = \frac{\delta n_c(\mathbf{r}z)}{\delta u_c(\mathbf{r}'z')} = -i \langle [\hat{n}_{\text{c,H}}[u_c](\mathbf{r}z), \hat{n}_{\text{c,H}}[u_c](\mathbf{r}'z')] \rangle, \quad (5.19)$$

where the Heisenberg representation of the density operator  $\hat{n}(\mathbf{r})$  is

$$\hat{n}_{c,H}[u_c](\mathbf{r}z) = \hat{U}_c^\dagger[u_c](z, z_i) \hat{n}(\mathbf{r}) \hat{U}_c[u_c](z, z_i) . \quad (5.20)$$

Eq. (5.19) is valid if  $z$  is later than  $z'$ , and we set  $\chi_c(\mathbf{r}z, \mathbf{r}'z') = 0$  if  $z'$  is later than or equal to  $z$ .

The inverse first order response function  $\chi_c^{-1}[n_c](\mathbf{r}z, \mathbf{r}'z') = \delta u_c(\mathbf{r}z)/\delta n_c(\mathbf{r}'z')$ , according to the RG theorem extended to the  $\mathcal{C}$ , must also satisfy causality in the contour, e.g.,  $\chi_c^{-1}(\mathbf{r}z, \mathbf{r}'z') = 0$  if  $z = z'$  or  $z'$  is later than  $z$ . When a physical potential is used, the Heisenberg operators recover their usual form in real-time. Therefore, we obtain a physical density  $\bar{n}_c(\mathbf{r}t^\pm) = n(\mathbf{r}t)$ . From Eq. (5.19) we can show that the first order response function satisfies the antisymmetry relationship:

$$\chi_c(\mathbf{r}t^+, \mathbf{r}'t'^+) \Big|_{u_c=\bar{u}_c} = -\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-) \Big|_{u_c=\bar{u}_c} , \quad (5.21)$$

where  $u_c = \bar{u}_c$  denotes evaluation at the physical regime. Note that  $\chi_c$  also satisfies  $\chi_c(\mathbf{r}t^+, \mathbf{r}'t'^+) = \chi_c(\mathbf{r}t^-, \mathbf{r}'t'^+)$  and  $\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^+) = \chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-)$  if  $t > t'$  and  $u_c = \bar{u}_c$ .

The response of the density in the Keldysh space is [22]:

$$\delta n_c[u_c](\mathbf{r}z) = \int_{z_i}^{z_f} dz' \int d^3\mathbf{r}' \chi_c[u_c](\mathbf{r}z, \mathbf{r}'z') \delta u_c(\mathbf{r}'z') . \quad (5.22)$$

To obtain the response in real-time, the variation of a physical potential must satisfy  $\delta \bar{u}_c(\mathbf{r}t^+) = \delta \bar{u}_c(\mathbf{r}t^-) = \delta u(\mathbf{r}t)$ . Using the aforementioned properties of  $\chi_c$  to calculate the above integral, the response of the density turns out to be independent of the time location in the contour, i.e.  $\delta n_c(\mathbf{r}t^+) = \delta n_c(\mathbf{r}t^-) = \delta n(\mathbf{r}t)$ . Hence, it is determined by:

$$\delta n_c[\bar{u}_c](\mathbf{r}t) = \int_{t_0}^{t^\pm} dt' \int d^3\mathbf{r}' \chi_c[\bar{u}_c](\mathbf{r}t^\pm, \mathbf{r}'t'^+) \delta \bar{u}_c(\mathbf{r}'t'^+) . \quad (5.23)$$

This result allows us to identify the response in real-time  $\chi(\mathbf{r}t, \mathbf{r}'t')$  as  $\chi_c(\mathbf{r}t^\pm, \mathbf{r}'t'^+) \Big|_{u_c=\bar{u}_c}$  or  $-\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-) \Big|_{u_c=\bar{u}_c}$ , which are causal. Exchanging variables in the integral of  $\chi_c \chi_c^{-1}$  reveals that  $\chi_c^{-1}$  satisfies the same relationships of  $\chi_c$  regarding exchange of variables at physical densities.

Let us extend the functional  $A_v$  to the Keldysh space:

$$\mathcal{A}_{\bar{v}_c}[n_c] = \mathcal{B}[n_c] - \int_{z_i}^{z_f} dz \int d^3\mathbf{r} n_c(\mathbf{r}z) \bar{v}_c(\mathbf{r}z) , \quad (5.24)$$

where  $\mathcal{B}[n_c] = \int_{z_i}^{z_f} dz \langle \psi_c[n_c](z) | i\partial_z - \hat{T} - \hat{W} | \psi_c[n_c](z) \rangle$ ,  $\bar{v}_c$  is some external physical potential, and  $\partial f(z)/\partial z = \partial f(t^\sigma)/\partial t$ , where  $\sigma = +, -$ . Vignale equation in this case reads:

$$\begin{aligned} \left. \frac{\delta \mathcal{B}}{\delta n_c(\mathbf{r}z)} \right|_{n_c = \bar{n}_c, \bar{v}_c} - \bar{v}_c(\mathbf{r}z) &= i \langle \psi_c(z_f) | \frac{\delta \psi_c(z_f)}{\delta n_c(\mathbf{r}z)} \rangle \Big|_{n_c = \bar{n}_c, \bar{v}_c} \\ &= \int_z^{z_f} dz' \int d^3\mathbf{r}' \bar{n}_{c, \bar{v}_c}(\mathbf{r}'z') \chi_c^{-1}[\bar{n}_{c, \bar{v}_c}](\mathbf{r}'z', \mathbf{r}z) . \end{aligned} \quad (5.25)$$

The left hand side of the above equation corresponds to  $\delta \mathcal{A}_{\bar{v}_c} / \delta n_c(\mathbf{r}z)$  evaluated at the density that yields  $\bar{v}_c$ ,  $\bar{n}_{c, \bar{v}_c}$ . Additionally, the above equation also gives the functional derivative  $\delta \mathcal{B} / \delta n_c(\mathbf{r}z)$  for an arbitrary density  $n_c$ ; in this case, we replace  $\bar{v}_c$  by  $u_c[n_c](\mathbf{r}z)$ ,  $\bar{n}_{c, \bar{v}_c}$  by  $n_c$ , and the inverse response function has to be evaluated at  $n_c$ .

Let us introduce the KS action functional:

$$\mathcal{A}_{s, \bar{v}_{c,s}}[n_c] = \mathcal{B}_s[n_c] - \int_{z_i}^{z_f} dz \int d^3\mathbf{r} n_c(\mathbf{r}z) \bar{v}_{c,s}(\mathbf{r}z) , \quad (5.26)$$

where  $\bar{v}_{c,s}(\mathbf{r}z)$  is some effective external potential and  $\mathcal{B}_s[n_c] = \int_{z_i}^{z_f} dz \langle \Phi_{c,s}[n_c](z) | i\partial_z - \hat{T} | \Phi_{c,s}[n_c](z) \rangle$ . The KS wave function is a Slater determinant of TD KS orbitals  $\{\phi_{c,i}(\mathbf{r}z)\}$  that satisfy:

$$i \frac{\partial \phi_{c,i}}{\partial z} = \left( -\frac{1}{2} \nabla_{\mathbf{r}}^2 + u_{c,s}[n_c](\mathbf{r}z) \right) \phi_{c,i}(\mathbf{r}z) , \quad (5.27)$$

where  $u_{c,s}[n_c]$  is the KS potential that represents  $n_c(\mathbf{r}z)$ . Thus, if we differentiate  $\mathcal{B}_s$  with respect to the TD density we obtain:

$$\frac{\delta \mathcal{B}_s}{\delta n_c(\mathbf{r}z)} = u_{c,s}[n_c](\mathbf{r}z) + \int_z^{z_f} dz' \int d^3\mathbf{r}' n_c(\mathbf{r}'z') \chi_{c,s}^{-1}[n_c](\mathbf{r}'z', \mathbf{r}z) , \quad (5.28)$$

where  $\chi_{c,s}^{-1}(\mathbf{r}z, \mathbf{r}'z') = \delta u_{c,s}(\mathbf{r}'z') / \delta n_c(\mathbf{r}z)$ .

Recall the Hartree functional:

$$\mathcal{A}_H[n_c] = \frac{1}{2} \int_{z_i}^{z_f} dz \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n_c(\mathbf{r}'z) n_c(\mathbf{r}z)}{|\mathbf{r} - \mathbf{r}'|} . \quad (5.29)$$

Let us introduce the XC action functional:

$$\mathcal{A}_{\text{XC}}[n_c] = \mathcal{B}_s[n_c] - \mathcal{B}[n_c] - \mathcal{A}_H[n_c] . \quad (5.30)$$

Using Eqs. (5.25) and (5.28) it is found that the functional derivative of the XC action functional can be expressed as:

$$u_{c,\text{xc}}(\mathbf{r}z) + \int_z^{z_f} dz' \int d^3\mathbf{r}' n_c(\mathbf{r}'z') [\chi_{c,s}^{-1}(\mathbf{r}'z', \mathbf{r}z) - \chi_c^{-1}(\mathbf{r}'z', \mathbf{r}z)] = \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n_c(\mathbf{r}z)} . \quad (5.31)$$

Here  $u_{c,\text{xc}}(\mathbf{r}z) = u_{c,s}(\mathbf{r}z) - u_c(\mathbf{r}z) - u_{c,H}(\mathbf{r}z)$ , where the Hartree potential is  $u_{c,H}[n_c](\mathbf{r}z) = \int d^3\mathbf{r}' n_c(\mathbf{r}'z)/|\mathbf{r}-\mathbf{r}'|$ . Now introduce the XC kernel  $f_{c,\text{xc}}(\mathbf{r}z, \mathbf{r}'z') = \delta u_{c,\text{xc}}(\mathbf{r}z)/\delta n_c(\mathbf{r}'z')$ , which satisfies:

$$\chi_{c,s}^{-1}(\mathbf{r}z, \mathbf{r}'z') = \chi_c^{-1}(\mathbf{r}z, \mathbf{r}'z') + \frac{\delta_c(z - z')}{|\mathbf{r} - \mathbf{r}'|} + f_{c,\text{xc}}(\mathbf{r}z, \mathbf{r}'z') . \quad (5.32)$$

The delta function in  $\mathcal{C}$  space is defined such that  $\int_{z_i}^{z_f} dz' f_c(z') \delta_c(z - z') = f_c(z)$ . The KS response function and the XC kernel satisfy the same properties of  $\chi_c$  regarding exchange of variables.

In order to simplify Eq. (5.31), suppose that the density is physical,  $n_c = \bar{n}_c$ . This imposes that the XC potential is the same in both  $\mathcal{C}^+$  and  $\mathcal{C}^-$  spaces. For example, if  $z = t^+$  then the integral in time can be split up into two integrals: The first one runs from  $t^+$  to  $t^-$ , and the second one from  $t^-$  to  $t_0^-$ . There is no contribution from the first integral due to the symmetry properties of  $\chi_c^{-1}$  and  $\chi_{c,s}^{-1}$  at physical densities. For the second integral we can use the antisymmetry relation to obtain in real-time that:

$$u_{\text{XC}}(\mathbf{r}t) + \int_{t_0}^t dt' \int d^3\mathbf{r}' f_{\text{XC}}(\mathbf{r}t, \mathbf{r}'t') n(\mathbf{r}'t') = \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n(\mathbf{r}t)} , \quad (5.33)$$

where  $u_{\text{XC}}(\mathbf{r}t) = \bar{u}_{c,\text{xc}}(\mathbf{r}t^\pm)$  and

$$\frac{\delta \mathcal{A}_{\text{XC}}}{\delta n(\mathbf{r}t)} = \left. \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n_c(\mathbf{r}t^\pm)} \right|_{n_c = \bar{n}_c} . \quad (5.34)$$

Setting  $z = t^-$  in Eq. (5.31) also leads to Eq. (5.33) when  $n_c = \bar{n}_c$ ; for this reason we expressed the final result in real-time. Because  $f_{c,\text{xc}}$  in the  $\mathcal{C}$  space also has

the same properties as  $\chi_c^{-1}$  we identify the XC kernel in real-time,  $f_{\text{XC}}(\mathbf{r}t, \mathbf{r}'t')$ , as  $f_{\text{c,xc}}(\mathbf{r}t^\pm, \mathbf{r}'t'^\pm)|_{n_c=\bar{n}_c}$ , or  $-f_{\text{c,xc}}(\mathbf{r}'t'^-, \mathbf{r}t^-)|_{n_c=\bar{n}_c}$ . Thus, the XC kernel is causal in real-time.

Given that we assumed that the response functions  $\chi_c$  and  $\chi_{c,s}$  are strictly causal in  $\mathcal{C}$ , the integral in Eq. (5.31) is taken over the interval  $(z, z_f]$ . This implies that the Hartree kernel  $\delta_c(z - z')/|\mathbf{r} - \mathbf{r}'|$  lies outside the integration limits and thus it has no contribution to Eq. (5.33). Based on this, the integral in Eq. (5.33) is carried out strictly over the past of  $t$ , i.e.,  $[t_0, t)$ . Hence, our causality assumption avoids singularities at equal-times and simplifies the transition to real-time.

Eq. (5.33) is the main result of this work. It is a variational equation that establishes a causal connection between  $u_{\text{XC}}$  in real-time with an XC action functional in the Keldysh space, and the memory of the system. If an approximation to the XC action functional is known, then Eq. (5.33) can be used to estimate the XC potential. The potentials  $u(\mathbf{r}t)$  and  $u_s(\mathbf{r}t)$  also satisfy the same type of equation as that of  $u_{\text{XC}}$ ; one has to replace  $f_{\text{XC}}$  and  $\mathcal{A}_{\text{XC}}$  by  $\chi^{-1}$  and  $\mathcal{B}$ , or  $\chi_s^{-1}$  and  $\mathcal{B}_s$ .

Note that the left-hand side of Eq. (5.33) is a functional of the density  $\bar{n}_c(\mathbf{r}t^\pm)$ , or simply  $n(\mathbf{r}t)$ . This implies that the second functional derivative of  $\mathcal{A}_{\text{XC}}$  with respect to the density in real-time is not symmetric, i.e.:

$$\frac{\delta}{\delta n(\mathbf{r}'t')} \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n(\mathbf{r}t)} = 0 \quad t' \geq t. \quad (5.35)$$

Here, the symbol  $\delta/\delta n(\mathbf{r}'t')$  represents regular functional differentiation in real-time because the operation  $\delta/\delta n(\mathbf{r}t)$  already involves evaluation at the physical regime. The above result is a consequence of implementing causality in the  $\mathcal{C}$  space explicitly using the path-ordering operator. Furthermore, recursive differentiation of Eq. (5.33) also allows us to express its solution as a series of functional derivatives of  $\mathcal{A}_{\text{XC}}$ . This reads

$$u_{\text{XC}}(\mathbf{x}_1) = \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n(\mathbf{x}_1)} + w_{\text{XC}}(\mathbf{x}_1) \quad (5.36)$$

where

$$w_{\text{XC}}(\mathbf{x}_1) = \sum_{m=2}^{\infty} \frac{(-1)^{m+1}}{m!} \int d\mu(\mathbf{x}_2) \cdots d\mu(\mathbf{x}_m) \frac{\delta^{m-1}}{\delta n(\mathbf{x}_m) \cdots \delta n(\mathbf{x}_2)} \frac{\delta \mathcal{A}_{\text{XC}}}{\delta n(\mathbf{x}_1)}. \quad (5.37)$$

Here  $\mathbf{x}_m = \mathbf{r}_m, t_m$ ,  $m = 1, 2, \dots$  and  $d\mu(\mathbf{x}_m) = n(\mathbf{x}_m)d^4\mathbf{x}_m$ . The functional derivatives in the integral are zero if, for any  $i > j$ ,  $t_i \geq t_j$ . This series shows that the XC potential depends on perturbations of the XC potentials in all orders. However, in order to achieve convergence the functional derivatives must decrease as their order increases.

Now let us apply our variational equation to the derivation of the ALDA XC potential:

$$\mathcal{A}_{\text{XC}}^{\text{ALDA}}[n_c] = \int_{z_i}^{z_f} dz \int d^3\mathbf{r} [\epsilon_{\text{XC}}(n)n] \Big|_{n=n_c(\mathbf{r}z)}, \quad (5.38)$$

where  $\epsilon_{\text{XC}}$  is the local XC energy density. To solve Eq. (5.33) the memory term can be neglected to yield

$$\bar{u}_{c,\text{xc}}^{\text{ALDA}}(\mathbf{r}z) = \frac{d}{dn}[\epsilon_{\text{XC}}(n)n] \Big|_{n=n_c(\mathbf{r}z)}. \quad (5.39)$$

Further differentiation leads to the kernel formula:

$$f_{\text{XC}}^{\text{ALDA}}(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \frac{d^2}{dn^2}[\epsilon_{\text{XC}}(n)n] \Big|_{n=n(\mathbf{r}t)}. \quad (5.40)$$

The singularity of the XC kernel does not contribute to the integral term of Eq. (5.33) because the end point is not included, or in other words, the end point is approached in a limiting procedure. Hence, the above equation satisfies Eq. (5.33) and thus it is the solution of it. The singularity of the XC kernel arises from the definition of the XC potential, which implies that at equal-times the XC kernel must cancel the singularity of the Hartree kernel. However, the ALDA XC kernel does not cancel the singularity of the Hartree kernel due to the self-interaction error.

Another application is the TDOPM. The exchange functional form remains the same as the one proposed by [22]:

$$\mathcal{A}_{\text{x}}[n_c] = \int_{z_i}^{z_f} dz \langle \Phi_c[n_c](z) | \hat{W} | \Phi_c[n_c](z) \rangle - \mathcal{A}_{\text{H}}[n_c]. \quad (5.41)$$

To derive the TDOPM one has to assume that (for example, see [3]):

$$\frac{\delta \mathcal{A}_{\bar{v}_c}}{\delta n(\mathbf{r}z)} = \frac{\delta \mathcal{A}_{\text{s}, \bar{v}_{c,s}}}{\delta n(\mathbf{r}z)}. \quad (5.42)$$

If we set  $\mathcal{A}_{\text{xc}} = \mathcal{A}_{\text{x}}$  and expand  $A_{\bar{v}_c}$  using Eq. (5.30) we find that the memory term in Eq. (5.33) can be discarded. Hence we can write:

$$u_{\text{x}}(\mathbf{r}t) = \frac{\delta \mathcal{A}_{\text{x}}}{\delta n(\mathbf{r}t)} . \quad (5.43)$$

The right hand side of the above equation can be calculated using the chain rule. If the result is multiplied by  $\chi_s$  and then integrated, the final result coincides with that of [26].

Ground-state DFT is also accessible with this theory. We can introduce a slowly varying density  $n_{\text{c}}^T(\mathbf{r}z) = n_{\text{c}}(\mathbf{r}z/T)$ , where  $T \rightarrow \infty$ . One can use the adiabatic theorem to show that:

$$\lim_{T \rightarrow \infty} A_{\text{XC}}[n_{\text{c}}^T] = \lim_{T \rightarrow \infty} \int_{z_i}^{z_f} dz E_{\text{XC}}[n_{\text{c}}^T(\cdot, z)] , \quad (5.44)$$

where  $E_{\text{XC}}$  is the XC energy functional of DFT. The above equation is local in time. As in the previous case, the solution of Eq. (5.33) has to be of the form:

$$\lim_{T \rightarrow \infty} u_{\text{XC}}[n^T](\mathbf{r}t) = \lim_{T \rightarrow \infty} \left. \frac{\delta E_{\text{XC}}}{\delta n(\mathbf{r})} \right|_{n=n^T(\mathbf{r}t)} . \quad (5.45)$$

where  $n^T = \bar{n}_{\text{c}}^T$ .

## 5.4 Conclusions

The RG action functional was revisited in this chapter. The problem leading to the causality paradox is the misinterpretation of a composition of maps. To eliminate the dependency of the functionals derivatives of the actions on the total time of the propagation, I extended the RG action functional to the Keldysh space and found a variational equation for the XC potential, from which the ALDA and the TDOPM are suitable solutions.



## 5.5 References

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## 6. PARTITION CURRENT-DENSITY FUNCTIONALS

The electronic density is a variable that is sufficient to determine the external potential of a molecule. Nevertheless, when a molecule is subject to a vector potential, the electronic density is not the main variable to determine such vector potential but the 1-particle *current-density*. The basic ideas of TDDFT can be extended to consider current-densities and electromagnetic (EM) fields. However, some subtleties may arise when studying the maps relating currents and EM fields.

The ALDA XC potential at a given space-time point only depends on the value of the density at such point; the exact XC potential depends on the density at all points in space and all previous times. It is quite challenging to include density-memory without violating the zero force theorem [1], stating that the XC potential cannot exert a net force on the system. This condition is met by the ALDA but not by the generalized-gradient approximation. The density does not yield enough information of the system locally (for example, not every current density is  $n$ -representable [2]). There might be regions in space where the density does not yield information about in what direction the density will displace [3]. Therefore, even in the absence of EM fields, the current-density is an important observable.

Time-dependent Current-density-functional Theory (TDCDFT) is rooted on a map relating vector potentials, that vary by more than gauge transformation, with the current-density of the system [4–6]. The current-density is a quantity that depends on time, and ground-state systems usually do not display a net current. Thus the current-density is a suitable variable to study dynamics (although the ground-state must be accessible through an appropriate limiting procedure).

Most researchers on functional development in TDCDFT focus on approximating the stress tensor of the system [7, 8], with quite elegant promising schemes proposed in the field of quantum continuum mechanics [9]. The current, main approximation in TDCDFT within its KS formulation is that of Vignale and Kohn [10]. This approximation is valid as long as the perturbations applied to the system are slowly varying and the system is periodic. Hence Vignale-Kohn functional is reliable [11–15] for solids and molecules with delocalized  $\pi$ -electron clouds.

The formulation to study the dynamics of molecular fragments within TDCDFT is presented in this chapter. I assign each fragment in the molecule a Hamiltonian including an auxiliary EM potential that represents the current-density of the system. I show that there exists a map that uniquely associates a current-density with a family of EM potential that only differ by a gauge transformation. The linear response formulation of this theory and a numerical inversion methodology to study EM fields is shown in this chapter as well.

### 6.1 Theory

This section is centered on the electronic dynamics of non-relativistic molecules with fixed nuclei, where the electrons interact with classical electromagnetic fields. The Hamiltonian representing the molecule is:

$$\hat{H}(t) = \hat{T}_{\mathbf{A}}(t) + \hat{W} + \int d^3\mathbf{r} \, \hat{n}(\mathbf{r})[v(\mathbf{r}t) - \phi(\mathbf{r}t)] , \quad (6.1)$$

where  $\mathbf{A}$  and  $\phi$  are the vector and scalar potentials, respectively. We refer to the pair  $\mathbf{A}, \phi$  as the 4-potential. The operator  $\hat{T}_{\mathbf{A}}(t)$  is defined as:

$$T_{\mathbf{A}}(t) = \frac{1}{2} \int d^3\mathbf{r} \, \hat{\psi}^\dagger(\mathbf{r})(-i\nabla + \mathbf{A}(\mathbf{r}t))^2\hat{\psi}(\mathbf{r}) . \quad (6.2)$$

Define the paramagnetic current operator:  $\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i}(\hat{\psi}^\dagger(\mathbf{r})\nabla\hat{\psi}(\mathbf{r}) - \nabla\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}))$  , and the total current operator:  $\hat{\mathbf{j}}(\mathbf{r}t) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{n}(\mathbf{r})\mathbf{A}(\mathbf{r}t)$  . These operators allow us to express the Hamiltonian as:

$$\hat{H}(t) = \hat{T} + \hat{W} + \int d^3\mathbf{r} \, \{\hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}t) + \hat{n}(\mathbf{r})[v(\mathbf{r}) - \phi(\mathbf{r}t) + \frac{1}{2}\mathbf{A}^2(\mathbf{r}t)]\} . \quad (6.3)$$

Here we can regard the Hamiltonian as a functional of  $\mathbf{A}$ ,  $\phi$ . These potentials are related to electromagnetic field  $\mathbf{E}$ ,  $\mathbf{B}$  by the following expressions:

$$\mathbf{E}(\mathbf{r}t) = -\nabla\phi(\mathbf{r}t) - \partial_t\mathbf{A}(\mathbf{r}t) , \quad (6.4)$$

and

$$\mathbf{B}(\mathbf{r}t) = \nabla \times \mathbf{A}(\mathbf{r}t) . \quad (6.5)$$

Let us define the average of an operator  $\hat{O}(\mathbf{r}t)$  as

$$O(\mathbf{r}t) = \text{tr}\{\hat{\Gamma}(t)\hat{O}(\mathbf{r}t)\} , \quad (6.6)$$

where  $\hat{\Gamma}$  is the density matrix of the system, which is the solution of the Liouville equation:

$$i\partial_t\hat{\Gamma}(t) = [\hat{H}(t), \hat{\Gamma}(t)] . \quad (6.7)$$

The density matrix  $\hat{\Gamma}(t)$  in general represents a mixed state in the fermionic Liouville space. This ensures that states with any number of particles, including real numbers, are considered in our formalism. The initial state is of the form:  $\hat{\Gamma}(t_0) = \sum_{M,k} w_{M,\mathbf{k}} |\psi_{M,\mathbf{k}}\rangle \langle \psi_{M,\mathbf{k}}|$ , where  $M$  is the number of electrons and  $\mathbf{k}$  is a label running over states.

The density of the system satisfies the continuity Eq.:

$$\partial_t n(\mathbf{r}t) = -\nabla \cdot \mathbf{j}(\mathbf{r}t) , \quad (6.8)$$

where this equation is valid for states with a real number of particles. The current density can be shown to satisfy the hydrodynamical-like equation:

$$\partial_t \mathbf{j}(\mathbf{r}t) = -\mathbf{q}(\mathbf{r}t) - n(\mathbf{r}t)[\mathbf{E}(\mathbf{r}t) + \nabla v(\mathbf{r})] - \mathbf{j}(\mathbf{r}t) \times \mathbf{B}(\mathbf{r}t) , \quad (6.9)$$

where the term  $\mathbf{q}(\mathbf{r}t)$  is defined as:

$$\mathbf{q}(\mathbf{r}t) = -i \text{tr}\{\hat{\Gamma}(t_0)[\hat{T} + \hat{W}, \hat{\mathbf{j}}_p(\mathbf{r})]\} . \quad (6.10)$$

This quantity can also be expressed as the gradient of the stress tensor, which causes the non-classical behavior of the current.

Ghosh and Dhara [5] proved there is a one-to-one mapping, up to a gauge transformation, between 4-potentials and current-densities. Their proof is quite analogous to that of Runge and Gross [16]. First assume that the 4-potential  $\mathbf{A}, \phi$  can be written as a power series around the initial time  $t = t_0$ . Suppose that there is another analytic 4-potential  $\mathbf{A}', \phi'$ , which differs from  $\mathbf{A}, \phi$  by more than a gauge transformation and yields the current density  $\mathbf{j}'(\mathbf{r}t)$ . Additionally, the initial conditions demand that  $\mathbf{A}'(\mathbf{r}t_0) = \mathbf{A}(\mathbf{r}t_0)$ . The proof requires that the power series exists. However, we just need to find the lowest number  $l$  and  $k$  such that:

$$\partial_t^n(\mathbf{A}(\mathbf{r}t) - \mathbf{A}'(\mathbf{r}t)) \Big|_{t=t_0} \neq \text{Const} , \quad n \geq l \quad (6.11)$$

$$\partial_t^n(\phi(\mathbf{r}t) - \phi'(\mathbf{r}t)) \Big|_{t=t_0} \neq \text{Const} , \quad n \geq k \quad (6.12)$$

$$(6.13)$$

Ghosh and Dhara [5] showed that if the above holds then:

$$\begin{aligned} i^n \partial_t^n [\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)] \Big|_{t=t_0} = & \\ \begin{cases} n(\mathbf{r}t_0) \nabla \left[ i^k \partial_t^k (\phi(\mathbf{r}t) - \phi'(\mathbf{r}t)) \Big|_{t=t_0} \right] , & n = k+1, l > k+1 \\ n(\mathbf{r}t_0) i^l \partial_t^l (\mathbf{A}(\mathbf{r}t) - \mathbf{A}'(\mathbf{r}t)) \Big|_{t=t_0} , & n = l, l < k+1 \\ -n(\mathbf{r}t_0) i^{k+1} \partial_t^k (\mathbf{E}(\mathbf{r}t) - \mathbf{E}'(\mathbf{r}t)) \Big|_{t=t_0} , & n = k+1, l = k+1 \end{cases} \end{aligned} \quad (6.14)$$

This set of equations shows that if the power series of the 4-potentials differ by more than a time-dependent constant then they cannot yield the same current density after  $t = t_0$ .

The above result suggests that the current-density is a fundamental variable that determines the state of the system. This result is also valid for extended systems because it only requires that the current densities of the unprimed and primed systems differ locally. This is a useful feature for application in solid state theory and periodic systems in general. However, the electron-electron interaction makes the solution of Eq. (6.9) very difficult. Vignale [17] found that the van Leeuwen theorem can be extended to the TDCDFT case as well. The theorem states that the current-density

of a system described by  $\mathbf{A}, \phi$  with particle interaction  $\hat{W}$  and initial state  $\hat{\Gamma}(t_0)$  can be reproduced exactly by another system under the influence of  $\mathbf{A}', \phi'$ , where the particle interaction is described by another operator  $\mathbf{W}'$  and the initial state is  $\hat{\Gamma}'(t_0)$ . Again, the 4-potential must vary from the original 4-potential by more than a gauge transformation. The van Leeuwen theorem also requires the initial state of the alternative system to be given such that the initial current in both cases coincide.

The van Leeuwen theorem is particularly useful when the particle interaction is neglected, e.g.  $\hat{W}' = 0$ , which is the Kohn-Sham system of non-interacting electrons. For the sake of simplicity, let us choose a gauge in which the scalar field is dropped. This facilitates the formulation for practical purposes because the vector potential  $\mathbf{A}$  and the current-density  $\mathbf{j}$  are both 3-dimensional quantities. If we denote  $\hat{\Gamma}(t_0)$  and  $\mathbf{A}_s$  as the initial state and 4-potential, respectively, yielding the current density  $\mathbf{j}$ , then the evolution of the current density is given by:

$$\partial_t \mathbf{j}(\mathbf{r}t) = -\mathbf{q}_s(\mathbf{r}t) - n(\mathbf{r}t) \left[ -\frac{\partial \mathbf{A}_s}{\partial t}(\mathbf{r}t) + \nabla v(\mathbf{r}) \right] - \mathbf{j}(\mathbf{r}t) \times \nabla \times \mathbf{A}_s(\mathbf{r}t) , \quad (6.15)$$

where  $\mathbf{q}(\mathbf{r}t) = -i \text{tr} \{ \hat{\Gamma}(t) [\hat{T}, \mathbf{j}_p(\mathbf{r})] \}$ . Now let us introduce the splitting of  $\mathbf{A}_s$ :  $\mathbf{A}_s = \mathbf{A} + \mathbf{A}_H + \mathbf{A}_{XC}$ , where

$$\partial_t \mathbf{A}_H(\mathbf{r}t) = -\nabla \int d^3 \mathbf{r}' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} . \quad (6.16)$$

If we subtract Eq. (6.9) from (6.15) and employ the above definition we find that:

$$n(\mathbf{r}t) \partial_t \mathbf{A}_{HXC}(\mathbf{r}t) - \mathbf{j}(\mathbf{r}t) \times \nabla \times \mathbf{A}_{HXC}(\mathbf{r}t) = \mathbf{q}_s(\mathbf{r}t) - \mathbf{q}(\mathbf{r}t) , \quad (6.17)$$

where  $\mathbf{A}_{HXC} = \mathbf{A}_{XC} + \mathbf{A}_H$ . The solution of Eq. (6.17) determines the XC vector potential as a functional of the current-density (note that the right hand side terms are functionals of  $\mathbf{j}$ ). If the HXC vector potential is expanded as a Taylor series then the above equation can be shown to provide a recursive scheme to calculate the coefficients of the Taylor expansion of the XC vector potential [17].

## 6.2 Partition Current-density-functional Theory

An electron in a molecule, when the nuclei are fixed in space, is subject to the influence of an external potential  $v(\mathbf{r})$  that is a sum of Coulomb potentials. Each of these potentials corresponds to the interaction between an electron and a particular nucleus. We can divide the set of nuclei into smaller subsets, or fragments. If we labelled a fragment as  $\alpha$  and its external potential as  $v_\alpha(\mathbf{r})$ , then the latter quantity describes the interaction between an electron and the nuclei in the subset  $\alpha$ . If there are  $N_f$  fragments then we require that  $v(\mathbf{r}) = \sum_\alpha v_\alpha(\mathbf{r})$ . A fragment that is infinitely separated from the molecule is isolated and its properties are not affected by the other fragments. Hence, we can assume that the current-density around such fragment is determined by its interaction with the 4-potential uniquely. Moreover, if the system is always bound while it interacts with the 4-potential then the current-density, and the electronic density, will remain localized around the fragment.

For molecules around their equilibrium distances we can also imagine that the current-densities are localized as long as the 4-potential is not ionizing the electrons. It is plausible to assume that the current-density can be split into current-densities that are localized around their corresponding fragment. This requires to define a fragment formally: It is a potential  $v_\alpha$ , a TD Hamiltonian  $\hat{H}_\alpha(t)$ , and a density matrix  $\hat{\Gamma}_\alpha(t)$  that satisfies the Liouville Eq.:

$$i\partial_t \hat{\Gamma}_\alpha(t) = [\hat{H}_\alpha(t), \hat{\Gamma}_\alpha(t)] \quad (6.18)$$

and its initial state is  $\hat{\Gamma}_\alpha(t_0)$ . The Hamiltonian  $\hat{H}_\alpha$  of the fragment  $\alpha$  is:

$$\hat{H}_\alpha(t) = \hat{T} + \hat{W} + \int d^3\mathbf{r} \left( \hat{\mathbf{j}}_\mathbf{p}(\mathbf{r}) \cdot \mathbf{A}_\mathbf{p}(\mathbf{r}t) + \hat{n}(\mathbf{r})[v_\alpha(\mathbf{r}) - \phi_\mathbf{p}(\mathbf{r}t) + \frac{1}{2}\mathbf{A}_\mathbf{p}^2(\mathbf{r}t)] \right) \quad (6.19)$$

An observable quantity of a fragment,  $O_\alpha(\mathbf{r}t)$ , is obtained by averaging over the fragment's ensemble:

$$O_\alpha(\mathbf{r}t) = \text{tr}\{\hat{O}(\mathbf{r}t)\hat{\Gamma}_\alpha(t)\} \quad (6.20)$$

For example the current-density of the fragment is  $\hat{\mathbf{j}}_\alpha(\mathbf{r}t) = \text{tr}\{\hat{\Gamma}_\alpha(t)\hat{\mathbf{j}}(\mathbf{r}t)\}$ . Let us denote  $\mathbf{A}_\mathbf{p}, \phi_\mathbf{p}$  as the partition 4-potential, whose purpose is to enforce that  $\mathbf{j}(\mathbf{r}t) = \sum_\alpha \mathbf{j}_\alpha(\mathbf{r}t)$  where  $\mathbf{j}(\mathbf{r}t)$  is the current-density of the “real” molecule of interest.



The motion equation for the current-density of a fragment satisfies:

$$\partial_t \mathbf{j}_\alpha(\mathbf{r}t) = -\mathbf{q}_\alpha(\mathbf{r}t) - n_\alpha(\mathbf{r}t)[\mathbf{E}_P(\mathbf{r}t) + \nabla v_\alpha(\mathbf{r})] - \mathbf{j}_\alpha(\mathbf{r}t) \times \mathbf{B}_P(\mathbf{r}t) \quad (6.21)$$

where  $\mathbf{q}_\alpha(\mathbf{r}t) = -i \text{tr}\{\hat{\Gamma}_\alpha(t)[\hat{T} + \hat{W}, \hat{\mathbf{j}}_P(\mathbf{r})]\}$ . The quantities that define a fragment are quite similar to those that define a quantum system in Ghosh and Dhara proof. The only difference is that the physical 4-potential has been replaced by the partition field. Therefore  $\hat{\mathbf{j}}_\alpha$  uniquely determines the partition field up to a gauge transformation. Note also that the motion Eq. of the current-densities can be added up, yielding:

$$\partial_t \mathbf{j}(\mathbf{r}t) = -\sum_\alpha (\mathbf{q}_\alpha + n_\alpha \nabla v_\alpha) - (n\mathbf{E}_P + \mathbf{j} \times \mathbf{B}_P) \quad (6.22)$$

again we find that the present formulation is analogous to that of Ghosh and Dhara. Hence, there is a 1-1 correspondence between  $\mathbf{j}$  and the partition EM, up to a gauge transformation. The properties of this map are determined by those of the  $\mathbf{j}_\alpha \leftrightarrow \mathbf{A}_P, \phi_P$  maps.

It is also easy to show the van Leeuwen theorem: The current density of a fragmented molecule defined by  $\hat{W}, \mathbf{A}_P, \phi$  can be represented by an alternative system with  $\hat{W}', \mathbf{A}'_P, \phi'$ . The initial state of the real system and the partition scheme are fixed. The proof follows the same steps shown by Vignale [17] applied to the motion equation of the current.

### 6.3 Extended Operators and the Partition 4-potential

The partitioned molecule can be thought of as a single object. One says that the density matrix of a fragment belongs to the Liouville space  $\mathcal{L}$ , and that the density matrix operates on the fermionic Fock space of the fragment. We define the space of the partitioned molecule as  $\mathcal{L}_f = \underbrace{\mathcal{L} \otimes \mathcal{L} \otimes \cdots \otimes \mathcal{L}}_{N_f \text{ times}}$ . The density matrix:  $\hat{\Gamma}_f(t) = \bigotimes_{\alpha=1}^{N_f} \hat{\Gamma}_\alpha(t)$  is the state of a partitioned molecule with  $N_f$  fragments and contains all the information required to calculate the total current density of the system. The Hamiltonian for such molecule is given by:

$$\hat{H}_f(t) = \hat{H}_1(t) \oplus \hat{H}_2(t) \oplus \cdots \oplus \hat{H}_{N_f}(t) \quad (6.23)$$

where  $\hat{H}_\alpha(t)$  is the Hamiltonian of fragment  $\alpha$ . For example, for a system with two fragments the operation  $\hat{H}_f(t)\hat{\Gamma}_f(t)$  yields:

$$\hat{H}_f(t)\hat{\Gamma}_f(t) = (\hat{H}_1(t)\hat{\Gamma}_1(t)) \otimes \hat{\Gamma}_2(t) + \hat{\Gamma}_1(t) \otimes (\hat{H}_2(t)\hat{\Gamma}_2(t)) \quad (6.24)$$

The role of the direct summation and product employed in our definition is to ensure that the energy of the system remains always additive. Other quantities such as the density and the current are also additive, e.g.:  $\hat{n}_f(\mathbf{r}) = \bigoplus_\alpha \hat{n}_\alpha(\mathbf{r})$ ,  $\hat{\mathbf{j}}(\mathbf{r}t) = \bigoplus_\alpha \hat{\mathbf{j}}_\alpha(\mathbf{r}t)$ . This allows us to write:

$$\mathbf{j}(\mathbf{r}t) = \text{tr}\{\hat{\Gamma}_f(t)\hat{\mathbf{j}}_f(\mathbf{r})\} = \sum_\alpha \mathbf{j}_\alpha(\mathbf{r}t) \quad (6.25)$$

The evolution of the system is thus described by the Liouville equation:

$$i\partial_t \hat{\Gamma}_f(t) = [\hat{H}_f(t), \hat{\Gamma}_f(t)] \quad (6.26)$$

Now, note that the Hamiltonian has the form:

$$\hat{H}_f = \hat{T}_f + \hat{W}_f + \int d^3\mathbf{r} [\hat{\mathbf{j}}_f(\mathbf{r}t) \cdot \mathbf{A}_P(\mathbf{r}t) + \hat{n}(\mathbf{r})(v(\mathbf{r}) - \phi_P(\mathbf{r}t) - \frac{1}{2}\mathbf{A}_P^2(\mathbf{r}t))] \quad (6.27)$$

Where  $\hat{T}_f = \bigoplus_\alpha \hat{T}_\alpha$  and  $\hat{W}_f = \bigoplus_\alpha \hat{W}_\alpha$ , being  $\hat{T}_\alpha$  and  $\hat{W}_\alpha$  operators that only apply to the fermionic Fock space of fragment  $\alpha$ .

Eq. (6.26) has the same form of the Liouville equation of the real system, Eq. (6.7). Differentiation of  $\text{tr}\{\hat{\mathbf{j}}(\mathbf{r}t)\hat{\Gamma}_f\}$  with respect to time gives rise to the evolution equation of the partitioned molecule as a whole. The evolution equation is the same as that shown in Eq. (6.22), where the term in the summation over the fragments,  $\sum_\alpha \mathbf{q}_\alpha + n_\alpha \nabla v_\alpha$ , is simply  $-i \text{tr}\{\hat{\Gamma}_f(t)[\hat{\mathbf{j}}_f(\mathbf{r}t), \hat{H}_f^0]$ , where  $\hat{H}_f^0$  is the Hamiltonian of the partitioned molecule in absence of electromagnetic fields. The previous commutator and the commutator  $-i \text{tr}\{[\hat{\mathbf{j}}(\mathbf{r}t), \hat{T} + \hat{W}]\hat{\Gamma}(t)\}$  are analogous: They are both free of the EM field and they are determined by the initial state. This analogy is what allows us to extend the Ghosh and Dhara proof to fragmented molecules in presence of partition EM fields.

Let us define the partition Kohn-Sham hamiltonian  $\hat{H}_{f,s}(t)$  of the fragmented molecule as follows:

$$\hat{H}_{f,s}(t) = \bigoplus_{\alpha} \left( \int d^3\mathbf{r} \hat{\psi}_{\alpha}^{\dagger}(\mathbf{r}) [-i\nabla + \mathbf{A}_{s,\alpha}(\mathbf{r}t)]^2 \hat{\psi}_{\alpha}(\mathbf{r}) + \int d^3\mathbf{r} \hat{n}_{\alpha}(\mathbf{r}) v_{\alpha}(\mathbf{r}) \right) \quad (6.28)$$

where  $\mathbf{A}_{s,\alpha} = \mathbf{A}_P + \mathbf{A}_{H,\alpha} + \mathbf{A}_{xc,\alpha}$  and

$$\partial_t \mathbf{A}_{H,\alpha}(\mathbf{r}t) = -\nabla \int d^3\mathbf{r}' \frac{n_{\alpha}(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} \quad (6.29)$$

The state of the partition KS system evolves according to:  $i\partial_t \hat{\Gamma}_{f,s}(t) = [\hat{H}_{f,s}(t), \hat{\Gamma}_{f,s}]$  The initial state is chosen such that:  $\text{tr}\{\hat{\Gamma}_{s,\alpha}(0)\hat{\mathbf{j}}_{\alpha}(\mathbf{r}0)\} = \mathbf{j}_{\alpha}(\mathbf{r}0)$  The XC potential is obtained by setting:  $\text{tr}\{\hat{\Gamma}_{s,\alpha}(t)\partial_t \hat{\mathbf{j}}(\mathbf{r}t)\} = \text{tr}\{\hat{\Gamma}_{\alpha}(t)\partial_t \hat{\mathbf{j}}(\mathbf{r}t)\}$  This yields:

$$\mathbf{j}_{\alpha} \times \nabla \times \mathbf{A}_{Hxc,\alpha} + n_{\alpha} \partial_t \mathbf{A}_{Hxc,\alpha} = \mathbf{q}_{\alpha} - \mathbf{q}_{s,\alpha} \quad (6.30)$$

where  $\mathbf{q}_{s,\alpha} = -i\text{tr}\{\hat{\Gamma}_{s,\alpha}(t)[\hat{T}_{\alpha}, \hat{\mathbf{j}}_{\alpha}]\}$ . The above is the conventional Hxc vector potential of TDCDFT and is a functional of  $\mathbf{j}_{\alpha}, \hat{\Gamma}_{\alpha}(0), \hat{\Gamma}_{s,\alpha}(0)$ . Now we can derive the equivalent of the zero-force theorem: Our objective is to represent the evolution of the current-density, Eq. 6.15, by means of the current-density shown in Eq. (6.22). As a consequence, the total momentum  $\mathbf{P}(t) = \int d^3\mathbf{r} \mathbf{j}(\mathbf{r}t)$  is represented by the partitioned molecule as well. Suppose the current-density  $\mathbf{j}$  is given and that we chose the proper partition field,  $\phi^*, \mathbf{A}_G^*$  that yields  $\mathbf{j}$ ; and, the EM field of the real system is  $\mathbf{E}^*$  and  $\mathbf{B}^*$ . Because the hydrodynamic-like quantities  $\mathbf{q}$  and  $\{\mathbf{q}_{\alpha}\}$  do not exert a net external force on the system, comparison of total momentum obtained in Eqs. (6.15) and (6.22) leads to the following exact condition for the partition potential:

$$\int d^3\mathbf{r} n \mathbf{E}_P^* + \mathbf{j} \times \mathbf{B}_P^* = \int d^3\mathbf{r} n \mathbf{E}^* + \mathbf{j} \times \mathbf{B}^* + n \nabla v - \sum_{\alpha} n_{\alpha} \nabla v_{\alpha} \quad (6.31)$$

This last equation suggests that the partition potential must have two types of contributions: one ensuring that the system is subject to the right external forces due to the EM field, and another introducing the right nuclear forces correcting for the fact that the system is partitioned. Other contribution to the partition field comes from the internal forces, i.e., the difference between the stress tensor of the real and

partitioned molecule. These internal forces do not contribute to Eq. (6.3) but they are essential to reproduce the dynamics of the real molecule.

Our simple extension of the proof of Ghosh and Dhara allows us to regard the partition 4-potential as a functional of the current for a given partition  $\{v_\alpha\}$ . The EM field of the real system in Eq. ( ) can be eliminated if we split the partition field as follows:

$$(\mathbf{A}_P, \phi_P)[\mathbf{j}; \hat{\Gamma}_f(0), \{v_\alpha\}] = (\mathbf{A}, \phi)[\mathbf{j}; \hat{\Gamma}(0), v] + (\mathbf{A}_G, \phi_G)[\mathbf{j}; \hat{\Gamma}(0), \hat{\Gamma}_f(0), v, \{v_\alpha\}] \quad (6.32)$$

where  $(\mathbf{A}_G, \phi_G)$  is the gluing 4-potential, a potential accounting for the time-dependent correlation between the fragments. It depends on the current density, where the initial states and external potentials of the real and partitioned system are given. If we evaluate the 4-potential at the current density  $\mathbf{j}^*$  and plug it into Eq. (6.3) we obtain the condition:

$$\int d^3\mathbf{r} \, n \mathbf{E}_G^* + \mathbf{j} \times \mathbf{B}_G^* = \int d^3\mathbf{r} \, \left( n \nabla v - n_\alpha \sum_\alpha \nabla v_\alpha \right) \quad (6.33)$$

This equation can be regarded as a generalization of the zero force theorem of TD-CDFT. In fact, if we only had one partition and eliminate the electron-electron repulsion from the only fragment's Hamiltonian we would obtain that the partition vector potential, in the Weyl Gauge, becomes the exact Hxc vector potential and the above equation becomes the zero-force theorem.

The initial density matrix  $\hat{\Gamma}_f$  is chosen to represent the initial current-density of the system  $\mathbf{j}_0 = \mathbf{j}(\mathbf{r}t_0)$ . We assumed it is given and found the properties that the partition field satisfies. There are several methods to find the initial state. If the molecule is initially in a stationary state (no current-density), then PDFT can be used to find the initial state, which only needs to represent the density. In such case we perform the operation

$$E_f[n(\cdot, t_0)] = \min\{\hat{\Gamma}_f \in \mathcal{L} : \text{tr}[\hat{\Gamma}_f \hat{H}_f^0] | \hat{\Gamma}_f \rightarrow n(\mathbf{r}t_0)\} \quad (6.34)$$

which requires only the introduction of the scalar partition potential  $\phi_P$  (or a longitudinal partition vector potential). On the other hand, if the system has an initial

current density  $\mathbf{j}_0$  then we replace the density  $n(\cdot, t_0)$  by the current-density  $\mathbf{j}_0$  as the constraint in Eq. (6.34). The density matrix that minimizes the right hand side of Eq. (6.34) can then be used as initial state. In a similar fashion we obtain the initial Kohn-Sham state for each fragment, we just apply the same procedure to each fragment Hamiltonian,  $\hat{T}_\alpha$ , which is the kinetic energy of non-interacting electrons. In each minimization, the constraint to satisfy is that the Kohn-Sham system must yield the initial fragment current-density  $\mathbf{j}_\alpha(\mathbf{r}t_0)$  (or density  $n_\alpha(\mathbf{r}t_0)$  in case there is no current-density).

#### 6.4 Variational Formulation

Let us consider the Keldysh space, which is defined by a pseudo-time  $z$  a vector of the form  $(t, \sigma)$ , where  $\sigma$  only takes to values,  $+$  or  $-$ . Here we denote  $z$  as  $t^\sigma$ . For convenience let us employ the Weyl gauge (or temporal gauge), that is, we set  $\phi_G = 0$ . The Hamiltonian of the fragmented molecule  $\hat{H}_f$  is a functional of the partition vector potential  $\mathbf{A}_P$ . These two objects,  $\hat{H}_f$  and  $\mathbf{A}_P$ , now depend on the pseudo-time  $z$ . In general we assume that  $\mathbf{A}_P(\mathbf{r}t^+) \neq \mathbf{A}_P(\mathbf{r}t^-)$ . Now define the functional:

$$F_P[\mathbf{A}] = i \ln \text{tr}\{\hat{\Gamma}_f(0)\hat{V}_f[\mathbf{A}](z_f, z_i)\} \quad (6.35)$$

where  $z_i = t_0^+$  and  $z_f = t_0^-$  and

$$\hat{V}[\mathbf{A}_P](z_f, z_i) = \hat{\mathcal{T}}_{\mathcal{K}} \exp \left( -i \int_{z_i}^{z_f} dz \hat{H}[\mathbf{A}_P](z) \right) \quad (6.36)$$

where the integration in Eq. (6.36) is taken over the  $\mathcal{K}$  space is defined as:

$$\int_{z_i}^z dz' \hat{H}[\mathbf{A}_P](z') := \begin{cases} \int_{t_0}^t dt' \hat{H}[\mathbf{A}_P](t'^+), & z = t^+ \\ \int_{t_0}^{t_1} dt' \hat{H}[\mathbf{A}_P](t'^+) + \int_{t_1}^t dt' \hat{H}[\mathbf{A}_P](t'^-), & z = t^-. \end{cases} \quad (6.37)$$

$t_1 > t_0$  is the upper limit of the propagation in real time.  $\hat{\mathcal{T}}_{\mathcal{K}}$  is the path-ordering operator in the Keldysh space. If  $z_2$  is later than  $z_1$  in the contour then  $\hat{\mathcal{T}}_{\mathcal{K}}[\hat{A}(z_1)\hat{A}(z_2)] = \hat{A}(z_2)\hat{A}(z_1)$ .  $z_2 = (t_2, \sigma_2)$  is later than  $z_1 = (t_1, \sigma_1)$  if: i)  $t_2 > t_1$  and  $\sigma_2 = \sigma_1 = +$ , or

ii)  $t_2 < t_1$  and  $\sigma_2 = \sigma_1 = -$ , or iii)  $\sigma_2 = -$  and  $\sigma_1 = +$  (regardless the value of  $t_2$  and  $t_1$ ).

It can be shown that:  $\frac{\delta F_P}{\delta \mathbf{A}_P(\mathbf{r}z)} = \tilde{\mathbf{j}}(\mathbf{r}z)$  where  $\tilde{\mathbf{j}}$  is pseudo-current:

$$\tilde{\mathbf{j}}(\mathbf{r}z) = \frac{\text{tr}\{\hat{\Gamma}_f(0)\hat{V}_f(z_f, z)(\hat{\mathbf{j}}_f(\mathbf{r}) + \hat{n}_f(\mathbf{r})\mathbf{A}_P(\mathbf{r}z))\hat{V}_f(z, z_i)\}}{\text{tr}\{\hat{\Gamma}_f(0)\hat{V}_f(z_f, z_i)\}} \quad (6.38)$$

The pseudo-current becomes the physical current of the fragmented molecule when  $\mathbf{A}_P(\mathbf{r}t^+) = \mathbf{A}_P(\mathbf{r}t^-)$ .

To relate the fragmented and real molecules' vector potentials define the real system's action:

$$F[\mathbf{A}] = i \ln \text{tr}\{\hat{\Gamma}_0 \hat{V}[\mathbf{A}](z_f, z_i)\} \quad (6.39)$$

Where  $\hat{V}$  has the same form  $\hat{V}_f$ ,  $\hat{H}_f$  is replaced by the Hamiltonian  $\hat{H}$  in Eq. (6.36).

Let us define the current-density-functional by means of the Legendre-transformation:

$$L[\tilde{\mathbf{j}}] = -F[\mathbf{A}] + \int d^3\mathbf{r}dz \tilde{\mathbf{j}}(\mathbf{r}z) \cdot \mathbf{A}(\mathbf{r}z) \quad (6.40)$$

The same transformation applied to the functional  $F_P$  yields the current-density-functional  $L_P$ . Finally let  $L_G$  be the gluing functional:

$$L_G[\tilde{\mathbf{j}}] = L_P[\tilde{\mathbf{j}}] - L[\tilde{\mathbf{j}}] \quad (6.41)$$

Functional differentiation of this functionals and insertion of Eq. (6.32) gives

$$\frac{\delta L_G}{\delta \tilde{\mathbf{j}}(\mathbf{r}z)} = \mathbf{A}_G[\tilde{\mathbf{j}}](\mathbf{r}z) \quad (6.42)$$

This last equation relates the gluing vector potential with its action functional (the dependency on the initial conditions are the same). The  $L_G$  action accounts for the interactions that take place in between the fragments without considering the external perturbation  $\mathbf{A}$ . The last step to obtain the gluing vector potential of the physical system is to evaluate at the physical current of the system, that is when  $\tilde{\mathbf{j}}(\mathbf{r}t^+) = \tilde{\mathbf{j}}(\mathbf{r}t^-)$ .

Further differentiation of Eq. (6.40) and evaluation at the physical regime leads us to the equation:

$$\chi_{\mu\nu}^{-1}(\mathbf{r}t, \mathbf{r}'t') = \chi_{\mu\nu, P}^{-1}(\mathbf{r}t, \mathbf{r}'t') - \chi_{\mu\nu, G}^{-1}(\mathbf{r}t, \mathbf{r}'t') \quad (6.43)$$

where  $\chi_{\mu\nu}^{-1}$  is the inverse first order response tensor of the super molecule, where

$$\chi_{\mu\nu}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta A_\mu(\mathbf{r}t)}{\delta j_\nu(\mathbf{r}'t')} \quad (6.44)$$

Similar equations define  $\chi_{\mu\nu,P}$  and  $\chi_{\mu\nu,G}$ ,  $\mathbf{A}$  has to be replaced by  $\mathbf{A}_P$  and  $\mathbf{A}_G$  respectively. One can derive Eq. (6.43) using only the above definition, avoiding the use of the Keldysh formalism. Eq. (6.43) can be recast in the form:

$$\underline{\chi} = \underline{\chi}_P + \underline{\chi}_P \underline{\chi}_G^{-1} \underline{\chi} \quad (6.45)$$

Where  $\underline{\chi}$  refers to the matrix form of the tensor(s). This equation can be used within the linear response regime to obtain the excitation energies of the super molecule. An interesting property of  $\chi_P^{-1}$  is that it is additive:

$$\underline{\chi}_P^{-1} = \sum_{\alpha} \underline{\chi}_{P,\alpha}^{-1} \quad (6.46)$$

where  $\chi_{P,\alpha}^{-1} = \delta \mathbf{j}_\alpha / \delta \mathbf{A}_P$ . However, in Eq. (6.45), the gluing linear response function must correct  $\underline{\chi}_P$  so the poles (excitation frequencies) of the super molecule are recovered.

### 6.5 Charged Particle in a Ring

To illustrate the existence of the partition field, let us consider the case of a charged particle in a ring under a external periodic potential. The particle is prepared in a linear combination of its ground state and second excited state. Later this state is propagated, and the partition field is found solving the inverse problem, that is, given the current-density find the partition field. The Hamiltonian of the system is:

$$\hat{H} = \frac{1}{2mR^2} \hat{L}_z^2 + V(\varphi) \quad (6.47)$$

where the external potential in this case is:  $V(\varphi) = -V_0 \cos(2\varphi - \pi)$  Define two fragments, left (L) and right (R), which are described by:

$$\hat{H}_\alpha(t) = \frac{1}{2mR^2} (\hat{L}_z - \lambda(\varphi, t) \Theta(t))^2 + V_\alpha(\varphi) + v_P(\varphi) \quad (6.48)$$

where  $\alpha = L, R$ ,  $\hat{L}_z = i\partial/\partial\phi$ ,  $\lambda = B_z R^2/2$ , and  $\Theta(t)$  is the Heaviside function:

$$\Theta(t) = \begin{cases} 1 & \text{if } t > 0 \\ 0 & \text{otherwise} \end{cases} \quad (6.49)$$

The potentials defining the partition are

$$V_L(\phi) = \begin{cases} V(\phi), & 0 \leq \phi < \pi \\ 0, & \text{otherwise} \end{cases} \quad (6.50)$$

and  $V_R(\phi) = V_L(\phi - \pi)$ ,  $0 \leq \phi \leq 2\pi$ .

We begin by finding the eigenvalues of the Hamiltonian shown in Eq. (6.47), that is  $\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$ , using the finite differences method. The objective is to reproduce the time-dependent density generated by the following linear combination:

$$|\psi(t)\rangle = c_0|\psi_0\rangle e^{-iE_0t} + c_2|\psi_2\rangle e^{-iE_2t} \quad (6.51)$$

where  $c_0 = \sqrt{0.98}$  and  $c_2 = \sqrt{0.02}$ . PDFT is used to obtain the initial state of the system: The density  $n^{\text{ref}}(\varphi, t=0) = |\psi(\varphi, t=0)|^2$  is used as a reference to minimize the error:

$$e[v_P]^2 = \|n^{\text{ref}}(\cdot, t=0) - n_0[v_P]\|_2^2 \quad (6.52)$$

by varying the partition potential  $v_P$  where  $n_0[v_P] = \nu_L|\psi_L[v_P]|^2 + \nu_R|\psi_R[v_P]|^2$  the error is minimized using sequential least-squares quadratic programming. The wavefunctions  $\psi_L$  and  $\psi_R$  are functionals of the partition potential and are obtained by solving the eigenvalue problem  $\hat{H}_\alpha(t=0)[v_P]|\psi_\alpha[v_P]\rangle = E_\alpha|\psi_\alpha[v_P]\rangle$ . The wavefunctions  $\psi_L$  and  $\psi_R$  are propagated by solving the Schrodinger equation  $i\partial\psi_\alpha(\varphi, t)/\partial t = \hat{H}_\alpha(t)\psi_\alpha(\varphi, t)$  with the Crank-Nicholson method. At each time step the following error functional is minimized:

$$e^2[\lambda] = \|j^{\text{ref}}(\cdot, t) - j[\lambda](\cdot, t)\|_2^2 \quad (6.53)$$

To reproduce the TD current-density of the system,  $j^{\text{ref}} = \text{Re}(i^{-1}\psi^*\partial_\varphi\psi)$ , the above functional was minimized using the MINPACK routine `lder`. Even though the current



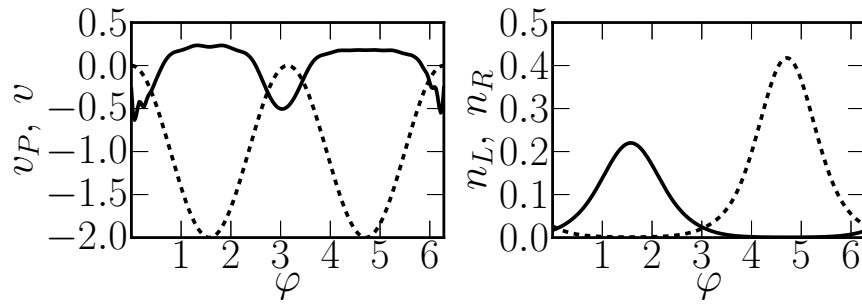
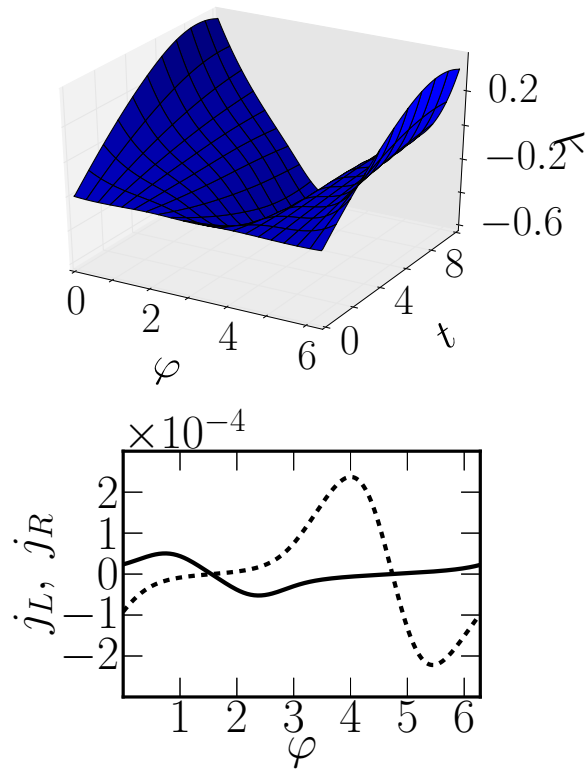


Figure 6.1. Partition potential and densities

Figure 6.2.  $\lambda$  potential, and fragment current-densities at  $t = 2.0$ .

density is nearly constant, the  $\lambda$  field varies significantly. An advantage of employing  $\lambda$  to reproduce the current is the explicit dependence of the latter on the former, i.e.:

$$j(\varphi, t) = j_p(\varphi, t) + n(\varphi, t)\lambda(\varphi, t) \quad (6.54)$$

Fig 1.a. shows the external potential of the system and the partition potential required to represent the initial density of the system. The partition potential has two wells: one around  $\phi = \pi/2$ , and another one at the boundaries. The partitioning scheme we chose localizes the current-densities of the fragments. The left fragment is isolated from the right fragment. Therefore, the partition potential must allow for some spreading of the left fragment density into the right fragments region. The depth of the partition potential depends on how high the barrier separating the fragment potentials is. If it is higher then the the partition potential depth should be higher as well. Fig. 1.b. shows the initial electronic densities of each fragment. In this case the addition of the second excited state adds some extra charge to the right fragment density.

In Fig 2.a the partition magnetic field is shown, initially it is zero because we used the scalar partition potential to represent the initial density and there is no current-density in the initial state. The partition magnetic potential is unique: There is no another one with the same initial condition that yields the current-density of the system. Similarly, for the partition chosen, the current densities shown in Fig 2.b are unique, and in this case they are localized around their respective fragments. Each fragments' current-density is in a 1-1 correspondence with the partition potential. However, in practice, the map between the total current-density and the partition magnetic field (or the partition 4-potential in general) is more useful. The reason is the following: If the current-density of a fragment is localized around the fragment, then it is not sensitive to variations 4-potential in regions far from the fragment nuclei, while the total-current density is sensitive far the fragment's nuclei, if it is close to the center of another fragment.

## 6.6 Concluding Remarks

In this chapter I presented the framework of quantum dynamics, based on the principles of DFT, of electronic fragments under scalar or vector potentials. A fictitious 4-potential that quantifies the correlation between the fragments was introduced. The properties that this potential satisfies were also derived in this chapter. For future work, new functionals for this framework are required, some directions are shown in chapter 7.

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## 7. FRAGMENT-BASED TIME-DEPENDENT DENSITY FUNCTIONALS

### 7.1 Introduction

Simple and productive methods to investigate dynamical features of solids and molecules are offered by Time-dependent Density-functional Theory (TDDFT) [1]. This theory embodies many concepts and formal exact results, but its core is the 1-1 correspondence [2] between time-dependent (TD) external potentials and TD electronic densities, provided the initial state of the system is given. Through the use of the TD Kohn-Sham (KS) equations [3], every observable of the system is expressed as a TD density-functional. The TD KS equations are single-particle Schrödinger equations that require an approximation to the exchange-correlation (XC) potential, a density-functional.

The adiabatic local density approximation (ALDA) [4] to the TD XC potential is, perhaps, the simplest, useful approximation to study the dynamics of atoms and solids. However, when applied to molecules, especially when the distance between atoms is large, ALDA yields unphysical results. For example, atoms with fractional charges, underestimated charge transfer excitation energies, missing double excitations, among others. Alternative TD XC potentials are obtained by careful introduction of functions that depend on KS orbitals, and, sometimes, fitting parameters. However, it is very challenging to enhance the performance of ALDA while preserving computational simplicity and elegance.

The TD KS equations describe all the electrons as part of a single entity, imposing a limit on the number of atoms that can be simulated in a reasonable amount of time. This limit can be increased dividing a molecule into fragments to perform calculations on each individual fragment. Several approximated methods to investi-

gate the electron dynamics of molecules are available [5–8]. These consist in assigning every fragment in the molecule a set of TD single-particle Schrödinger equations (not necessarily TD KS equations) in which the electrons are subject to a potential representing the interactions between the electrons of the fragment, and an extra potential accounting for the interaction between the fragments is added. Successful applications to the calculation of solvachromatic shifts [9, 10] and excitation energy of monomers [6] are reported.

A rigorous extension of TDDFT, fragment-based TDDFT, for molecules made of chemical fragments is presented in Ref. [11]. In this extension a molecule is divided into fragments, each one is a set of atoms. Every fragment is assigned an initial state, and a Hamiltonian including a global, auxiliary potential, termed partition potential (partition potential), which enforces that the total electronic density is the true TD electronic density of the molecule. We proved that the partition potential is uniquely determined by the TD electronic density of the system; thus, it can be expressed as a density-functional. The linear response and extension to consider electromagnetic fields is presented in Ref. [12].

The Hamiltonians used in Refs. [11] and [12], and the aforementioned approximated methods, are particle-conserving, i.e., the average number of electrons in a fragment is time-independent. The purpose of this paper is to extend fragment-based TDDFT to allow for variable number electrons in each fragment, and preserving the uniqueness of observables as density-functionals. The formalism introduced in this paper can serve as a theoretical foundation for the development of methods accounting for electronic excitations and processes of electron-transfer, without sacrificing the use of the ALDA and computational efficiency.

## 7.2 Fragment-based TDDFT

### 7.2.1 Formulation

An electron in a fragment, labeled  $\alpha$ , is subject to a 1-body external potential, denoted as  $v_\alpha$ . For example,  $v_\alpha(\mathbf{r}) = \sum_{i \in I_\alpha} -Z_i/|\mathbf{r} - \mathbf{R}_i|$ .  $I_\alpha$  is a set of the indices corresponding to the atoms composing fragment  $\alpha$ . We assign each fragment in the molecule a Hamiltonian, including an auxiliary potential, here dubbed, partition potential:

$$\hat{H}_\alpha[v_p](t) = \hat{H}_\alpha^0 + \int d^3\mathbf{r} \hat{n}(\mathbf{r})v_p(\mathbf{r}t) , \quad (7.1)$$

where  $\hat{H}_\alpha^0 = \hat{T} + \hat{W} + \int d^3\mathbf{r} \hat{n}(\mathbf{r})v_\alpha(\mathbf{r})$ ,  $\hat{T}$  and  $\hat{W}$  are the kinetic, and coulombic repulsion energy operators, respectively, and  $\hat{n}(\mathbf{r})$  is the density operator. This Hamiltonian is in absence of any external driving force besides that due to the nuclei of the fragment  $\alpha$ . TD displacement of the positions of the nuclei can be described by introducing a time-dependent Hamiltonian where  $v_\alpha$  is replaced by the corresponding TD fragment-potential,  $\sum_{i \in I_\alpha} -Z_i/|\mathbf{r} - \mathbf{R}_i(t)|$ .

The state of a fragment is described by the evolution of the ket  $|\psi_\alpha[v_p](t)\rangle$  in Fock space, which satisfies the TD Schrödinger equation:

$$i\partial_t|\psi_\alpha[v_p](t)\rangle = \hat{H}_\alpha[v_p](t)|\psi_\alpha[v_p](t)\rangle , \quad (7.2)$$

where

$$|\psi_\alpha(t)\rangle = \sum_M \nu_{\alpha,M} |\psi_{\alpha,M}(t)\rangle . \quad (7.3)$$

$\{\psi_{\alpha,M}\}$  are kets corresponding to states with integer number of particles and  $\nu_{\alpha,M}$  is the weight amplitude of that state. Kets with different number of electrons are orthogonal,  $\langle\psi_{\alpha,M}|\psi_{\alpha,M'}\rangle = 0$  ,  $M \neq M'$ . The total density is defined as

$$n(\mathbf{r}t) = \sum_\alpha n_\alpha(\mathbf{r}t) , \quad (7.4)$$

and  $n_\alpha(\mathbf{r}t) = \langle\psi_\alpha(t)|\hat{n}(\mathbf{r})|\psi_\alpha(t)\rangle$ . In Ref. [11], the following theorem was proved: given a set  $\{\psi_{\alpha,0}, v_\alpha\}$ , two potentials  $v_p$  and  $v'_p$  that differ by more than a TD constant



cannot give rise to the same density. A corollary of this theorem is that there is a TD density-functional that, when evaluated at a given TD electronic-density, gives the corresponding TD partition potential.

The partition potential represents the TD electronic density of the supermolecule, it is decomposed as follows [12]:

$$v_p(\mathbf{r}t) = v_G(\mathbf{r}t) + v_d(\mathbf{r}t) . \quad (7.5)$$

$v_G$  is the gluing potential, accounting for the correlation between the fragments, and  $v_d$  is the driving potential the molecule is subject to (e.g. laser field). The gluing potential yields the shape of the potential such that the TD electronic density is recovered. The formal expression defining the gluing potential is:

$$\begin{aligned} \frac{1}{i} \nabla \cdot n(\mathbf{r}t) \nabla v_G(\mathbf{r}t) &= \langle \psi(t) | [\hat{H}^0, \nabla \cdot \hat{\mathbf{j}}(\mathbf{r})] | \psi(t) \rangle \\ &- \sum_{\alpha} \langle \psi_{\alpha}(t) | [\hat{H}_{\alpha}^0, \nabla \cdot \hat{\mathbf{j}}(\mathbf{r})] | \psi_{\alpha}(t) \rangle . \end{aligned} \quad (7.6)$$

The right hand side terms of the above equation are TD density-functionals. Approximation to the terms on the r.h.s of the above equation and solution to the resulting differential equation renders an estimation to the gluing potential. Another way of approximating  $v_G$  is assuming that the system evolves adiabatically through its ground states, driven by a very slowly-varying field. In such case the potential  $v_G$  is obtained from the adiabatic approximation in ground-state Partition DFT [13, 14]:

$$v_G^{\text{Ad}}[n(t)] = v_p^{\text{Ad}}[n(t)] - v^{\text{HK}}[n(t)] , \quad (7.7)$$

where  $v^{\text{HK}}[n(t)]$  is the external perturbation the interacting electrons are subject to in their ground-state in order to yield the density  $n(\mathbf{r}t)$  ( $v^{\text{HK}}$  follows from the Hohenberg-Kohn theorem). The partition potential,  $v_p^{\text{Ad}}[n(t)]$ , is the Lagrange multiplier required to solve the minimization:

$$\min_{\{\psi_{\alpha}\} \rightarrow n(t)} \sum_{\alpha} \langle \psi_{\alpha} | \hat{H}_{\alpha}^0 | \psi_{\alpha} \rangle . \quad (7.8)$$

The Lagrange multiplier for this problem is unique, up to an arbitrary constant [15].

For practical applications, the TD partition KS equations are:

$$i\partial_t\phi_{i,\alpha}(\mathbf{r},t) = \left( -\frac{1}{2}\nabla^2 + v_{\text{Hxc}}[n_\alpha](\mathbf{r},t) + v_\alpha(\mathbf{r}) + v_{\text{G}}[n](\mathbf{r},t) + v_{\text{d}}(\mathbf{r},t) \right) \phi_{i,\alpha}(\mathbf{r},t) . \quad (7.9)$$

The density is obtained by means of:  $n(\mathbf{r},t) = \sum_{i\alpha} f_{i\alpha} |\phi_{i\alpha}(\mathbf{r},t)|^2$ , where  $\{f_{i\alpha}\}$  are the occupation numbers (time-independent), chosen from a proper ensemble [11].

### 7.3 Classical Interpretation of the Partition Potential

We now show that, when the system is split into a subsystem made of a single massive particle, and bath formed by particles much smaller than the massive one, the partition potential is responsible for the Langevin dynamics. The evolution of the subsystem particle, labeled S, is dictated by Eq. (7.2). The average position of the particle is  $\bar{\mathbf{r}}_S(t) = \int d^3\mathbf{r} \mathbf{r} |\psi_S|^2(\mathbf{r},t)$ . By the Ehrenfest theorem and correspondence principle we have

$$m_S \frac{d^2 \bar{\mathbf{r}}_S}{dt^2} = -\mathbf{F}_{\text{p},S}(t) , \quad (7.10)$$

where  $\mathbf{F}_{\text{p},S}(t) = -\int d^3\mathbf{r} |\psi_S|^2(\mathbf{r},t) \nabla v_{\text{p}}(\mathbf{r},t)$ , and  $m_S$  is the mass of the particle. In the classical limit, comparison with the equation of motion of the real system indicates that  $-(\nabla v_{\text{p}})(\bar{r}_S(t)) = -(\nabla U_{\text{int}})(\bar{r}_S(t), \bar{r}_B(t))$ , where  $U_{\text{int}}$  is the total interaction potential between the particles.

As the mass of the subsystem particle is increased, the density tends to the classical Dirac distribution. Thus, the shape of the partition potential for any point but that of the particles is undefined. However, for given initial momenta and coordinates of the particles and bath, the evolution of the momenta of the total system is in a one-to-one correspondence with the partition forces exerted on each particle. Furthermore, if the assumptions of Langevin dynamics are applicable, the partition force of the massive particle can be interpreted as  $\mathbf{F}_{\text{p},S}(t) = -\gamma \mathbf{v}_S(t) + \mathbf{F}_{\text{ran}}(t)$ . Where  $\mathbf{v}_S(t) = -d\bar{\mathbf{r}}_S/dt$ ,  $\gamma$  is the friction coefficient, and  $\mathbf{F}_{\text{ran}}$  is the random force.

### 7.4 Numerical TD Potentials

TDDFT, which our formulation is built upon, concerns about the simplification of the problem:

$$(i\partial_t - \hat{H}^\lambda[v](t))|\psi(t)\rangle = 0, \quad |\psi(0)\rangle = |\psi_0\rangle, \quad (7.11)$$

where

$$\hat{H}^\lambda[v](t) = \hat{T} + \lambda\hat{W} + \int d^3 \mathbf{r} \hat{n}(\mathbf{r})v(\mathbf{r}t). \quad (7.12)$$

Runge and Gross [2] showed that if  $v$  is Taylor-expandable and does not display physical anomalies in the boundaries, then  $v$  determines  $n$  uniquely, up to a TD constant in the potential (this theorem can be extended to include non-analytic potentials [16]). Let us denote the RG map as  $\Lambda_{\psi_0}^\lambda$ ; thus,  $n(t) = \Lambda_{\psi_0}^\lambda[v](t)$ . The operator  $\hat{W}$  can be representative of different types of electron-electron interactions, such as screened coulombic repulsion. If  $\lambda = 0$ , then the electrons are free.

Suppose a well behaved density,  $n^{\text{ref}}$ , and a initial state  $\psi_0$  are known. If  $v_1$  and  $v_0$  exist, where  $v_\lambda(t) = (\Lambda_{\psi_0}^\lambda)^{-1}[n^{\text{ref}}](t)$ , then, the Hartree-exchange-correlation potential for the system, by definition, reads  $v_{\text{HXC}} = v_0 - v_1$ . For the exact TDDFT, one needs the map  $\Lambda_{\psi_0}$ , i.e., the TD Schrödinger equations has to be solved, which is what is to be avoided in practical calculations.

For the development of functionals, exploration of the map  $\Lambda_{\psi_0}^\lambda$  is fruitful; this map could be investigated by solving the problem  $n^{\text{ref}}(t) - \Lambda_{\psi_0}^\lambda[v](t) = 0$ , which is a root-finding problem. The first order response of the density for some perturbation  $\delta v$  is  $\delta n(\mathbf{r}t) = \int d^3 \mathbf{r}' dt' \chi^{-1}(\mathbf{r}t, \mathbf{r}'t')\delta v(\mathbf{r}'t')$ . The response function  $\chi^{-1}$  should decay in the asymptotics. Hence, large perturbations of  $v$  in the asymptotics have little response in  $n$ . In the ground-state case this problem can be alleviated by enforcing satisfaction of eigenvalue constraints. For three dimensional applications, capturing the asymptotic region is difficult if the Gaussian basis sets are used because they do not display the right asymptotic behavior. In practice, the root-finding problem is quite unstable.

Instead of solving the exact root-finding problem, one can solve a minimization problem:

$$\min_{v \in \mathcal{V}} \int_0^T \|n^{\text{ref}}(s) - \Lambda_{\psi_0}^\lambda[v](s)\|_\mu^2 ds . \quad (7.13)$$

This problem is still theoretical because the quantities  $n^{\text{ref}}(t)$  and  $\langle \psi[v](t) | \hat{n}(\mathbf{r}) | \psi[v](t) \rangle$  need to be approximated. Instead, we now write  $n^{\text{ref}}(t) - \Lambda_{\psi_0}^\lambda[v](t) = \tilde{n}^{\text{ref}}(t) - \tilde{\Lambda}_{\psi_0}^\lambda[v](t) + \epsilon[n^{\text{ref}}, v]$ .  $\tilde{n}^{\text{ref}}(t)$  is the approximation to  $n^{\text{ref}}(t)$  and  $\tilde{\Lambda}_{\psi_0}^\lambda[v]$  is the approximation to  $\Lambda_{\psi_0}^\lambda$ . If  $v^*$  is the exact potential representing  $n^{\text{ref}}$ , then the problem becomes  $\tilde{n}^{\text{ref}} = \tilde{\Lambda}_{\psi_0}^\lambda[v^*] + \epsilon$ . Because we cannot use exact methods to determine  $n^{\text{ref}}$  and  $\Lambda_{\psi_0}^\lambda$ , we assume that  $\epsilon$  is a random function. Moreover, one would expect that  $\tilde{n}^{\text{ref}}$  and  $\Lambda_{\psi_0}^\lambda$  have smooth timespace gradients, and that  $\epsilon$  displays autocorrelation because the spacing between points is arbitrarily small.

#### 7.4.1 Estimation of the Partition Potential

Let  $\mathcal{V}_p$  be a space of TD partition potentials, and  $\mathcal{D}$  a space of TD densities and define the map:

$$\Lambda_{S_0} : \mathcal{V}_p \rightarrow \mathcal{D} , \quad (7.14)$$

where  $S_0 = \{\psi_{\alpha,0}, v_\alpha\}$ . For a given TD partition potential, the density is obtained by evaluation of the above map at the given partition potential, in other words,  $n(t) = \Lambda_{S_0}[v_p](t)$ . This map depends on the history of the partition potential, i.e., it has memory dependence [11].

Let  $v_p^*$  be the true partition potential. We assume that, due to numerical errors, the estimation to the reference density  $\tilde{n}^{\text{ref}}$  is of the form  $\tilde{n}^{\text{ref}} = \tilde{\Lambda}_{S_0} + \epsilon$ , where  $\epsilon$  is a *random function*. To estimate the partition potential corresponding to  $\tilde{n}^{\text{ref}}$  we minimize:

$$\|e[v_p]\|_\mu^2 = \|\tilde{n}^{\text{ref}} - \tilde{\Lambda}_{S_0}[v_p]\|_\mu^2 , \quad (7.15)$$

where  $d\mu(\mathbf{r}, t)$  is the measure.

Given  $\epsilon$  is a function, its probability density function (PDF) is a *functional*. The PDF depends on parameters, we denote them as  $\Theta$ , and the PDF as  $D([\epsilon]|\Theta)$ . The probability that  $\epsilon$  is observed in a set  $\mathcal{U}$  is given by the path integral:

$$P(\epsilon \in \mathcal{U}|\Theta) = \int_{\mathcal{U}} dm_L[\epsilon] D([\epsilon]|\Theta) , \quad (7.16)$$

Where the measure over the space of errors is  $m_L$ . The traditional methods of non-linear regression can be applied to estimate the best parameters of the distribution,  $\Theta^*$ , for a given set of observations. Then a Taylor expansion in terms of the parameters can be used to generate the PDF of the parameters, which can then be used to estimate the error in the parameters. In this case, the parameters are: The variance and the partition potential.

In the next section, we will expand the partition potential in a spline basis set. In this method the parameters are the values of the partition potential at the knots. The parameters are correlated: A perturbation of the partition potential at one knot affects the response of the density in other knots. Hence, we must employ a model of correlated errors. Finding the correct model is a quite demanding task, perhaps, beyond the scope of this work. For this reason, I choose a biased model based on the following observations: i) A measure of the error of the form  $\int d^3\mathbf{r}dt (\tilde{n}^{\text{ref}}(\mathbf{r}, t) - \tilde{\Lambda}_{S_0}[v_p])^2$  suffers of autocorrelation. ii) Far from the molecule, the partition potential has little influence on the density. iii) Estimating the density is not sufficient, its spatio-temporal gradient is an important quantity. An error measure accounting for these observations is:

$$\|e[v_p]\|_{\mu}^2 = \int d\mu(\mathbf{r}, t) \{ |\nabla e(\mathbf{r}, t)|^2 + (\partial_t e(\mathbf{r}, t))^2 \} . \quad (7.17)$$

Based on ii), we choose a measure of the form  $d\mu(\mathbf{r}, t) = d^3\mathbf{r}dt \sum_i \tilde{n}^{\text{ref}}(\mathbf{r}_i, t) \delta(\mathbf{r} - \mathbf{r}_i)$ . Where  $\{\mathbf{r}_i\}$  are points selected in such a way that  $|\nabla e|^2 + (\partial_t e)^2$  resembles a  $\chi^2$ -distribution. To apply this measure of error in the next section, we need to transform the above measure into a vector norm. Then, the resultant distribution is expanded in terms of the gradient of the partition potential and asymptotic analysis is applied,

leading to the random variables required to reproduce the density within a small error tolerance.

#### 7.4.2 1d Electron in a Double-well Potential

Let us consider the following example: a one dimensional electron in a double well potential:

$$i\partial_t\phi_\alpha(x,t) = \left(-\frac{1}{2}\partial_x^2 + v_\alpha(x) + v_p(x,t)\right)\phi_\alpha(x,t) , \quad (7.18)$$

where  $\alpha = \text{L, R}$ . The potentials are  $v_\alpha(x) = v_0/\sqrt{(x-x_\alpha)^2+a}$ ; the parameters are:  $v_0 = -1$ ,  $x_R - x_L = 4$ , and  $a = 1$ . The density is obtained by averaging over the orbital densities of each well:

$$n(x,t) = \frac{1}{2}|\phi_L(x,t)|^2 + \frac{1}{2}|\phi_R(x,t)|^2 . \quad (7.19)$$

Suppose that the supermolecule evolves from the ground-state driven by a monochromatic laser, the evolution of the system is thus dictated by the solution of:

$$i\partial_t\psi(x,t) = \left(-\frac{1}{2}\partial_x^2 + v(x) + v_d(x,t)\right)\psi(x,t) , \quad (7.20)$$

where  $v_d(xt) = Ex \sin \omega t$ , and the external potential is  $v = v_L + v_R$ . The density obtained from the above evolution equation is  $n^{\text{ref}}(xt) = |\psi|^2(xt)$ , which is the target density we wish to represent.

The laser parameters are  $\omega = 0.3$ ,  $E_0 = 0.05$ . We propagate the states of the system using the Crank-Nicholson method; time step is 0.1, box length is 20, spatial step is 0.17, and total propagation time is 10 units. The partition potential is represented in a spline basis set with 40 knots equally spaced in the box. The initial partition potential is estimated by minimizing the error using sequential quadratic programming (as shown in Chapter 6). First the problem  $(-1/2\nabla^2 + v_\alpha + v_p^0)\phi_{n,\alpha} = \epsilon_{n,\alpha}\phi_{n,\alpha}$  is solved for both wells with some estimation of  $v_p^0$ ; then, the density is compared with that of the system of reference in order to propose the next estimation in the iterative procedure of sequential quadratic programming. The TD partition potential is also found using the steps shown chapter 6.

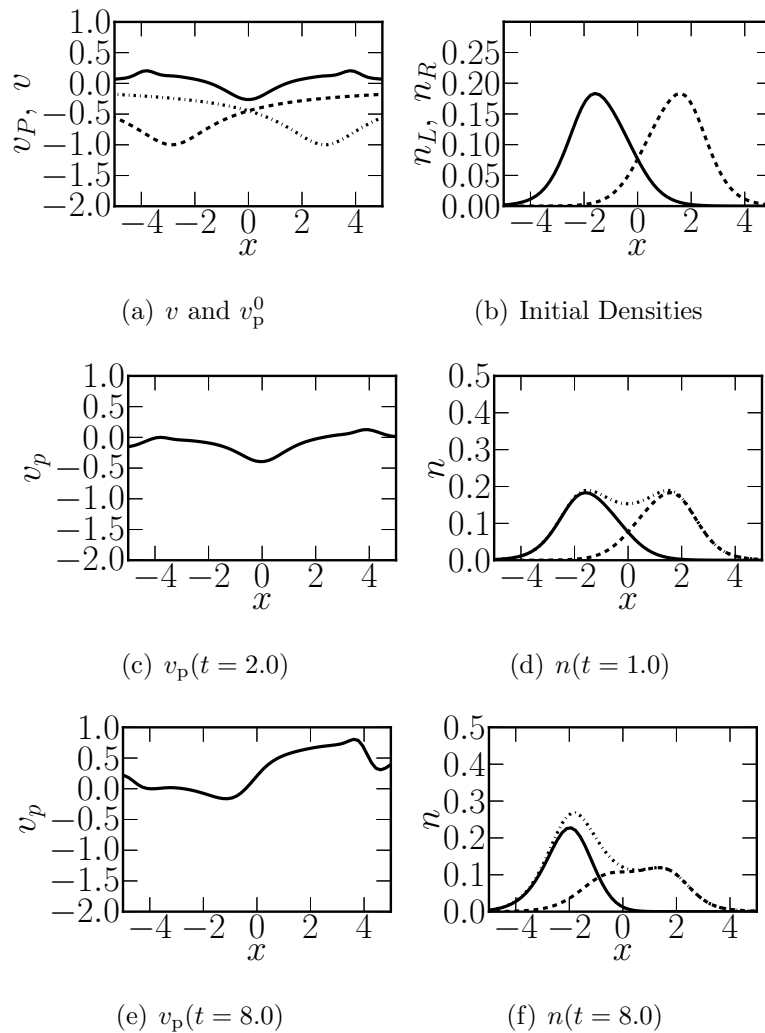


Figure 7.1. Snapshots of the partition potential. In a), solid line: Total external potential, dashed line: Left fragment external potential, dashed-dotted line: Right fragment potential. In b), c), and d), solid lines: Left electron-fragment density, dashed lines: Right electron-fragment density. In c) and d) the dashed-dotted line is the total density.

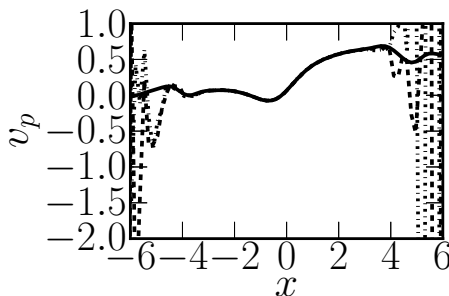


Figure 7.2. Error estimation of the partition potential at  $t = 6.2$ . The dashed and dashed-dotted lines correspond to two random-trajectory simulations.

Figure 1.a. shows the initial partition potential and external potentials of each well. The initial fragment densities that add up to the ground-state density of the supermolecule are displayed in Figure 1.b. Figure 1.c. shows the partition potential at  $t = 1.0$ ; it is localized in the intermediate region between the fragments. The electron-fragment densities (Figure 1.d) are also well localized at  $t = 1.0$ . Because in absence of the partition potential the fragment-densities would just be localized around their wells, the partition potential must be such that it induces the transfer of charge from the right fragment into the left fragment (Figure 1.e). However, as we note in Figure 1.f, the charge transfer in this case is represented by the spreading of the right fragment's density into the left one. Two observations: i) if one were to assign a grid that is fine around the center of the wells and then coarse as one moves away from the wells, then to describe the density spreading, the grid should be time-dependent to account for this. ii), The partition potential must induce the charge transfer and act like a “spoon”.

The result of the error estimation in the partition potential at  $t = 6.2$  is shown in Figure 2. As expected the error is quite significant in the boundary regions of the system. This implies that the shape of the potential in these regions is not reliable. Besides, since all space-time points obeying causality are coupled, the error will indeed spread to regions where the density is non-negligible. Despite the error shows large derivative fluctuations in the estimation, these can cause instabilities in



the minimization procedure, for this reason we recommend that the resulting potential should be smoothed using the local error as a smoothing parameter.

### 7.5 Variable Occupation Numbers

To avoid the physical and numerical problems described in the previous section, let us assign variable electron-occupation numbers to the fragments. First, divide the propagation time into blocks  $[0, \tau) \cup [\tau, 2\tau) \cup \dots \cup [(m-1)\tau, m\tau)$ , where  $m\tau$  is the total time of the propagation, and let

$$X_\alpha = \{|\xi_\alpha^0\rangle, |\xi_\alpha^1\rangle, \dots, |\xi_\alpha^m\rangle\} , \quad (7.21)$$

be a set of kets for fragment  $\alpha$ . At a single time  $t = k\tau$ , the following minimization is performed to obtain the set of kets describing the density of the fragmented molecule:

$$\begin{aligned} \{|\xi_\alpha^k\rangle\}_{\alpha=1}^{N_{\text{frag}}} = \arg \min \left\{ \sum_{\alpha} \langle \psi_\alpha^k | \hat{H}_\alpha^0 | \psi_\alpha^k \rangle \text{ s.t.} \right. \\ \left. \{|\psi_\alpha^k\rangle\} \rightarrow n(k\tau^-), \mathbf{j}(k\tau^-) \right\} , \end{aligned} \quad (7.22)$$

the occupation numbers of fragment  $\alpha$  are formally expressed as  $|\nu_{\alpha,M}(k\tau)|^2 = |\langle \xi_{\alpha,M}^k | \xi_\alpha^k \rangle|^2$ . These numbers, and  $\mathbf{j}$  (the current-density) as well, are density-functionals.

The evolution operator of fragment  $\alpha$  is:  $\hat{U}_\alpha[v_p](t_1, t_2) = \mathcal{T} \exp(-i \int_{t_0}^{t_1} ds \hat{H}_\alpha[v_p])$ . Introduce the displaced set of kets:

$$\begin{aligned} \tilde{X}_\alpha = \{\hat{U}_\alpha(\tau, 0)|\xi_\alpha^0\rangle, \\ \hat{U}_\alpha(2\tau, \tau)|\xi_\alpha^1\rangle, \dots, \hat{U}_\alpha(m\tau, (m-1)\tau)|\xi_\alpha^{m-1}\rangle\} . \end{aligned} \quad (7.23)$$

Now let us define the following dyadic product:  $(X_\alpha \tilde{X}_\alpha^\dagger)(k) = |\xi_\alpha^k\rangle \langle \tilde{\xi}_\alpha^{k-1}|$ . The symbol  $X_\alpha \tilde{X}_\alpha^\dagger$  is the set of dyadic products where the  $k$ -th component is the dyadic product between the ket at the beginning of the  $k$ -th block and the displaced ket from the  $k-1$ -th block. Now, let  $\hat{B}_\alpha$  be the TD operator:

$$\begin{aligned} \hat{B}_\alpha(t) &= (\text{III}_\tau * \ln X_\alpha \tilde{X}_\alpha^\dagger)(t) \\ &= \sum_{k=1}^m \delta(t - k\tau) \ln |\xi_\alpha^k\rangle \langle \tilde{\xi}_\alpha^{k-1}| . \end{aligned} \quad (7.24)$$

where  $\text{III}_\tau$  is the Dirac-Comb kernel. Addition of the operator  $\hat{B}_\alpha$  to the Hamiltonian  $\hat{H}_\alpha(t)$  yields the non-Hermitian operator:

$$\hat{H}_{c,\alpha}[v_p](t) = \hat{H}_\alpha[v_p](t) + i\hat{B}_\alpha[v_p](t) . \quad (7.25)$$

The evolution of the system is now determined by  $|\psi_\alpha[v_p]\rangle$ , which obeys

$$i\partial_t|\psi_\alpha[v_p](t)\rangle = \hat{H}_{c,\alpha}[v_p](t)|\psi_\alpha[v_p](t)\rangle , \quad (7.26)$$

the total density is  $n(\mathbf{r}t) = \sum_\alpha \langle \psi_\alpha(t) | \hat{n}(\mathbf{r}) | \psi_\alpha(t) \rangle$  and the number of particles in fragment  $\alpha$  is  $N_\alpha(t) = \langle \psi_\alpha(t) | \hat{N} | \psi_\alpha(t) \rangle$ . In general, any observable,  $\hat{O}(t)$ , is expressed as a functional of the partition potential,  $\langle \psi_\alpha[v_p](t) | \hat{O}(t) | \psi_\alpha[v_p](t) \rangle$ .

Given the partition potential and occupation numbers as density-functionals, the scheme to determine the evolution of the molecule is: First the kets  $\{|\psi_\alpha\rangle\}$  are propagated in the interval  $[0, \tau)$  with fixed populations on each fragment. Then, at  $t = \tau$  new occupation numbers are obtained from Eq. (7.22) as well as new states to propagate, and the propagation continues in the block  $[\tau, 2\tau)$ . The procedure continues similarly for the rest of the propagation. The density of the system is then obtained as  $n(\mathbf{r}, t) = \sum_\alpha \langle \psi_\alpha(t) | \hat{n}(\mathbf{r}) | \psi_\alpha(t) \rangle$ . The theorem discussed in section 2 also applies in this case. Therefore, the partition potential for this scheme is uniquely determined by the TD electronic density, up to an arbitrary constant.

The partition potential is discontinuous at the relaxation nodes (points where  $t$  is an integer multiple of  $\tau$ ). Discontinuities in time can be eliminated by using an integral transformation that smooths the observable at the relaxation nodes. In practice, however, it is convenient to propagate the occupation numbers and gluing potential assuming that they are continuously differentiable functions of time. It can be shown, assuming that the dynamics of the occupation numbers is much slower than that of the partition potential, that the 1-1 map between the former and the density still holds. This follows from the scheme we have shown here because the electronic populations are fixed in the first block, allowing us to apply the Runge-Gross theorem in such block.

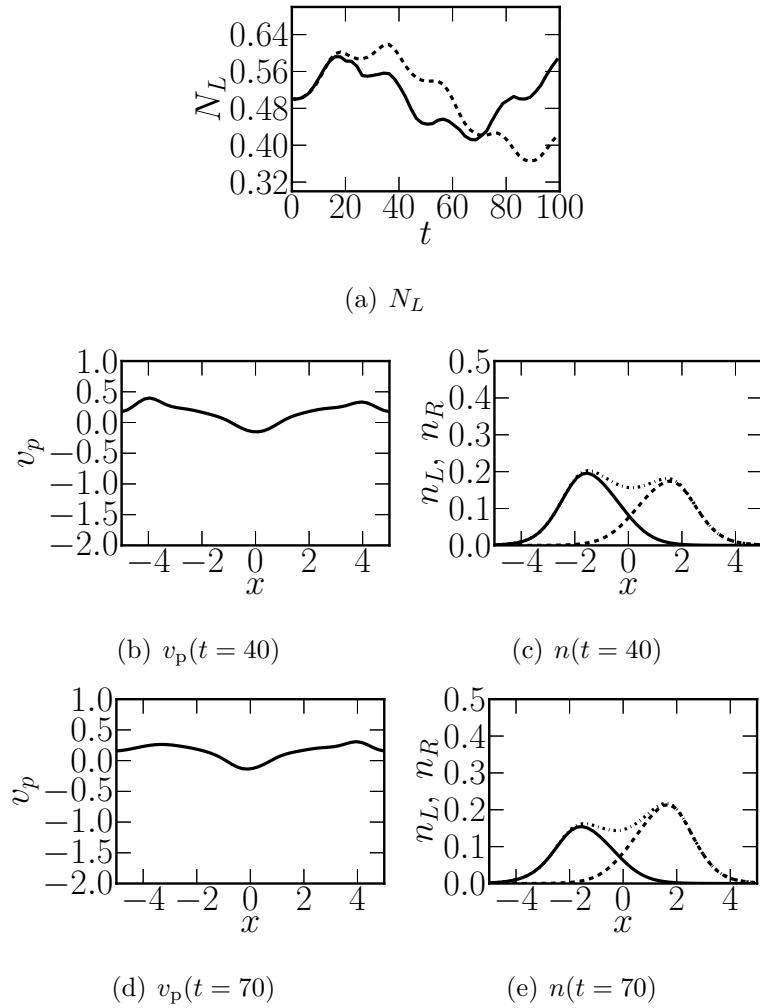


Figure 7.3. Evolution of the fragments with TD electron populations. In a) the solid line is the result from the inversion, and the dashed line is the result from the two-state approximation. In c), e), and g), solid line:  $n_L$ , dashed line:  $n_R$ , dashed-dotted:  $n$ .

A density-functional approximation to the occupation numbers is the last step to apply the theory illustrated in this chapter. The dynamics of the occupation numbers can be investigated using master equations, where the rate coefficients are determined by Dirac's golden rule, or transition elements that couple the fragments. Here, we illustrate a simple approach: A trial wave function to investigate the evolution of the occupation numbers is  $|\eta(t)\rangle = \xi_L(t)|\varphi_L\rangle + \xi_R(t)|\varphi_R\rangle$ , where  $|\varphi_\alpha\rangle$  is the ground-state of the electron described only by  $\hat{H}_\alpha^0$  (This hamiltonian in coordinate representation is

$-1/2\partial_x^2 + v_\alpha(x)$ ). The dynamics of electron transfer is governed by a two-component wave-function  $\boldsymbol{\xi} = (\xi_L, \xi_R)^T$ . We assume that the Hamiltonian coupling that relates the two fragments is of the form:

$$\hat{\mathcal{H}}(t) = \hat{H}_f + \int dx (v_G(x, 0) + v_d(x, t))\hat{n}(x) \quad (7.27)$$

where  $\hat{H}_f = \hat{H}_L \oplus \hat{H}_R$ , is the uncoupled Hamiltonian;  $\hat{H}_\alpha|\varphi_\beta\rangle = 0$  if  $\alpha \neq \beta$ . Here we further assume, for the sake of the illustration, that the gluing field is frozen; hence, it serves as a “bridge” for the charge to be transferred from one well into the other.

From the evolution Eq.  $i\partial_t|\eta(t)\rangle = \hat{\mathcal{H}}(t)|\eta(t)\rangle$  we infer that the state vector,  $\boldsymbol{\xi}$ , satisfies:

$$i\partial_t\boldsymbol{\xi}(t) = \mathbf{S}^{-1}(\boldsymbol{\epsilon}_0 + \boldsymbol{\Delta}(t))\boldsymbol{\xi}(t) \quad (7.28)$$

where  $S_{\alpha\beta} = \int dx \varphi_\alpha^*(x)\varphi_\beta(x)$ ,  $\boldsymbol{\epsilon}_0 = \text{diag}(\epsilon_0, \epsilon_0)$ , and

$$\Delta_{\alpha\beta}(t) = \int dx \varphi_\alpha^*(x)(v_G(x, 0) + v_d(x, t))\varphi_\beta(x) . \quad (7.29)$$

The occupation numbers are obtained from the “density” of  $\xi$ :  $N_\alpha(t) = |\tilde{\xi}_\alpha|^2(t) + \text{Re}(\xi_L^*(t)\xi_R(t)S_{LR})$ . The last term arises from the overlap of the functions  $\varphi_L$  and  $\varphi_R$ , guaranteeing that  $N_L + N_R = 1$ .

Let us revisit the example of section 7.4.2. The parameters for the propagation now are  $\tau = 2$ ,  $\Delta t = 1$ ,  $\omega = 0.3$ ,  $E_0 = 0.02$ . The exact dependency of the average number of electrons of the left fragment on time is shown in Figure 3.a. The two-state approximation works very well at short times, and displays deviations after  $t = 20$ . The dynamics of the two-state approximation would be quite challenging to capture by fixing the occupation numbers and finding the corresponding partition potential. Improvements over the two-state approximation can proceed by either refining the gluing potential (going beyond the frozen approximation) or increasing the number of states considered to couple the fragments. The first alternative has the advantage that the equations can be solved very fast. Nonetheless, it must be remarked, for functional development, that the gluing potential is also a determinant factor for the evolution of the shape of the electronic fragment-density ( $\int n_\alpha/N_\alpha$ ).

Figure 3.b shows a snapshot of the “exact” partition potential at  $t = 10$ . In contrast with the results of section 3.2, the partition potential now remains well localized (Figures 3.d and 3.f). This suggests that the standard methods of ground-state PDFT can be used to estimate the partition potential through the use of the adiabatic approximation (a report on a complete framework to apply PDFT in molecules is underway). The fragment densities also remain localized (Figure 3.c, 3.e, and 3.g). Qualitatively, the partition potential is in charge of the shape of the electronic densities of the fragments, while the occupation numbers are responsible for their height.

## 7.6 Conclusions

We formulated a TDDFT for treating a molecule as composed of smaller composite units. To successfully apply these theories we need approximations to the partition potential and the occupation numbers, this can be accomplished by a proper approximation to the Hamiltonians  $\{\hat{H}^c(t)\}$ , or the auxiliary evolution equations of the electron populations in the fragments; the approximations I discussed in chapter 4 will assist the estimation of gluing potentials. The error analysis was also presented. It leads to a simple form of estimating the errors in the potentials. In agreement with the classical interpretation, the problem is ill-posed for regions where the density is small. However, as time increases, the error might propagate from the boundaries into the regions where the density is high.

## 7.7 References

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## 8. CONCLUDING REMARKS

The formulation of the principles and mathematical framework to study the quantum mechanics of molecular fragments has been completed in this thesis. Future work requires attention to the numerics for applications in large molecules. The machinery developed here is sufficient to develop methods that are applicable to systems with large number of atoms.

The author believes that the local spin-density approximation must be conserved for large systems. For example, better approximation to the *kinetic* partition energy can be useful for calculations. There is great flexibility in the formalism of partition density functional theory to “rescue” local approximations to the XC energy and TD potential.



VITA

## VITA

Martín Alonso Mosquera Tabares was born in Palmira, Colombia, November 25, 1986. He studied one year of Chemistry in Universidad del Valle, Cali, Colombia. Frustrated by so many labs and lack of numbers he decided to study Chemical Engineering (2004-2009), obtaining a BS degree. While being an engineering student, he took several courses of Quantum Mechanics, and found it very interesting. He later pleaded forgiveness with Chemistry and was admitted at Purdue University in Fall 2010. He spent a large number of hours working in theoretical physics and chemistry at Purdue.

## PUBLICATIONS

## RESEARCH ARTICLE

### Partition density functional theory and its extension to the spin-polarized case

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*(Received 14 August 2012; final version received 5 September 2012)*

Partition density functional theory (PDFT) [P. Elliott, K. Burke, M.H. Cohen, and A. Wasserman, *Phys. Rev. A* 82 (2), 024501 (2010)] is a formally exact method for obtaining molecular properties from Kohn–Sham calculations on isolated fragments. Here, we express the partition energy of PDFT as an implicit functional of the molecular spin-densities for a given choice of fragmentation, and use the principle of von Barth and Hedin to formulate the spin-decomposed version of PDFT. We introduce a partition energy functional of the spin-up and spin-down electronic densities and derive the associated polarized partition potentials, which are found to be global quantities that influence every fragment in the molecule. Along with the formal theory, we propose a simplified approach to computing the spin-partition potentials, and illustrate its utility and accuracy with two simple examples. Finally, we propose a viable approach to including external electric and magnetic fields in the framework of spin-PDFT.

**Keywords:** Partition theory; Density functional theory; spin polarization; partition potential; Kohn–Sham equations

#### 1. Introduction

The success of Density Functional Theory (DFT) to describe the ground-state properties of many-electron systems has positioned it as one of the top choices for quantum chemistry calculations of molecules and materials. The extension of ground-state DFT to the spin-dependent case was first proposed by von Barth and Hedin [1]. They showed that in the presence of a static magnetic field there is an energy functional of the spin-densities which yields the correct energy of the system when it is minimized with respect to variations of the spin-densities. Even if the external potential is spin independent, the principle of von Barth and Hedin [1] (BH) holds, thus subsuming the original principle of Hohenberg and Kohn [2] (HK), which did not initially consider spin-dependent external fields. A comparison of these two variational principles, HK and BH, reveals that the HK principle offers a direct minimization with respect to the electronic density, whereas the BH principle entails a two-step energy minimization. One reason to choose SDFT in practice is that the correlation of electrons with anti-parallel spins is a significant contribution to the correlation energy [3], making the explicit functional dependence on the spin-densities a useful one. However, both HK and BH principles are equivalent in the absence of magnetic fields. Both lead to the correct ground state energy.

The applications of these ground-breaking principles to physics and chemistry have been made possible through the Kohn–Sham (KS) method [4], in which the real system of particles is mapped into a fictitious system of non-interacting particles. This method introduces the exchange-correlation functional, whose accurate approximation has been a major challenge for the theoretical community during the last 50 years.

The scaling of the computational cost tends to be a limiting issue in quantum-chemical simulations. Even an approximate DFT calculation may be expensive for systems with hundreds of atoms. For this reason, several theories of molecular fragmentation have been proposed, whose purpose is to allow for a divide-and-conquer approach [5] (for example, see recent special issue of *Phys. Chem. Chem. Phys.* on fragment and localized orbital methods in electronic-structure theory [6]); this also permits one to assign electrostatic charges to individual fragments. The key is the division of a large molecular system into simpler and smaller subsystems for which arbitrarily accurate calculations are feasible. The division of a molecule into its atomic fragments is one of the most natural choices, and DFT offers several appealing ways to define ‘atoms in molecules’ [7–10]. The basic idea is to take advantage of the fact that the external potential is the sum of nuclear attractive potentials. An energy functional can

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then be defined for an electron density associated with each individual nucleus; such an energy functional only depends on a localized density corresponding to that fragment and (ideally) tends to localize around the fragment's nucleus. Two constraints are imposed: (i) the total number of electrons must be conserved; and (ii) the sum of localized densities must coincide with the total molecular density. The first constraint gives rise to the well-known chemical potential, and the second one yields a Lagrange multiplier which is a function of the position [9].

A mathematical formulation of the above 'Partition Theory' (PT) was proposed in a series of papers by Cohen and Wasserman [11]. By merging PT with Kohn-Sham DFT, Elliott *et al.* [12] then found a method to obtain ground-state molecular properties by carrying out self-consistent calculations on isolated fragments. They introduced an energy functional  $E_f$  which is the minimum sum of the energies of the isolated fragments under the constraint that the sum of the fragments' electronic densities add up to the total molecular density. In order to match  $E_f$  with the true energy functional, a residual functional was introduced, the 'partition energy',  $E_p$ . Its associated potential, the *partition potential*, is a global potential in the sense that every fragment is influenced by it. This Partition Density Functional Theory (PDFT) is an *exact* reformulation of the ground state problem. It is consistent with the density-partitioning ideas of Parr and co-workers [7–10], close to embedding methods whose original purpose was to treat a particular region within a larger system [13–17], and also similar in practice to the self-consistent atomic deformation theory of Mehl and co-workers [18–21]. Some similarities and differences have been discussed elsewhere [12,22], and a more detailed and extensive comparative analysis is forthcoming.

In this paper we do three things: (1) express the partition energy of [12] as an implicit functional of the molecular density for a given choice of fragmentation (Section 2); (2) use the BH principle to formulate Partition *Spin* Density Functional Theory (Section 3), along with a simplified approach to computing the spin-partition potentials (Section 3.2), which we illustrate with two simple examples (Section 3.3); and (3) propose a viable approach to including external electric and magnetic fields in the PDFT formalism (Section 3.4).

## 2. Partition energy as an implicit density functional

The algorithm proposed in [12] (PDFT) provides a way to find the ground-state energy  $E_v$  and density  $n(\mathbf{r})$  for a system of  $N$  interacting electrons moving under the

influence of an external potential  $v(\mathbf{r})$ , without having to solve the problem directly for  $v(\mathbf{r})$  but indirectly via fragment calculations. Paving the way for the developments of the next sections, we start by unveiling an important aspect of PDFT that was not made explicit in the presentation of [12].

To find  $E_v$ , the functional

$$E_v[n] = F[n] + \int d\mathbf{r} v(\mathbf{r})n(\mathbf{r}) \quad (1)$$

needs to be minimized with respect to density variations subject to the constraint that the density integrates to  $N$  electrons:

$$E_v = \min_n E_v[n] \text{ s.t. } \int d\mathbf{r} n(\mathbf{r}) = N. \quad (2)$$

In Equation (1),  $F[n]$  is the Levy-Lieb universal functional [23]. Now choose  $N_f$  fragments by partitioning the external potential as

$$v(\mathbf{r}) = \sum_{\alpha}^{N_f} v_{\alpha}(\mathbf{r}), \quad (3)$$

and define  $\tilde{E}_p[n; \{n_{\alpha}\}]$  as

$$\tilde{E}_p[n; \{n_{\alpha}\}] = E_v[n] - \tilde{E}_f[\{n_{\alpha}\}], \quad (4)$$

where  $\tilde{E}_f[\{n_{\alpha}\}]$  is the sum of fragment energies, an explicit functional of a set of  $N_f$  fragment densities  $\{n_{\alpha}\}$ ,

$$\tilde{E}_f[\{n_{\alpha}\}] = \sum_{\alpha}^{N_f} E_{v_{\alpha}}[n_{\alpha}]. \quad (5)$$

The prescription of [11,12] minimizes  $\tilde{E}_f[\{n_{\alpha}\}]$  subject to the constraint that the sum of fragment densities equals the total molecular density. The corresponding Euler-Lagrange equation is:

$$\frac{\delta \tilde{E}_f[\{n_{\alpha}\}]}{\delta n_{\alpha}(\mathbf{r})} + \tilde{v}_p(\mathbf{r}) - \mu = 0, \quad (6)$$

where the potential  $\tilde{v}_p(\mathbf{r})$  enters as the Lagrange multiplier guaranteeing satisfaction of the density constraint, and is thus  $\alpha$ -independent. The chemical potential  $\mu$  also enters here as a Lagrange multiplier to ensure that the sum of fragment occupations equals the total number of electrons. Inserting Equation (5) into Equation (6):

$$\frac{\delta E_{v_{\alpha}}[\{n_{\alpha}\}]}{\delta n_{\alpha}(\mathbf{r})} + \tilde{v}_p(\mathbf{r}) - \mu = 0. \quad (7)$$

Although Equation (7) can be solved for all  $\alpha$  to find the optimum set of fragment densities  $\{\tilde{n}_{\alpha}\}$  yielding a pre-set density, the goal PDFT sets itself is to find the

unique  $v_p(\mathbf{r}) \equiv \tilde{v}_p(\mathbf{r}) \mapsto n(\mathbf{r})$  [24] that yields the *correct* ground-state density  $n(\mathbf{r})$ . To achieve this, recast Equation (2) as:

$$E_v = \min_n \{E_t[n] + E_p[n]\} \quad \text{s.t.} \quad \int d\mathbf{r} n(\mathbf{r}) = N, \quad (8)$$

where we have defined

$$E_t[n] = \min_{\{n_\alpha\} \mapsto n} \tilde{E}_t[\{n_\alpha\}], \quad (9)$$

$$E_p[n] = \min_{\{n_\alpha\} \mapsto n} \tilde{E}_p[n; \{n_\alpha\}] \quad (10)$$

as *implicit* functionals of the total density, with the symbol  $\{n_\alpha\} \mapsto n$  indicating that  $\sum_\alpha n_\alpha(\mathbf{r}) = n(\mathbf{r})$ . The search in Equations (9) and (10) is carried out over all ensemble  $v$ -representable (EVR) densities, and the search of Equation (8) over all EVR-decomposable densities, those that can be expressed as a sum of EVR fragments [24]. The Euler–Lagrange equation associated with the minimization procedure of Equation (8) is:

$$\frac{\delta E_t[n]}{\delta n(\mathbf{r})} + \frac{\delta E_p[n]}{\delta n(\mathbf{r})} - \mu = 0. \quad (11)$$

The proofs of [25–27] indicating that all densities are EVR suggest that the search above is not problematic. Furthermore, the need for  $v$ -representability could be circumvented by reformulating the method in terms of Legendre transforms [27,28] or via potential functionals [29–32]. From Equation (9), one can see that the functional derivative of  $E_t[n]$  with respect to the  $n_\alpha(\mathbf{r})$  must vanish if the total density is held fixed, but if it is allowed to vary as  $\delta n(\mathbf{r}) = \delta n_\alpha(\mathbf{r})$ , then Equations (5) and (11) lead to:

$$\frac{\delta E_{v_\alpha}[n_\alpha]}{\delta n_\alpha(\mathbf{r})} + \frac{\delta E_p[n]}{\delta n_\alpha(\mathbf{r})} - \mu = 0, \quad (12)$$

where the second term on the left is independent of  $\alpha$ , in spite appearances, because

$$\frac{\delta E_p[n = \sum_\alpha n_\alpha]}{\delta n_\alpha(\mathbf{r})} = \int d\mathbf{r}' \frac{\delta E_p[n]}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta n_\alpha(\mathbf{r})} = \frac{\delta E_p[n]}{\delta n(\mathbf{r})}. \quad (13)$$

The unique partition potential  $v_p(\mathbf{r}) \equiv \tilde{v}_p(\mathbf{r}) \mapsto n(\mathbf{r})$  is, from Equations (7) and (12):

$$v_p(\mathbf{r}) = \left. \frac{\delta E_p[n]}{\delta n(\mathbf{r})} \right|_{\min}. \quad (14)$$

Although  $v_{p,\alpha}(\mathbf{r}) \equiv \delta E_p[n]/\delta n_\alpha(\mathbf{r})$  is  $\alpha$ -independent for the *exact*  $E_p[n]$  at convergence,  $v_{p,\alpha}(\mathbf{r})$  may depend on  $\alpha$  at intermediate steps of any iteration procedure used to solve Equation (12). It may also depend on  $\alpha$  at convergence when employing approximate functionals for  $E_p[n]$ . Thus, we will find it

convenient to define the  $Q$ -functions of Section 3.2. They measure the response of the fragment densities to variations of the total density, and will allow us to propose a practical expression for calculating  $v_p(\mathbf{r})$ .

### 3. Partition spin density functional theory

#### 3.1. Scalar external fields

In the absence of external electric or magnetic fields, and when the external potential  $v(\mathbf{r})$  is spin independent, the extension of PDFT to spin-densities is straightforward. We only need to add a new index to the densities of the previous section. Under the BH variational principle we need to minimize the following functional to obtain the ground state energy and spin-densities:

$$E_v[n_\uparrow, n_\downarrow] = F[n_\uparrow, n_\downarrow] + \int d\mathbf{r} v(\mathbf{r})n(\mathbf{r}), \quad (15)$$

where  $F$  is:

$$F[n_\uparrow, n_\downarrow] = \min_{\hat{T} \rightarrow n_\uparrow, n_\downarrow} \text{Tr}\{\hat{T}(\hat{T} + \hat{V}_{ee})\}. \quad (16)$$

Here  $\hat{T}$  is the zero-temperature density matrix of the molecular system, and  $\hat{T}$  and  $\hat{V}_{ee}$  are the total kinetic and electron–electron interaction operators. The external potential is again partitioned as shown in Equation (3). Now, however, each fragment has two spin-densities associated with it. We denote the electronic density of fragment  $\alpha$  as  $n_\alpha(\mathbf{r}) = n_{\uparrow\alpha}(\mathbf{r}) + n_{\downarrow\alpha}(\mathbf{r})$ . Hence, the total spin-density  $n_\sigma(\mathbf{r})$  is expressed as:

$$n_\sigma(\mathbf{r}) = \sum_\alpha n_{\sigma\alpha}(\mathbf{r}). \quad (17)$$

Now, let us define the partition energy functional as an implicit functional of the total spin-densities:

$$E_p[n_\uparrow, n_\downarrow] = E_v[n_\uparrow, n_\downarrow] - E_t[n_\uparrow, n_\downarrow], \quad (18)$$

where

$$E_t[n_\uparrow, n_\downarrow] = \min_{\{n_{\sigma\alpha}\} \mapsto n_\sigma} \sum_\alpha E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}]. \quad (19)$$

To minimize  $\tilde{E}_t[\{n_{\sigma\alpha}\}] = \sum_\alpha E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}]$  subject to the constraint that the fragment spin-densities add up to the molecular spin-densities, we introduce the following Lagrangian functional:

$$\begin{aligned} \mathcal{L}[\{n_{\sigma\alpha}\}, \{n_\sigma\}] = & \tilde{E}_t[\{n_{\sigma\alpha}\}] \\ & + \sum_\sigma \int d\mathbf{r} \tilde{v}_{p,\sigma}(\mathbf{r}) \left\{ \sum_\beta n_{\sigma\beta}(\mathbf{r}) - n_\sigma(\mathbf{r}) \right\} \\ & + \mu \left\{ N - \int d\mathbf{r} \sum_{\sigma\beta} n_{\sigma\beta}(\mathbf{r}) \right\}. \end{aligned} \quad (20)$$

Unconstrained minimization of  $\mathcal{L}[\{n_{\sigma\alpha}\}, \{n_\sigma\}]$  with respect to the fragment densities yields the equation of motion:

$$\frac{\delta E_{v_\alpha}[n_{\sigma\alpha}]}{\delta n_{\sigma\alpha}(\mathbf{r})} + v_{p,\sigma}(\mathbf{r}) = \mu, \quad (21)$$

$$v_{p,\sigma}(\mathbf{r}) = \left. \frac{\delta E_p[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} \right|_{\min}. \quad (22)$$

The fact that  $\tilde{v}_{p,\sigma}(\mathbf{r}) = v_{p,\sigma}(\mathbf{r})$  in Equation (21) follows from comparing it with the Euler equation obtained when minimizing  $E_v[n_\uparrow, n_\downarrow] = E_p[n_\uparrow, n_\downarrow] + E_t[n_\uparrow, n_\downarrow]$  subject to the number constraint. The spin-fragment densities  $n_{\sigma\alpha}(\mathbf{r})$  integrate in general to a non-integer number of electrons  $N_{\sigma\alpha}$ . The energy functionals  $E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}]$  should therefore be taken to be of the PPLB form [33]:

$$E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = (1 - v_\alpha)E_{v_\alpha}[n_{p_{1\alpha}}, n_{p_{1\alpha}}] + v_\alpha E_{v_\alpha}[n_{p_{1\alpha}+1}, n_{p_{1\alpha}+1}], \quad (23)$$

where  $p_{\sigma\alpha}$  and  $p_{\sigma\alpha+1}$  are the bordering integers of  $N_{\sigma\alpha} = p_{\sigma\alpha} + v_{\sigma\alpha}$ , and  $v_\alpha = v_{\uparrow\alpha} + v_{\downarrow\alpha}$ . Here, however, for simplicity, we follow the recent approach of Huang and Carter [34] and fractionally occupy the fragment Kohn–Sham orbitals of the  $(p_{\sigma\alpha} + 1)$ -electron system, defined as those that minimize the non-interacting kinetic energy for each fragment. The non-interacting kinetic energy functional of fragment  $\alpha$  is defined as:

$$T_{s,\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = \min_{\{\phi_{i\alpha}\} \rightarrow n_{\sigma\alpha}} \sum_{i\sigma} f_{i\alpha\sigma} \langle \phi_{i\alpha\sigma} | \hat{t} | \phi_{i\alpha\sigma} \rangle, \quad (24)$$

where  $\hat{t}$  is the one-electron kinetic energy operator, and the occupation numbers  $\{f_{i\alpha\sigma}\}$  can be chosen to match those that would be obtained from PPLB. Consequently, the localized spin-densities are expressed by:

$$n_{\sigma\alpha}(\mathbf{r}) = \sum_i f_{i\alpha\sigma} |\phi_{i\alpha\sigma}(\mathbf{r})|^2. \quad (25)$$

The total number of orbitals in PSDFT is approximately the same as that in standard SDFT. For example, suppose we have a molecule with three spin-up electrons and a partition with two fragments has been chosen such that there are 1.5 electrons in each fragment. In SDFT we would need three spin-up orbitals to describe these electrons, while four orbitals are required in PSDFT. Hence, in terms of number of orbitals, the amount of computation does not increase significantly.

If the fragment spin-densities are non-interacting  $v$ -representable, then these can be obtained from the KS equations (atomic units used throughout):

$$\left[ -\frac{1}{2} \nabla^2 + v_{s,\sigma\alpha}(\mathbf{r}) \right] \phi_{i\alpha\sigma}(\mathbf{r}) = \epsilon_{i\alpha\sigma} \phi_{i\alpha\sigma}(\mathbf{r}), \quad (26)$$

which follow from

$$\frac{\delta T_{s,\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}]}{\delta n_{\sigma\alpha}(\mathbf{r})} + v_{s,\sigma\alpha}(\mathbf{r}) = \mu. \quad (27)$$

Writing the fragment energies in terms of Kohn–Sham quantities,

$$E_{v_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = T_{s,\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + E_{\text{HXC}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d\mathbf{r} n_\alpha(\mathbf{r}) v_\alpha(\mathbf{r}) \quad (28)$$

and differentiating with respect to the spin fragment densities, comparison of Equations (21) and (27) leads to:

$$v_{s,\sigma\alpha}(\mathbf{r}) = v_{\text{H}}[n_\alpha](\mathbf{r}) + v_\alpha(\mathbf{r}) + v_{\text{XC},\sigma}[n_{\uparrow\alpha}, n_{\downarrow\alpha}](\mathbf{r}) + v_{p,\sigma}(\mathbf{r}). \quad (29)$$

Thus,  $v_{s,\sigma\alpha}(\mathbf{r})$  differs from its usual expression only by the polarized partition potential. These effective potentials are input into the corresponding KS equations of each fragment which can be solved self-consistently. First, a reasonable approximation to the KS orbitals  $\{\phi_{i\alpha\sigma}\}$  is required, for which we calculate all the relevant densities to make a first estimation of the KS potentials; the resulting potentials are then used to generate a new approximation to the densities and the KS potentials as well. If a tolerance in the spin-densities estimation has not been achieved then the procedure is repeated.

### 3.2. Local- $Q$ approximation

Let us denote as  $\{\tilde{n}_{\sigma\alpha}\}$  the set of fragment densities that minimizes  $E_t[\{n_{\sigma\alpha}\}]$  for a given spin-density pair  $n_\uparrow, n_\downarrow$ . Each one of these fragment spin-densities is a functional of the total spin-densities, i.e.  $\tilde{n}_{\uparrow,\alpha} = \tilde{n}_{\uparrow,\alpha}[n_\uparrow, n_\downarrow]$ . In order to investigate the mutual influence of fragments we define the ‘ $Q$ ’ function:

$$Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) = \frac{\delta \tilde{n}_{\sigma'\alpha}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})}, \quad (30)$$

which satisfies the rule:

$$\sum_\alpha Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) = \delta_{\sigma,\sigma'} \delta(\mathbf{r} - \mathbf{r}'). \quad (31)$$

Let  $A$  be a functional that can be written as an explicit functional of the set of fragment densities  $\{\tilde{n}_{\sigma\alpha}\}$ , and therefore as an implicit functional of  $n_\uparrow$  and  $n_\downarrow$ ,  $A[\{\tilde{n}_{\sigma\alpha}[n_\uparrow, n_\downarrow]\}]$ . Invoking the chain rule,

$$\frac{\delta A}{\delta n_\sigma(\mathbf{r})} = \sum_{\sigma'} \int d\mathbf{r}' \frac{\delta A}{\delta \tilde{n}_{\sigma'\alpha}(\mathbf{r}')} Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}). \quad (32)$$

For example, applying this formula to the polarized partition potential:

$$v_{p,\sigma}(\mathbf{r}) = \sum_{\sigma'\alpha} \int d\mathbf{r}' v_{p,\sigma'\alpha}(\mathbf{r}') Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}), \quad (33)$$

where  $v_{p,\sigma'\alpha}(\mathbf{r})$  is a spin-fragment partition potential:

$$v_{p,\sigma'\alpha}(\mathbf{r}) = \frac{\delta E_p}{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r})}. \quad (34)$$

Because  $n_\sigma(\mathbf{r}) = \sum_\alpha \bar{n}_\alpha(\mathbf{r})$ , again by the chain rule we obtain:

$$v_{p,\sigma\alpha}(\mathbf{r}) = v_{p,\sigma\beta}(\mathbf{r}) \quad \forall \alpha, \beta, \quad (35)$$

as discussed in Section 1.

We now propose a useful approximation for  $Q$ . Consider an idealized system in which a perturbation of the form  $\delta n_\sigma(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{z})n_\sigma(\mathbf{r})$  induces a similar response in the  $\sigma\alpha$ -fragment as  $\delta \bar{n}_{\sigma\alpha}(\mathbf{r}') = \delta(\mathbf{r}' - \mathbf{z})\bar{n}_{\sigma\alpha}(\mathbf{r}')$ . Given that

$$\delta \bar{n}_{\sigma\alpha}(\mathbf{r}') = \int d\mathbf{r} Q_{\sigma\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \delta n_\sigma(\mathbf{r}), \quad (36)$$

then we obtain the crude approximation to  $Q$ :

$$Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \approx \delta_{\sigma'\alpha} \delta(\mathbf{r}' - \mathbf{r}) \frac{\bar{n}_{\sigma'\alpha}(\mathbf{r}')}{n_\sigma(\mathbf{r})}, \quad (37)$$

in which ' $Q$ ' plays the role of a weighting factor, analogous to a molar fraction. Also note that this approximation is consistent with the rule shown in Equation (31). To avoid confusion and for convenience we refer to Equation (37) as the *local- $Q$  approximation*.

Although in light of Equation (35) it is not necessary to apply Equation (32) for the partition energy (setting  $A = E_p$  in Equation (32)), doing so turns out to be convenient in practice to keep  $v_{p,\sigma}(\mathbf{r})$  independent of  $\alpha$  at each step throughout the iteration process. Moreover, the fragment densities used during the iterative procedure are not the same as the  $\{\bar{n}_{\sigma\alpha}\}$ . In other words, during the iterations, we set the partition potentials to be of the form shown in Equation (33) where they depend on the fragments' densities instead of the total density. We define such partition potential as follows:

$$u_{p,\sigma}[\{n_{\sigma\alpha}\}](\mathbf{r}) = \sum_{\sigma'\alpha} \int d\mathbf{r}' \frac{\delta E_p}{\delta \bar{n}_{\sigma'\alpha}(\mathbf{r}')} \bigg|_{\bar{n}_{\mu\beta} = n_{\mu\beta}} Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}) \bigg|_{\bar{n}_{\mu\beta} = n_{\mu\beta}} \quad (38)$$

and

$$u_{p,\sigma\alpha}(\mathbf{r}) = \frac{\delta E_p}{\delta \bar{n}_{\sigma\alpha}(\mathbf{r})} \bigg|_{\bar{n}_{\mu\beta} = n_{\mu\beta}}. \quad (39)$$

For example, under the local- $Q$  approximation we get:

$$u_{p,\sigma}[\{n_{\sigma\alpha}\}](\mathbf{r}) = \sum_\alpha u_{p,\sigma\alpha}(\mathbf{r}) \frac{\bar{n}_{\sigma\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})}. \quad (40)$$

Once self-consistency has been achieved then all the fragment partition potentials for the channel  $\sigma$  become identical ( $u_{p,\sigma} \rightarrow v_{p,\sigma}$ ).

Now introduce the spin-fragment average:

$$\langle f_{\sigma',\alpha} \rangle_{sf}(\mathbf{r}) = \sum_{\sigma'\alpha} \int d^3\mathbf{r}' f_{\sigma',\alpha}(\mathbf{r}') Q_{\sigma'\alpha,\sigma}(\mathbf{r}', \mathbf{r}). \quad (41)$$

Therefore  $u_{p,\sigma}(\mathbf{r}) = \langle u_{p,\sigma'\alpha} \rangle_{sf}(\mathbf{r})$ , i.e. the polarized partition potential is an average over fragments and spins, and the  $Q$  function plays the role of weighting factor. It is plausible to conceive a fragment-localized approximation in which the spin-fragment partition potential is averaged only over its closest neighbours. This might be used to save computing time in practical calculations.

Using the expression of Equation (28) for  $E_{v_\sigma}[n_{\uparrow,\alpha}, n_{\downarrow,\alpha}]$ , and the definitions of Equations (18)–(19), the local- $Q$  expression to the partition potential, Equation (40), leads to a sum of three terms arising from the usual kinetic, Hartree-exchange-correlation, and external potential contributions:

$$u_{p,\sigma}(\mathbf{r}) = u_{k,\sigma}^p(\mathbf{r}) + u_{\text{HXC},\sigma}^p(\mathbf{r}) + u_{\text{ext}}^p(\mathbf{r}), \quad (42)$$

where:

$$u_{k,\sigma}^p(\mathbf{r}) = \frac{\delta T_s[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} - \sum_\alpha \frac{n_{\sigma,\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})} \frac{\delta T_s[\bar{n}_{\uparrow,\alpha}, \bar{n}_{\downarrow,\alpha}]}{\delta \bar{n}_{\sigma,\alpha}(\mathbf{r})} \bigg|_{n_{\uparrow,\alpha}, n_{\downarrow,\alpha}}, \quad (43)$$

$$u_{\text{HXC},\sigma}^p(\mathbf{r}) = \frac{\delta E_{\text{HXC}}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} - \sum_\alpha \frac{n_{\sigma,\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})} \frac{\delta E_{\text{HXC}}[\bar{n}_{\uparrow,\alpha}, \bar{n}_{\downarrow,\alpha}]}{\delta \bar{n}_{\sigma,\alpha}(\mathbf{r})} \bigg|_{n_{\uparrow,\alpha}, n_{\downarrow,\alpha}}, \quad (44)$$

$$u_{\text{ext}}^p(\mathbf{r}) = v(\mathbf{r}) - \sum_\alpha \frac{n_{\sigma,\alpha}(\mathbf{r})}{n_\sigma(\mathbf{r})} v_\alpha(\mathbf{r}). \quad (45)$$

We emphasize that the bar on the  $\bar{n}_{\sigma,\alpha}$  indicates that these fragment densities are implicit functionals of  $n_\uparrow, n_\downarrow$  as explained at the beginning of Section 3.2.

At first sight this method seems to be difficult to implement computationally because it is a more involved formulation of DFT than the original KS theory. However, its rigorous focus on fragments permits one to develop approximations that might help decreasing the computing time even below standard approximate DFT calculations. Another advantage of the partition method is that the SIE can be



treated locally by selecting those fragments for which the SIE is relevant. Also, note that different levels of theory can be employed for different fragments.

In some respects, this method follows the philosophy of the generalized KS method [35], extending the non-interacting KS system such that an alternative fictitious system with interactions can be included. In principle any type of interaction can be introduced in the fictitious system, e.g. one may include a system defined within Hartree-Fock only, where the electron-electron interactions are described by Coulomb and exchange operators, or a system of fictitious electrons interacting via screened Coulomb potentials. To impose the restriction that the sum of squared modulus of each orbital yields the density one needs a local multiplicative potential. In analogy with the partition potential, the residual potential of Seidl *et al.* [35] turns out to be the functional derivative of a residual functional with respect to the electronic density. If the energy of the fictitious system is close enough to the actual energy, then the residual potential should have a small contribution to the ground state energy.

The chemical potential equalization determines the occupation numbers for the fragments when the energy functionals are differentiable with respect to their corresponding spin-densities. If the energy of a fragment is defined by means of the PPLB functional, then its energy is not differentiable when the number of electrons is an integer because the fragment does not have a definite chemical potential. To overcome this difficulty the energy has to be minimized with respect to the fragment occupations without resorting to the chemical potential equalization. This requires a derivative-free algorithm to minimize the energy. Despite this, the fragment KS equations remain valid.

### 3.3. Simple illustrations

#### 3.3.1. One electron

Consider one electron moving in one dimension under the double-well potential (see Figure 1a):

$$v(x) = V_0 \left( \frac{1}{\cosh((x+d/2)/a)} + \frac{1}{\cosh((x-d/2)/a)} \right), \quad (46)$$

where  $V_0 < 0$  is the depth of each well,  $d$  is the distance between the wells, and  $a$  is the width of each well. We omit in this example the spin subindex in the electronic densities because there is only one electron. We want to find the ground state energy and density for this

system. The more intuitive choice for the fragment potentials is:

$$\begin{aligned} v_1(x) &= \frac{V_0}{\cosh((x+d/2)/a)}, \\ v_2(x) &= \frac{V_0}{\cosh((x-d/2)/a)}. \end{aligned} \quad (47)$$

Since there is only one electron and the double-well potential is symmetric around  $x=0$ , we can set the occupation numbers as 1/2 for each well. Denoting by  $\phi_1$  and  $\phi_2$  the KS orbitals of fragments 1 and 2, respectively, the partition KS equations (26) are:

$$\left[ -\frac{1}{2} \frac{d^2}{dx^2} + v_\alpha(x) + u_p(x) \right] \phi_\alpha(x) = \epsilon_\alpha \phi_\alpha(x), \alpha = 1, 2. \quad (48)$$

There are in this case only two contributions to the partition potential,  $u_p(x) = u_k^p(x) + u_{\text{ext}}^p(x)$ . The first one comes from the kinetic energy relaxation, which we can calculate exactly using the 1d-von Weizsäcker functional  $T_s^{VW}[n] = \frac{1}{8} \int dx [ |dn(x)/dx|^2 / n(x) ]$ . From Equation (43):

$$\begin{aligned} u_k^p(x) &= -\frac{1}{2(n(x))^{1/2}} \nabla^2 (n(x))^{1/2} \\ &+ \frac{1}{2n(x)} \sum_{\alpha=1}^2 (n_\alpha(x))^{1/2} \nabla^2 (n_\alpha(x))^{1/2}. \end{aligned} \quad (49)$$

The second contribution comes from the relaxation with the external field. From Equation (45):

$$u_{\text{ext}}^p(x) = v(x) - \frac{n_1(x)}{n(x)} v_1(x) - \frac{n_2(x)}{n(x)} v_2(x). \quad (50)$$

The density is:

$$n(x) = n_1(x) + n_2(x) = \frac{1}{2} |\phi_1(x)|^2 + \frac{1}{2} |\phi_2(x)|^2. \quad (51)$$

Equations (48)–(51) were solved self-consistently and the results for the density and partition potential are shown with dashed lines in Figure 1. The solid lines indicate an alternative numerically exact solution found by solving directly the Schrödinger equation via the finite difference method. A simple inversion algorithm was employed to obtain the exact partition potential from the exact density: first, the partition potential is estimated by solving the fragment KS equations with the partition potential given by our local-Q expression, then the KS equations are solved iteratively. The partition potential generated by this

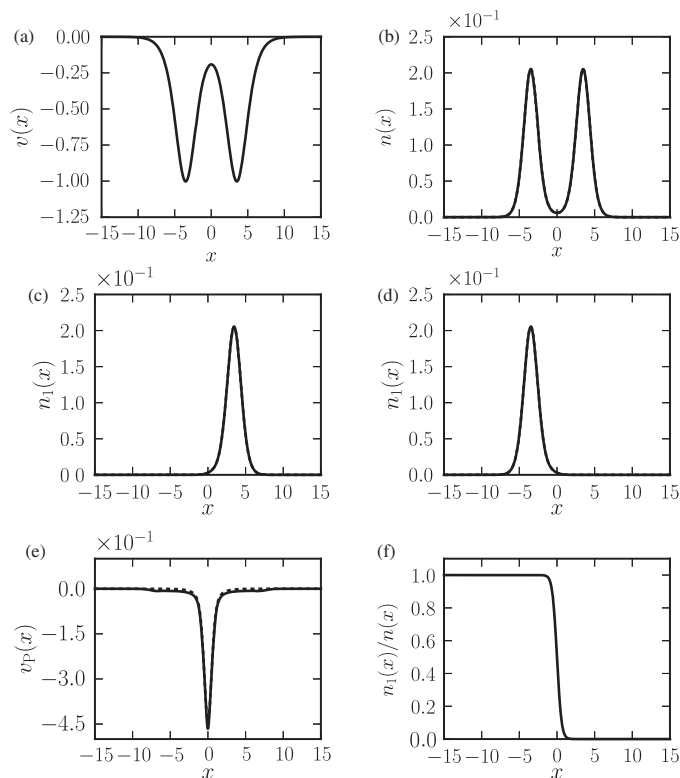


Figure 1. Results for one electron in a double-cosh potential, parameter values:  $a=2.0$ ,  $V_0=-1.0$ , and  $d=7.0$ . Dashed lines: local- $Q$  PDFT, solid line: direct solution. (a) Symmetric double-cosh potential; (b) exact density; (c) density of fragment 1; (d) density of fragment 2; (e) partition potential; and (f) integrated density-density response of fragment 1.

calculation is used as initial input to obtain a new approximation by means of the iterative scheme [36]:

$$u_p^{(i+1)}(x) = u_p^{(i)}(x) + \gamma(n^{(i)}(x) - n(x)), \quad (52)$$

where  $n^0$  and  $n$  are the estimated and reference electronic density respectively, and  $\gamma$  is a positive constant. This procedure is performed until a convergence criterion is satisfied. The formula shown above is rather slow, and might not be suitable for large scale inversion problems, but it performs well for our purposes.

Figure 1(a) shows the potential employed to generate the densities; a box of length 30 au was set for the simulation and a grid of size 600 was used to solve the KS equations. The convergence criterion to stop the inversion iterations was  $n^{(i+1)} - n_\infty^{(i)} < 10^{-5}$ .

The electronic density is shown in Figure 1(b). Note that the local- $Q$  PDFT density and partition potential are indistinguishable from the exact quantities. The numerical error in the density estimation is 0.01% and the error in the energy is negligible; both local- $Q$  PDFT and the exact solution yield a ground state energy of  $-0.698$  au. If we neglect the partition potential, which is equivalent to assuming that the fragments do not interact, then the energy rises to  $-0.690$  au. By having set the occupation numbers on the left and right as  $1/2$  we obtain equal eigenvalues on both sides. Figure 1(c) and (d) display the fragment densities. As expected, they are localized around their respective potential well. Figure 1(e) shows the integrated response  $\int dx Q_1(x, x')$ , which behaves like a step function.

Table 1. Eigenvalues and energies of the pseudo HeH molecule, Equation (54). A box of length 30 au and a grid of size 500 were employed. In the case of PDFT and local-Q\*, the subindices '1' and '2' label the fragments. In the case of KS-DFT, they label the molecular orbital eigenvalues.

Method	Energy (au)	$\epsilon_{\uparrow 1}$ (au)	$\epsilon_{\uparrow 2}$ (au)	$\epsilon_{\downarrow 1}$ (au)	$E_p$ (au)
KS-SDFT	-1.6473	-0.9405	-0.3366	-0.1649	—
PSDFT	-1.6473	-0.9127	-0.3531	-0.1635	$-7.5 \times 10^{-4}$
Local-Q*	-1.6488	-0.9400	-0.3366	-0.1641	$-1.9 \times 10^{-3}$

### 3.3.2. Three interacting electrons

Now consider three contact-interacting electrons in an asymmetrical double-well potential:

$$v(x) = \frac{V_{0,a}}{\cosh((x+d/2)/a)} + \frac{V_{0,b}}{\cosh((x-d/2)/a)}, \quad (53)$$

and the three-electron Hamiltonian:

$$\hat{H} = \sum_{i=1}^3 -\frac{1}{2} \frac{\partial^2}{\partial x_i^2} + \lambda \sum_{i>j} \delta(x_i - x_j) + \sum_i v(x_i). \quad (54)$$

The potential of Equation (53) is partitioned as in the previous case:

$$\begin{aligned} v_1(x) &= \frac{V_{0,a}}{\cosh((x+d/2)/a)}, \\ v_2(x) &= \frac{V_{0,b}}{\cosh((x-d/2)/a)}. \end{aligned} \quad (55)$$

We solved this problem in three different ways: (1) by directly solving the Kohn-Sham equations using the exchange-only Magyar-Burke functional (MB) [37] for contact-interacting electrons; (2) by exact PSDFT with the same MB functional; (3) by neglecting the kinetic term  $v_k^p(\mathbf{r})$  of Equations (42)–(43) within the local-Q approximation (we refer to this as the local-Q\* results in Table 1).

In the MB functional [37],

$$E_X[n, \zeta] = -\frac{\lambda}{4} \int dx n^2(x) [1 + \zeta^2(x)], \quad (56)$$

where  $\zeta$  is the magnetization density  $\zeta(x) = (n_{\uparrow}(x) - n_{\downarrow}(x))/n(x)$ . The contribution from the external field to the partition potential is approximated with Equation (45). The partition term associated with the Hartree energy can be regarded as electrostatic repulsion between the fragments:

$$E_H^p = \int dx dx' n_1(x) v(x - x') n_2(x'), \quad (57)$$

where  $v(x - x') = \lambda \delta(x - x')$ . Given that the fragment densities overlap, some exchange takes place in the contacting region. The MB partition potentials were obtained by a simple inversion procedure similar to

that shown in the previous subsection. First we make an approximation to the partition potentials and KS orbitals; the potentials are fixed until self-consistency is achieved; if the total density differs from the 'exact' density then the following scheme is used to obtain a new estimate of the partition potentials [38]:

$$u_{p,\sigma}^{(i+1)}(x) = u_{p,\sigma}^{(i)}(x) + \gamma_{\sigma}(n_{\sigma}^{(i)}(x) - n_{\sigma}(x)), \quad (58)$$

and the procedure is repeated until the density converges. In this example we set the convergence tolerance as  $1.0 \times 10^{-5}$  for the estimation of the total density.

We found that there is essentially one spin-up electron on the left, one spin-up electron on the right, and one spin-down electron on the left. This is consistent with the physical picture obtained from applying the unrestricted Hartree-Fock method to the HeH molecule. Moreover, this integer-occupation phenomenon has been found to be persistent at both small and large internuclear separations [39]. As expected the approximation used here tends to localize the densities around the corresponding potential wells.

Table 1 and Figure 2 show the results. They demonstrate that PSDFT is *exactly* equivalent to KS-SDFT as it yields identical total energy and spin-densities. The partition potentials are shown in Figure 2(c) and (d). Although the approximation employed for the spin-up  $v_{p,\uparrow}$  might not be quantitative, it reproduces qualitatively the behaviour of the 'exact' partition potential obtained from the inversion in the bonding region. This potential shows a repulsive barrier for negative positions and an attractive well for positive positions. This basically shrinks the zero-order spin-up density of the left fragment, and it spreads out the spin-up density of the right fragment. By zero-order density we refer to that density obtained by neglecting the partition potentials while keeping the occupation numbers fixed. Therefore the local approximation employed for the  $Q$  function might be suitable as a first estimation in the inversion procedure and on further refinements of the partition functional.

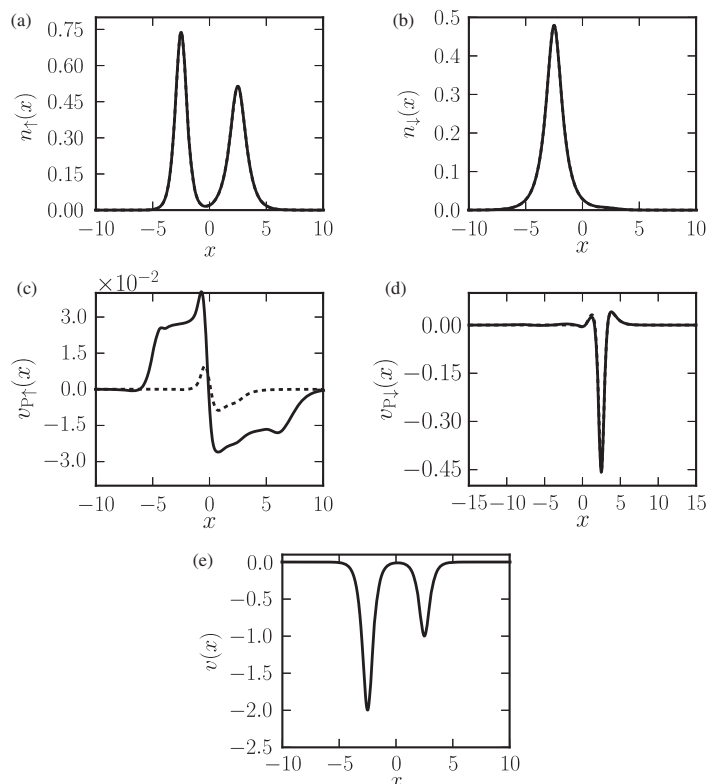


Figure 2. Results for three contact-interacting electrons in a double well potential; parameters:  $\lambda=1.0$ ,  $a=0.4$ ,  $d=5.0$ ,  $V_{0,a}=-2$ ,  $V_{0,b}=-1$ . A box of length 30 with a grid of size 500 was used. Dashed lines: local-Q\* PSDFT; solid line: 'exact' (PSDFT and direct solution). (a) Spin-up densities; (b) spin-down densities; (c) spin-up partition potential; (d) spin-down partition potential; and (e) potential.

Due to the non-differentiability of  $E_F$ , it is not possible to equalize the chemical potentials on both spin channels. This is reflected in the numerical values of the KS eigenvalues shown in Table 1. On the other hand, the partition energy was found to be small compared to the energy values. This is due to the particular choice of fragmentation energy, which includes the contributions from kinetic energy, electron–electron repulsion, and electron–nucleus interaction.

### 3.4. Inclusion of static electric and magnetic fields

We now propose a way to extend PSDFT to include other global fields such as static electric and

magnetic fields. It might not be convenient to partition an external electric potential of the form  $v_E(\mathbf{r}) = -\mu(\mathbf{r}) \cdot \mathcal{E}(\mathbf{r})$  as shown in Equation (3) because that would introduce unphysical spatial discontinuities. A simpler and more physical alternative is to allow each fragment (which is defined by means of Equation (3)) to interact with the electric field. Thus, the electrons in fragment  $\alpha$  are now subject to the external potential:

$$\bar{v}_\alpha(\mathbf{r}) = v_\alpha(\mathbf{r}) + v_E(\mathbf{r}). \quad (59)$$

Note that Equation (3) does not hold for this type of partitioning because of the global character of the electric field.

The energy of a fragment now reads

$$E_{\tilde{v}_\alpha}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = F[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} \tilde{v}_\alpha(\mathbf{r})n_\alpha(\mathbf{r}). \quad (60)$$

Given that the electric potential is global as well, then the partition energy functional, which is a difference between the ‘true’ energy and the fragmentation energy, does not depend on the electric field explicitly. The spin-polarized KS potentials turn into

$$\begin{aligned} v_{s,\sigma\alpha}(\mathbf{r}) &= v_H[n_\alpha](\mathbf{r}) + v_\alpha(\mathbf{r}) + v_E(\mathbf{r}) \\ &+ v_{xc,\sigma}[n_{\uparrow\alpha}, n_{\downarrow\alpha}](\mathbf{r}) + v_{p,\sigma}(\mathbf{r}). \end{aligned} \quad (61)$$

This scheme enables one to calculate the polarizability of the ground state. A simple approximated approach is to calculate the ground state and find the partition potential; then this can be fixed and the density of the system estimated by solving the KS equations under the influence of the electric field.

The inclusion of magnetic fields is somewhat more involved. For example consider the Hamiltonian:

$$\hat{H}_{v,\mathbf{B}} = \hat{T} + \hat{V}_{ee} + \int d\mathbf{r} \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) + \int d\mathbf{r} \hat{n}(\mathbf{r})v(\mathbf{r}), \quad (62)$$

where  $\hat{\mathbf{m}}$  and  $\mathbf{B}$  are the local magnetization and magnetic field, respectively. It is known that there is no one-to-one correspondence between  $v, \mathbf{B}$  and the local magnetization-density pair [1]. Capelle and Vignale [40] showed that if  $|\psi\rangle$  satisfies  $\hat{H}_{v,\mathbf{B}}|\psi\rangle = E|\psi\rangle$ , then it is possible to find perturbations  $\Delta v(\mathbf{r})$  and  $\Delta \mathbf{B}(\mathbf{r})$  such that:

$$\int d\mathbf{r} (\hat{n}(\mathbf{r})\Delta v(\mathbf{r}) + \hat{\mathbf{m}}(\mathbf{r})\Delta \mathbf{B}(\mathbf{r}))|\psi\rangle = \Delta E|\psi\rangle, \quad (63)$$

valid as long as there is no level-crossing induced by the magnetic field. This poses a fundamental difficulty in applying PSDFT to the Kohn–Sham formalism of von Barth and Hedin [1] and Rajagopal and Callaway [41]. A simple solution is to regard the magnetic field as a fixed variable [42], thus the energy

$$E_{v,\mathbf{B}}[n_\uparrow, n_\downarrow] = G_{\mathbf{B}}[n_\uparrow, n_\downarrow] + \int d\mathbf{r} n(\mathbf{r})v(\mathbf{r}) \quad (64)$$

is a functional of the spin-densities. The functional  $G$  is defined in the above equation as follows:

$$G_{\mathbf{B}}[n_\uparrow, n_\downarrow] = \min_{\psi \rightarrow n_\uparrow, n_\downarrow} \langle \psi | \hat{T} + \hat{V}_{ee} + \int d^3\mathbf{r} \hat{\mathbf{m}}(\mathbf{r})\mathbf{B}(\mathbf{r}) | \psi \rangle. \quad (65)$$

Our partitioning approach is easily applicable to the functional given by Equation (64). If the energy of a fragment is written as

$$E_{\tilde{v}_\alpha, \mathbf{B}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] = G_{\mathbf{B}}[n_{\uparrow\alpha}, n_{\downarrow\alpha}] + \int d^3\mathbf{r} n(\mathbf{r})\tilde{v}_\alpha(\mathbf{r}), \quad (66)$$

where the search is now over density matrices, then one may now define the analogue of  $\tilde{E}_f$ , Equation (5), as the sum of all such fragment energies. And the partition energy functional can be defined as the difference between the true energy functional and  $\tilde{E}_f$ . The partition energy functional can thus be expanded in terms of the corresponding Kohn–Sham contributions, which include a new term due to the presence of the magnetic field. This procedure avoids the non-uniqueness problems mentioned before. However it introduces more complexity to the energy functional because the magnetic field is treated as an inherent property of the system.

In summary, we highlighted the importance of viewing the partition energy as an implicit functional of the total density for a given choice of fragmentation. Based on this, we proposed an approach to construct the partition potential of PDFT, and extended PDFT to include electronic spin-densities in the absence and presence of external electric and magnetic fields.

#### Acknowledgements

The authors thankfully acknowledge financial support provided by the Department of Energy under grant No. DE-FG02-10ER16196.

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**Action formalism of time-dependent density-functional theory**

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(Received 20 December 2012; published 26 August 2013)

The Runge-Gross [E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984)] action functional of time-dependent density-functional theory leads to a well-known causality paradox; that is, a perturbation of the electronic density in the future affects the response of the system in the present. This paradox is known to be caused by an inconsistent application of the Dirac-Frenkel variational principle. In view of the recent solutions to this problem, the action functional employed by Runge and Gross in their formulation of time-dependent density-functional theory is analyzed in the context of the Keldysh contour technique. The time-dependent electronic density and the concept of causality are extended to the contour. We derive a variational equation that obeys causality and relates the exchange-correlation potential with its kernel and the functional derivative of the exchange-correlation action functional with respect to the density. It is shown that the adiabatic local-density approximation is a consistent solution of this equation and that the time-dependent optimized potential method can also be derived from it. The formalism presented here can be used to find new approximation methods for the exchange-correlation potential and to avoid the causality dilemma.

DOI: 10.1103/PhysRevA.88.022515

PACS number(s): 31.15.ee

**I. INTRODUCTION**

Time-dependent density-functional theory (TDDFT) [1–3] establishes the time-dependent (TD) electronic density as the primary object of study to understand the dynamics of molecular systems. TDDFT is widely used to calculate spectroscopic properties of molecules and solids, especially when TD perturbation theory is not applicable [4]. However, TDDFT can also be used to study electronic excitations in the linear regime or predict the electronic ground-state energy and density [5,6]. The foundation of TDDFT is the theorem of Runge and Gross (RG) [7] stating that there is a one-to-one mapping, given an initial state, between electronic TD densities and TD external potentials. Later, van Leeuwen [8] showed that it is possible to reproduce the TD electronic density of the system of interacting electrons by a system of noninteracting electrons, which makes possible the use of the TD Kohn-Sham (KS) equations. Challenges in TDDFT include the correct description of charge-transfer excitation [9,10], electronic transport through a molecule connected to metallic leads under a bias [11–13], high-order-harmonic generation [14], double excitations [15], and van der Waals interactions, among others [16].

In TDDFT, the prediction of the evolution of the electronic density is reformulated in terms of the TD KS equations, which are easier to solve than the time-dependent Schrödinger equation (TDSE). Moreover, every observable of the system can be expressed as a functional of the density because the wave function is a density functional as well. However, Runge and Gross [7] proved that the one-to-one mapping between TD densities and TD potentials is valid under the restriction that the TD external potential is Taylor expandable in terms of the time variable. The question as to how vast the set of TD potentials (or TD densities) of the RG theorem should be is still an open question. The proof shown by Ruggenthaler and van Leeuwen [17] and Ruggenthaler et al. [18] suggests

that the Runge-Gross theorem can be extended to a wider set of TD potentials, including those that are nonanalytic in time. Although it is known that this map exists and there is a formal procedure to construct KS potentials, it is still a challenge to calculate the TD potential from a given TD density [18–20].

In ground-state density-functional theory (DFT), the exchange-correlation (XC) potential is expressed as the functional derivative of the XC energy functional with respect to the time-independent electronic density. In TDDFT, an analogous variational relation between the TD XC potential and its action functional has been sought for the last three decades. Peuckert [21] first suggested that the Dirac-Frenkel action functional and its variational principle should be used in TDDFT. Later, Runge and Gross [7] showed that the Dirac-Frenkel action functional extended to TDDFT leads to identifying the TD XC potential as a functional derivative of the XC action functional with respect to the density. However, it was later found by Gross et al. [22] that this gives rise to a *paradox* in which a variation of the density in the future induces a perturbation of the potential in the past. According to this, the inverse first-order response functional would not be causal. Gross et al. [22] conjectured that the paradox could be solved by incorporating the causality principle explicitly into the action formalism.

To resolve this causality paradox several works have been published. Rajagopal [23] introduced an action based on the work of Jackiw and Kerman [24] in quantum field theory. However, this formalism does not use the density as a basic variable but as a transition density that can be negative valued; this quantity is unsuitable as a basic quantity for TDDFT.

van Leeuwen [25] proposed a functional in the Keldysh contour with similar properties to that of a free energy. This functional depends on a pseudo-density in the Keldysh space that reduces to the density of the system when the potential in the Keldysh space corresponds to a physical potential. Due to the symmetry properties of the first-order response function of the pseudo-density, the causality is restored when the density is mapped to the real-time regime. However, the van Leeuwen

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formalism requires expansion of the action functional in terms of Feynman diagrams, while the functional of RG does not require such expansion. Furthermore, the operator used in this formalism for the pseudodensity is not Hermitian in general, and thus the pseudodensity does not integrate to the total number of electrons of the system, except when the density is physical.

Recently, Vignale [26] solved the causality paradox in real time by showing that the source of the problem in the RG formulation is a boundary condition. He showed that only the initial condition is necessary in the Runge-Gross functional to recover the causality restriction in general and derived an expression for the XC potential that is causal.

In this paper I review Vignale's solution of the causality paradox in real time from the perspective of unitary propagation and later use Vignale's theory to extend the RG action functional to the *Keldysh contour*. The RG action functional in the Keldysh space, unlike the van Leeuwen functional, does not require diagrammatic expansion and uses an electronic density that is a causal functional of the potential in the Keldysh space. By the RG theorem applied to the Keldysh space and under the assumption that the density is a *strictly causal* functional of the potential in the contour, I show that a *variational equation* relating the XC potential to the XC action functional arises. This equation shows an explicit dependence on the *memory* of the system through the XC kernel. I show that the adiabatic local-density approximation (ALDA) is consistent with this equation, how the TD optimized potential method (TDOPM) can be obtained, and also how the ground-state XC potential can be recovered.

## II. REAL-TIME ANALYSIS

The Dirac-Frenkel variational principle provides a method to derive the TDSE and its approximations by finding a stationary value of the action functional:

$$W[\psi; v] = \int_{t_0}^{t_1} dt \langle \psi(t) | i \frac{\partial}{\partial t} - \hat{H}[v](t) | \psi(t) \rangle. \quad (1)$$

In this work we consider Hamiltonians of the form

$$\hat{H}[v](t) = \hat{T} + \hat{W} + \int d^3\mathbf{r} v(\mathbf{r}t) \hat{n}(\mathbf{r}), \quad (2)$$

where  $\hat{T}$  and  $\hat{W}$  are the kinetic energy and electron-electron repulsion energy operators, respectively, and  $\hat{n}(\mathbf{r})$  is the density operator. The Dirac-Frenkel functional is defined over a *Hilbert space of antisymmetric wave functions* representing bound systems of  $N$  electrons. The TDSE is thus obtained by setting

$$\delta_\psi W[\psi; v] = 0. \quad (3)$$

This variational principle supposes that  $\delta\psi(t_0) = \delta\psi(t_1) = 0$ . The solution of the above equation, denoted as  $\psi[v](t)$ , is the solution of the TDSE:

$$i \frac{\partial}{\partial t} |\psi[v](t)\rangle = \hat{H}[v](t) |\psi[v](t)\rangle. \quad (4)$$

$|\psi[v](t)\rangle$  is said to be a  $v$ -representable ket in real time, which, expressed in terms of the unitary evolution operator, is

$$|\psi[v](t)\rangle = \hat{U}[v](t, t_0) |\psi(t_0)\rangle, \quad (5)$$

where

$$\hat{U}[v](t, t_0) = \hat{T} \exp \left( -i \int_{t_0}^t ds \hat{H}[v](s) \right). \quad (6)$$

Here  $\hat{T}$  is the time-ordering operator in real time. In this work we interpret the integral determining the unitary evolution in the above equation to be taken over the interval  $[t_0, t]$ ; that is, we define it as

$$\int_{t_0}^t ds \hat{H}[v](s) := \lim_{\epsilon \rightarrow 0} \int_{t_0}^{t-\epsilon} ds \hat{H}[v](s). \quad (7)$$

The above definition, when inserted into Eq. (6) and the result is applied to the initial state, determines the evolution of the system. We refer to the dependency on the potential of Eq. (6) as the *strict causality assumption*, which will be used in the next section to simplify the corresponding calculations.

Our choice of integration is related to the question, Does a perturbation of the form  $\delta v_1(\mathbf{r}'t'; t) = c(\mathbf{r}')\delta(t - t')$  cause a response in any observable at time  $t$ , i.e., at the very moment when the perturbation occurs? In this work I elect to postulate that the instantaneous perturbation  $\delta v_1$  does only affect the system strictly after it has occurred, enforcing the intuitive notion that the time delay between a cause and its effect has to be greater than zero. This choice on how the integration in time is taken excludes any response to  $\delta v_1(\mathbf{r}'t'; t)$  when  $t' \leq t$ .

We may state, under the strict causality assumption, that  $\delta\hat{U}(t, t_0)/\delta v(\mathbf{r}'t') = 0$  if  $t = t'$  and that the ket  $|\psi[v](t)\rangle$  is a strictly causal functional of the potential: It is determined by the potential  $v$  at times less than  $t$ . Furthermore, every observable of the form  $O[v](t) = \langle \psi(t_0) | \hat{O}^\dagger[v](t, t_0) \hat{O}[v](t, t_0) | \psi(t_0) \rangle$  is also a strictly causal functional of  $v$ , i.e.,

$$\frac{\delta O[v](t)}{\delta v(\mathbf{r}'t')} = 0 \quad t' \geq t. \quad (8)$$

For example, the density of the system,

$$n[v](\mathbf{r}t) = \langle \psi(t_0) | \hat{U}^\dagger[v](t, t_0) \hat{n}(\mathbf{r}) \hat{U}[v](t, t_0) | \psi(t_0) \rangle, \quad (9)$$

is determined by the evolution of  $v$  in the interval  $[t_0, t]$  [3].

By the RG theorem, given a fixed initial state, the potential  $v$  at times in  $[t_0, t]$  uniquely determines  $n$  in the interval  $[t_0, t]$  and vice versa. If we denote as  $u[n]$  the external potential as a functional of the TD density, then a first-order variation in  $u$  is given by a variation of  $n$  over the interval  $[t_0, t]$ :

$$\delta u[n](\mathbf{r}t) = \int_{t_0}^t dt' \int d^3\mathbf{r}' \chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t'), \quad (10)$$

where

$$\chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') = \frac{\delta u(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}. \quad (11)$$

This indicates that  $\delta u(\mathbf{r}t)/\delta n(\mathbf{r}'t')$  for  $t \leq t'$  is not defined because it does not contribute to the integral of Eq. (10). However, for convenience we set

$$\chi^{-1}[n](\mathbf{r}t, \mathbf{r}'t') = 0 \quad t \leq t'. \quad (12)$$

Vignale [26], however, employing the evolution equation of the current, showed that  $\delta u(\mathbf{r}t)/\delta n(\mathbf{r}'t')$  is related to  $\delta(t - t')$  and its first- and second-order time derivatives when  $t = t'$ . This result is obtained under two assumptions different from



ours: First,  $u(\mathbf{r}t)$  is determined by  $n(\mathbf{r}'t')$  for  $t' \leq t$ . Second, the functional derivative of the *stress* tensor with respect to the density vanishes at equal times. Our assumption avoids this singularity in  $\chi^{-1}$  and will be used to simplify our calculations in the Keldysh space.

Now let us consider the Runge-Gross action functional:

$$A_v[n] = \int_{t_0}^{t_1} dt \langle \psi[n](t) | i \frac{\partial}{\partial t} - \hat{H}[v](t) | \psi[n](t) \rangle, \quad (13)$$

where  $|\psi[n](t)\rangle = |\psi[u[n]](t)\rangle$ ,  $v$  is some TD external potential, and  $t_1 > t_0$ . Note that the ket  $|\psi[n](t)\rangle$  is causal; that is, it is determined by  $n$  in the interval  $[t_0, t]$ . Runge and Gross [7], based on the Dirac-Frenkel variational principle, imposed  $\delta\psi(t_0) = \delta\psi(t_1) = 0$  and

$$\frac{\delta A_v}{\delta n(\mathbf{r}t)} = 0, \quad (14)$$

which leads to the following alternative form of the variational principle:

$$\frac{\delta B[n]}{\delta n(\mathbf{r}t)} - v(\mathbf{r}t) = 0, \quad (15)$$

where  $B[n]$  is the internal action:

$$B[n] = \int_{t_0}^{t_1} dt \langle \psi[n](t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{W} | \psi[n](t) \rangle. \quad (16)$$

If Eq. (15) were valid, then we could assert that [27]

$$u[n](\mathbf{r}t) = \frac{\delta B[n]}{\delta n(\mathbf{r}t)}. \quad (17)$$

Unfortunately, when the above function is further differentiated with respect to  $n$ ,

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta^2 B[n]}{\delta n(\mathbf{r}'t') \delta n(\mathbf{r}t)}, \quad (18)$$

one finds an inconsistency because the above equation implies that  $\chi(\mathbf{r}t, \mathbf{r}'t') \neq 0$  for  $t < t'$ . This is known as the *causality paradox* [22]. The solution to the paradox was found by Vignale [26], who pointed out that, according to the definition of the  $v$ -representable wave function, we can only set  $\delta\psi(t_0) = 0$  because a perturbation  $\delta n(\mathbf{r}t)$ , in general, will induce a response  $\delta\psi(t_1) \neq 0$ .

The solution of Vignale [26] can be viewed as a direct implementation of the causality principle into the RG functional. For example, the internal action  $B[n]$ , using the TDSE, can be written as [3]

$$B[n] = \int_{t_0}^{t_1} dt u[n](\mathbf{r}t) n(\mathbf{r}t). \quad (19)$$

The density functional  $u[n]$  is causal by the RG theorem. If we differentiate the above functional with respect to the density and insert the result into the functional derivative of the RG action functional, we obtain

$$\begin{aligned} \frac{\delta A_v}{\delta n(\mathbf{r}t)} &= u[n](\mathbf{r}t) - v(\mathbf{r}t) \\ &+ \int_{t_0}^{t_1} dt' \int d^3\mathbf{r}' \chi^{-1}[\mathbf{r}t, \mathbf{r}'t'] n(\mathbf{r}'t'). \end{aligned} \quad (20)$$

Now let  $n_v$  be the TD density corresponding to  $v$ ; then

$$\left. \frac{\delta A_v}{\delta n(\mathbf{r}t)} \right|_{n=n_v} = \int_{t_0}^{t_1} dt' \int d^3\mathbf{r}' \chi^{-1}[\mathbf{r}t, \mathbf{r}'t'] n_v(\mathbf{r}'t'). \quad (21)$$

This last equation is an alternative form of the Vignale variational formulation that shows that  $n_v$  is not a stationary value of  $A_v[n]$ . This is a consequence of constraining the wave functions of the RG functional to be density functionals of the form  $\psi[u[n]]$ . Ruggenthaler and Leeuwen [27] showed that not every TD wave function can be associated with a TD external potential (or a TD density). Hence the domain of the RG functional is just a subset of the domain of the Dirac-Frenkel functional, explaining why the RG and the Dirac-Frenkel functionals lead to different results.

### III. KELDYSH-SPACE ANALYSIS

Let us add a superscript index  $+$  or  $-$  to the time variable  $t$ . The Keldysh contour  $\mathcal{C}$  is expressed as  $\mathcal{C} = \mathcal{C}^+ \cup \mathcal{C}^-$ , where  $\mathcal{C}^+ = [t_0^+, t_1^+]$  and  $\mathcal{C}^- = [t_0^-, t_1^-]$ . We denote  $z$  as a variable in the contour  $\mathcal{C}$  and let  $z_i = t_0^+$  and  $z_f = t_1^-$ . The arrow of time in  $\mathcal{C}$  points from  $t_0^+$  to  $t_1^+$  and from  $t_1^-$  to  $t_0^-$  (see Fig. 1). Thus, any  $z \in \mathcal{C}^-$  is said to be later than any  $z' \in \mathcal{C}^+$ . If  $z, z' \in \mathcal{C}^-$ , we say that  $z$  is later than  $z'$  if  $t(z) < t(z')$ , where  $t(z)$  is the real value of  $z$ . A ket in  $\mathcal{C}$  is denoted as  $|\psi_c[u_c](z)\rangle$ , where  $u_c(\mathbf{r}z)$  is some potential in  $\mathcal{C}$ . A physical potential in  $\mathcal{C}$  is denoted as  $\tilde{u}_c$ , and it satisfies  $\tilde{u}_c(\mathbf{r}t^+) = \tilde{u}_c(\mathbf{r}t^-)$ . Thus a potential in real time is mapped to the Keldysh space when setting  $\tilde{u}_c(\mathbf{r}t^\pm) = u(\mathbf{r}t)$  ( $t^\pm$  denotes evaluation at  $\mathcal{C}^+$  or  $\mathcal{C}^-$ ).

We now extend the unitary propagator  $\hat{U}$  to the Keldysh space as follows:

$$\hat{U}_c[u_c](z, z_i) = \hat{T}_C \exp \left[ -i \int_{z_i}^z dz' \hat{H}_c[u_c](z') \right], \quad (22)$$

where  $\hat{T}_C$  is the path-ordering operator in  $\mathcal{C}$  (for example,  $\hat{T}_C[\hat{B}_c(z')\hat{A}_c(z)] = \hat{A}_c(z)\hat{B}_c(z')$  if  $z$  is later than  $z'$ ). The Hamiltonian in the Keldysh space now reads  $\hat{H}_c[u_c](z) = \hat{T} + \hat{W} + \int d^3\mathbf{r} u_c(\mathbf{r}z) \hat{n}(\mathbf{r})$ . The integration over the pseudotime is defined as

$$\int_{z_i}^z dz' f_c(z') := \lim_{\epsilon \rightarrow 0} \begin{cases} \int_{t_0^+}^{t_1^+} dt' f_c(t'^+), & z = t^+ \\ \int_{t_0^+}^{t_1^+} dt' f_c(t'^+) + \int_{t_1^-}^{t_0^-} dt' f_c(t'^-), & z = t^- \end{cases} \quad (23)$$

The above expresses, in analogy with the real-time case, that the end point of the integral in Eq. (22) is not included by definition. This is the strict causality assumption in the Keldysh contour.

A  $v$ -representable ket in  $\mathcal{C}$  is thus expressed as  $|\psi_c[u_c](z)\rangle = \hat{U}_c[u_c](z, z_i) |\psi_c(z_i)\rangle$ , where  $|\psi_c(z_i)\rangle = |\psi(t_0)\rangle$  is the initial state of the system. Note that  $\psi_c(z)$  does not depend on the potential  $u_c$  at later times than  $z$ . We define the

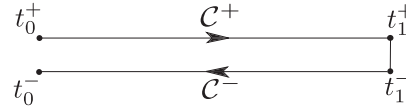


FIG. 1. Keldysh contour.

density in  $\mathcal{C}$  as [28]

$$n_c[u_c](\mathbf{r}z) = \langle \hat{U}_c^\dagger[u_c](z, z_i) \hat{n}(\mathbf{r}) \hat{U}_c[u_c](z, z_i) \rangle, \quad (24)$$

where  $\langle \hat{O} \rangle = \langle \psi_c(z_i) | \hat{O} | \psi_c(z_i) \rangle$ . To prove that there is a one-to-one mapping between  $n_c$  and  $u_c$ , it is sufficient to notice that  $\psi_c$  satisfies the Schrödinger equation in  $\mathcal{C}^+$ . Therefore, if the potential can be expressed as a power series around  $z_i$ , then the RG theorem and its extension [17] including nonanalytic potentials apply in this case.

Let us examine the action functional proposed by van Leeuwen [25], which reads

$$A_{vL}[u_c] = i \ln \langle \hat{U}_c[u_c](z_f, z_i) \rangle. \quad (25)$$

The functional derivative of this functional with respect to the potential  $u_c$  yields the pseudodensity [25]:

$$n_{vL}(\mathbf{r}z) = \frac{\langle \hat{U}_c(z_f, z) \hat{n}(\mathbf{r}) \hat{U}_c(z, z_i) \rangle}{\langle \hat{U}_c(z_f, z_i) \rangle}. \quad (26)$$

However, the above density is an average of the operator:

$$\hat{n}_{vL,H}(\mathbf{r}) = \hat{U}_c(z_f, z) \hat{n}(\mathbf{r}) \hat{U}_c(z, z_i), \quad (27)$$

which is not a Hermitian operator. Therefore

$$\int d^3\mathbf{r} \hat{n}_{vL,H}(\mathbf{r}z) = \hat{N} \hat{U}_c(z_f, z_i), \quad (28)$$

where  $\hat{N}$  is the particle-number operator. This implies that  $n_{vL}$  does not integrate to  $N$ , except when the potential  $u_c$  is physical [25]. The density  $n_c$ , on the other hand, integrates to  $N$  and is always positive.

It can be shown that the response function of the density in  $\mathcal{C}$  is given by

$$\begin{aligned} \chi_c[u_c](\mathbf{r}z, \mathbf{r}'z') &= \frac{\delta n_c(\mathbf{r}z)}{\delta u_c(\mathbf{r}'z')} \\ &= -i \langle [\hat{n}_{c,H}[u_c](\mathbf{r}z), \hat{n}_{c,H}[u_c](\mathbf{r}'z')] \rangle, \end{aligned} \quad (29)$$

where the Heisenberg representation of the density operator  $\hat{n}(\mathbf{r})$  is

$$\hat{n}_{c,H}[u_c](\mathbf{r}z) = \hat{U}_c^\dagger[u_c](z, z_i) \hat{n}(\mathbf{r}) \hat{U}_c[u_c](z, z_i). \quad (30)$$

Equation (29) is valid if  $z$  is later than  $z'$ , and we set  $\chi_c(\mathbf{r}z, \mathbf{r}'z') = 0$  if  $z'$  is later than or equal to  $z$ .

The inverse first-order response function  $\chi_c^{-1}[n_c](\mathbf{r}z, \mathbf{r}'z') = \delta u_c(\mathbf{r}z) / \delta n_c(\mathbf{r}'z')$ , according to the RG theorem extended to  $\mathcal{C}$ , must also satisfy causality in the contour, e.g.,  $\chi_c^{-1}(\mathbf{r}z, \mathbf{r}'z') = 0$  if  $z = z'$  or  $z'$  is later than  $z$ . When a physical potential is used, the Heisenberg operators recover their usual form in real time. Therefore we obtain a physical density  $\bar{n}_c(\mathbf{r}t^\pm) = n(\mathbf{r}t)$ . From Eq. (29) we can show that the first-order response function satisfies the antisymmetry relationship:

$$\chi_c(\mathbf{r}t^+, \mathbf{r}'t'^+) \Big|_{u_c=\bar{u}_c} = -\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-) \Big|_{u_c=\bar{u}_c}, \quad (31)$$

where  $u_c = \bar{u}_c$  denotes evaluation at the physical regime. Note that  $\chi_c$  also satisfies  $\chi_c(\mathbf{r}t^+, \mathbf{r}'t'^+) = \chi_c(\mathbf{r}t^-, \mathbf{r}'t'^+)$  and  $\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^+) = \chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-)$  if  $t > t'$  and  $u_c = \bar{u}_c$ .

The response of the density in the Keldysh space is [25]

$$\delta n_c[u_c](\mathbf{r}z) = \int_{z_i}^{z_f} dz' \int d^3\mathbf{r}' \chi_c[u_c](\mathbf{r}z, \mathbf{r}'z') \delta u_c(\mathbf{r}'z'). \quad (32)$$

To obtain the response in real time, the variation of a physical potential must satisfy  $\delta \bar{u}_c(\mathbf{r}t^+) = \delta \bar{u}_c(\mathbf{r}t^-) = \delta u(\mathbf{r}t)$ . Using the aforementioned properties of  $\chi_c$  to calculate the above integral, the response of the density turns out to be independent of the time location in the contour, i.e.,  $\delta n_c(\mathbf{r}t^+) = \delta n_c(\mathbf{r}t^-) = \delta n(\mathbf{r}t)$ . Hence it is determined by

$$\delta n_c[\bar{u}_c](\mathbf{r}t) = \int_{t_0}^{t^\pm} dt' \int d^3\mathbf{r}' \chi_c[\bar{u}_c](\mathbf{r}t^\pm, \mathbf{r}'t'^+) \delta \bar{u}_c(\mathbf{r}'t'^+). \quad (33)$$

This result allows us to identify the response in real time  $\chi(\mathbf{r}t, \mathbf{r}'t')$  as  $\chi_c(\mathbf{r}t^\pm, \mathbf{r}'t'^+)|_{u_c=\bar{u}_c}$  or  $-\chi_c(\mathbf{r}'t'^-, \mathbf{r}t^-)|_{u_c=\bar{u}_c}$ , which are causal. Exchanging variables in the integral of  $\chi_c \chi_c^{-1}$  reveals that  $\chi_c^{-1}$  satisfies the same relationships of  $\chi_c$  regarding exchange of variables at physical densities.

Let us extend the functional  $A_v$  to the Keldysh space:

$$A_{\bar{v}_c}[n_c] = B[n_c] - \int_{z_i}^{z_f} dz \int d^3\mathbf{r} n_c(\mathbf{r}z) \bar{v}_c(\mathbf{r}z), \quad (34)$$

where

$$B[n_c] = \int_{z_i}^{z_f} dz \langle \psi_c[n_c](z) | i \frac{\partial}{\partial z} - \hat{T} - \hat{W} | \psi_c[n_c](z) \rangle, \quad (35)$$

$\bar{v}_c$  is some external physical potential, and  $\partial f(z)/\partial z = \partial f(t^\sigma)/\partial t$ , where  $\sigma = +, -$ . The Vignale equation in this case reads

$$\begin{aligned} \frac{\delta B}{\delta n_c(\mathbf{r}z)} \Big|_{n_c=\bar{n}_{c,\bar{v}_c}} &= -\bar{v}_c(\mathbf{r}z) \\ &= i \langle \psi_c(z_f) | \frac{\delta \psi_c(z_f)}{\delta n_c(\mathbf{r}z)} \rangle \Big|_{n_c=\bar{n}_{c,\bar{v}_c}} \\ &= \int_{z_i}^{z_f} dz' \int d^3\mathbf{r}' \bar{n}_{c,\bar{v}_c}(\mathbf{r}'z') \chi_c^{-1}[\bar{n}_{c,\bar{v}_c}](\mathbf{r}'z', \mathbf{r}z). \end{aligned} \quad (36)$$

The left-hand side of the above equation corresponds to  $\delta A_{\bar{v}_c} / \delta n_c(\mathbf{r}z)$  evaluated at the density that yields  $\bar{v}_c$ ,  $\bar{n}_{c,\bar{v}_c}$ . Additionally, the above equation also gives the functional derivative  $\delta B / \delta n_c(\mathbf{r}z)$  for an arbitrary density  $n_c$ ; in this case, we replace  $\bar{v}_c$  by  $u_c[n_c](\mathbf{r}z)$  and  $\bar{n}_{c,\bar{v}_c}$  by  $n_c$ , and the inverse response function has to be evaluated at  $n_c$ .

Let us introduce the KS action functional:

$$A_{s,\bar{v}_{c,s}}[n_c] = B_s[n_c] - \int_{z_i}^{z_f} dz \int d^3\mathbf{r} n_c(\mathbf{r}z) \bar{v}_{c,s}(\mathbf{r}z), \quad (37)$$

where  $\bar{v}_{c,s}(\mathbf{r}z)$  is some effective external potential and

$$B_s[n_c] = \int_{z_i}^{z_f} dz \langle \Phi_{c,s}[n_c](z) | i \frac{\partial}{\partial z} - \hat{T} | \Phi_{c,s}[n_c](z) \rangle. \quad (38)$$

The KS wave function is a Slater determinant of TD KS orbitals  $\{\phi_{c,i}(\mathbf{r}z)\}$  that satisfy

$$i \frac{\partial \phi_{c,i}}{\partial z} = \left( -\frac{1}{2} \nabla^2 + u_{c,s}[n_c](\mathbf{r}z) \right) \phi_{c,i}(\mathbf{r}z), \quad (39)$$

where  $u_{c,s}[n_c]$  is the KS potential that represents  $n_c(\mathbf{r}z)$ . Thus, if we differentiate  $B_s$  with respect to the TD density, we obtain

$$\begin{aligned} \frac{\delta B_s}{\delta n_c(\mathbf{r}z)} &= u_{c,s}[n_c](\mathbf{r}z) \\ &+ \int_{z_i}^{z_f} dz' \int d^3\mathbf{r}' n_c(\mathbf{r}'z') \chi_{c,s}^{-1}[n_c](\mathbf{r}'z', \mathbf{r}z), \end{aligned} \quad (40)$$

where  $\chi_{c,s}^{-1}(\mathbf{r}z, \mathbf{r}'z') = \delta u_{c,s}(\mathbf{r}'z')/\delta n_c(\mathbf{r}z)$ .

Recall the Hartree functional:

$$\mathcal{A}_H[n_c] = \frac{1}{2} \int_{z_1}^{z_f} dz \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n_c(\mathbf{r}'z)n_c(\mathbf{r}z)}{|\mathbf{r} - \mathbf{r}'|}. \quad (41)$$

Let us introduce the XC action functional:

$$\mathcal{A}_{xc}[n_c] = \mathcal{B}_s[n_c] - \mathcal{B}[n_c] - \mathcal{A}_H[n_c]. \quad (42)$$

Using Eqs. (36) and (40), it is found that the functional derivative of the XC action functional can be expressed as

$$u_{c,xc}(\mathbf{r}z) + \int_z^{z_f} dz' \int d^3\mathbf{r}' n_c(\mathbf{r}'z') [\chi_{c,s}^{-1}(\mathbf{r}'z', \mathbf{r}z) - \chi_c^{-1}(\mathbf{r}'z', \mathbf{r}z)] = \frac{\delta \mathcal{A}_{xc}}{\delta n_c(\mathbf{r}z)}. \quad (43)$$

Here  $u_{c,xc}(\mathbf{r}z) = u_{c,s}(\mathbf{r}z) - u_c(\mathbf{r}z) - u_{c,H}(\mathbf{r}z)$ , where the Hartree potential is  $u_{c,H}[n_c](\mathbf{r}z) = \int d^3\mathbf{r}' n_c(\mathbf{r}'z)/|\mathbf{r} - \mathbf{r}'|$ . Now introduce the XC kernel  $f_{c,xc}(\mathbf{r}z, \mathbf{r}'z') = \delta u_{c,xc}(\mathbf{r}z)/\delta n_c(\mathbf{r}'z')$ , which satisfies

$$\chi_{c,s}^{-1}(\mathbf{r}z, \mathbf{r}'z') = \chi_c^{-1}(\mathbf{r}z, \mathbf{r}'z') + \frac{\delta_c(z - z')}{|\mathbf{r} - \mathbf{r}'|} + f_{c,xc}(\mathbf{r}z, \mathbf{r}'z'). \quad (44)$$

The  $\delta$  function in  $\mathcal{C}$  space is defined such that  $\int_{z_1}^{z_f} dz' f_c(z') \delta_c(z - z') = f_c(z)$ . The KS response function and the XC kernel satisfy the same properties of  $\chi_c$  regarding exchange of variables.

In order to simplify Eq. (43), suppose that the density is physical,  $n_c = \bar{n}_c$ . This imposes that the XC potential is the same in both  $\mathcal{C}^+$  and  $\mathcal{C}^-$  spaces. For example, if  $z = t^+$  then the integral in time can be split up into two integrals: The first one runs from  $t^+$  to  $t^-$ , and the second one runs from  $t^-$  to  $t_0^-$ . There is no contribution from the first integral due to the symmetry properties of  $\chi_c^{-1}$  and  $\chi_{c,s}^{-1}$  at physical densities. For the second integral we can use the antisymmetry relation to obtain in real time that

$$u_{xc}(\mathbf{r}t) + \int_{t_0}^t dt' \int d^3\mathbf{r}' f_{xc}(\mathbf{r}t, \mathbf{r}'t') n(\mathbf{r}'t') = \frac{\delta \mathcal{A}_{xc}}{\delta n(\mathbf{r}t)}, \quad (45)$$

where  $u_{xc}(\mathbf{r}t) = \bar{u}_{c,xc}(\mathbf{r}t^\pm)$  and

$$\frac{\delta \mathcal{A}_{xc}}{\delta n(\mathbf{r}t)} = \frac{\delta \mathcal{A}_{xc}}{\delta n_c(\mathbf{r}t^\pm)} \Big|_{n_c = \bar{n}_c}. \quad (46)$$

Setting  $z = t^-$  in Eq. (43) also leads to Eq. (45) when  $n_c = \bar{n}_c$ ; for this reason we expressed the final result in real time. Because  $f_{c,xc}$  in the  $\mathcal{C}$  space also has the same properties as  $\chi_c^{-1}$ , we identify the XC kernel in real time  $f_{xc}(\mathbf{r}t, \mathbf{r}'t')$  as  $f_{c,xc}(\mathbf{r}t^\pm, \mathbf{r}'t'^\pm)|_{n_c = \bar{n}_c}$  or  $-f_{c,xc}(\mathbf{r}'t'^-, \mathbf{r}t^-)|_{n_c = \bar{n}_c}$ . Thus, the XC kernel is causal in real time.

Given that we assumed that the response functions  $\chi_c$  and  $\chi_{c,s}$  are strictly causal in  $\mathcal{C}$ , the integral in Eq. (43) is taken over the interval  $(z, z_f]$ . This implies that the Hartree kernel  $\delta_c(z - z')/|\mathbf{r} - \mathbf{r}'|$  lies outside the integration limits, and thus it has no contribution to Eq. (45). Based on this, the integral in Eq. (45) is carried out strictly over the past of  $t$ , i.e.,  $[t_0, t)$ . Hence, our causality assumption avoids singularities at equal times and simplifies the transition to real time.

Equation (45) is the main result of this work. It is a variational equation that establishes a causal connection between

$u_{xc}$  in real time with an XC action functional in the Keldysh space and the memory of the system. If an approximation to the XC action functional is known, then Eq. (45) can be used to estimate the XC potential. The potentials  $u(\mathbf{r}t)$  and  $u_s(\mathbf{r}t)$  also satisfy the same type of equation as that of  $u_{xc}$ ; one has to replace  $f_{xc}$  and  $\mathcal{A}_{xc}$  by  $\chi^{-1}$  and  $\mathcal{B}$  or  $\chi_s^{-1}$  and  $\mathcal{B}_s$ .

Note that the left-hand side of Eq. (45) is a functional of the density  $\bar{n}_c(\mathbf{r}t^\pm)$ , or simply  $n(\mathbf{r}t)$ . This implies that the second functional derivative of  $\mathcal{A}_{xc}$  with respect to the density in real time is not symmetric, i.e.,

$$\frac{\delta}{\delta n(\mathbf{r}'t')} \frac{\delta \mathcal{A}_{xc}}{\delta n(\mathbf{r}t)} = 0 \quad t' \geq t. \quad (47)$$

Here, the symbol  $\delta/\delta n(\mathbf{r}'t')$  represents regular functional differentiation in real time because the operation  $\delta/\delta n(\mathbf{r}t)$  already involves evaluation at the physical regime. The above result is a consequence of implementing causality in the  $\mathcal{C}$  space explicitly using the path-ordering operator. Furthermore, recursive differentiation of Eq. (45) also allows us to express its solution as a series of functional derivatives of  $\mathcal{A}_{xc}$ . This reads

$$u_{xc}(\mathbf{x}_1) = \frac{\delta \mathcal{A}_{xc}}{\delta n(\mathbf{x}_1)} + w_{xc}(\mathbf{x}_1), \quad (48)$$

where

$$w_{xc}(\mathbf{x}_1) = \sum_{m=2}^{\infty} \frac{(-1)^{m+1}}{m!} \int d\mu(\mathbf{x}_2) \cdots d\mu(\mathbf{x}_m) \times \frac{\delta^{m-1}}{\delta n(\mathbf{x}_m) \cdots \delta n(\mathbf{x}_2)} \frac{\delta \mathcal{A}_{xc}}{\delta n(\mathbf{x}_1)}. \quad (49)$$

Here  $\mathbf{x}_m = \mathbf{r}_m, t_m$ ,  $m = 1, 2, \dots$  and  $d\mu(\mathbf{x}_m) = n(\mathbf{x}_m) d^4\mathbf{x}_m$ . The functional derivatives in the integral are zero if, for any  $i > j$ ,  $t_i \geq t_j$ . This series shows that the XC potential depends on perturbations of the XC potentials in all orders. However, in order to achieve convergence the functional derivatives must decrease as their order increases.

Now let us apply our variational equation to the derivation of the ALDA XC potential. The ALDA XC action functional is:

$$\mathcal{A}_{xc}^{\text{ALDA}}[n_c] = \int_{z_1}^{z_f} dz \int d^3\mathbf{r} [\epsilon_{xc}(n)n] \Big|_{n=n_c(\mathbf{r}z)}, \quad (50)$$

where  $\epsilon_{xc}$  is the local XC energy density. To solve Eq. (45) the memory term can be neglected to yield

$$\bar{u}_{c,xc}^{\text{ALDA}}(\mathbf{r}z) = \frac{d}{dn} [\epsilon_{xc}(n)n] \Big|_{n=n_c(\mathbf{r}z)}. \quad (51)$$

Further differentiation leads to the kernel formula:

$$f_{xc}^{\text{ALDA}}(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \frac{d^2}{dn^2} [\epsilon_{xc}(n)n] \Big|_{n=n(\mathbf{r}t)}. \quad (52)$$

The singularity of the XC kernel does not contribute to the integral term of Eq. (45) because the end point is not included, or in other words, the end point is approached in a limiting procedure. Hence the above equation satisfies Eq. (45), and thus it is the solution of it. The singularity of the XC kernel arises from the definition of the XC potential, which implies that at equal times the XC kernel must cancel the singularity of the Hartree kernel. However, the ALDA XC kernel does

not cancel the singularity of the Hartree kernel due to the self-interaction error.

Another application is the TDOPM. The exchange functional form remains the same as the one proposed by van Leeuwen [25]:

$$\mathcal{A}_x[n_c] = \int_{z_i}^{z_f} dz \langle \Phi_c[n_c](z) | \hat{W} | \Phi_c[n_c](z) \rangle - \mathcal{A}_H[n_c]. \quad (53)$$

To derive the TDOPM one has to assume that (for example, see [3])

$$\frac{\delta \mathcal{A}_{\tilde{v}_c}}{\delta n(\mathbf{r}z)} = \frac{\delta \mathcal{A}_{s, \tilde{v}_{c,s}}}{\delta n(\mathbf{r}z)}. \quad (54)$$

If we set  $\mathcal{A}_x = \mathcal{A}_x$  and expand  $\mathcal{A}_{\tilde{v}_c}$  using Eq. (42), we find that the memory term in Eq. (45) can be discarded. Hence we can write

$$u_x(\mathbf{r}t) = \frac{\delta \mathcal{A}_x}{\delta n(\mathbf{r}t)}. \quad (55)$$

The right-hand side of the above equation can be calculated using the chain rule. If the result is multiplied by  $\chi_s$  and then integrated, the final result coincides with that of Ullrich *et al.* [29].

Ground-state DFT is also accessible with this theory. We can introduce a slowly varying density  $n_c^T(\mathbf{r}z) = n_c(\mathbf{r}z/T)$ , where  $T \rightarrow \infty$ . One can use the adiabatic theorem to show that

$$\lim_{T \rightarrow \infty} \mathcal{A}_{xc}[n_c^T] = \lim_{T \rightarrow \infty} \int_{z_i}^{z_f} dz E_{xc}[n_c^T(\cdot, z)], \quad (56)$$

where  $E_{xc}$  is the XC energy functional of DFT. The above equation is local in time. As in the previous case, the solution of Eq. (45) has to be of the form

$$\lim_{T \rightarrow \infty} u_{xc}[n^T](\mathbf{r}t) = \lim_{T \rightarrow \infty} \left. \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right|_{n=n^T(\mathbf{r}t)}, \quad (57)$$

where  $n^T = \tilde{n}_c^T$ .

#### IV. CONCLUSIONS

To summarize, we examined the RG action functional and the solution of the causality paradox by Vignale [26] from the point of view of unitary evolution. We extended this solution to the Keldysh space, and under the strict causality assumption, we found a variational equation for the XC potential that involves an XC memory term. The solution of this variational equation is a series in terms of functional derivatives of the XC action functional in the Keldysh space. We showed that it is possible to derive the ALDA XC and TDOPM exchange potentials from the present theory and that ground states are also accessible using the adiabatic theorem.

#### ACKNOWLEDGMENTS

The author thankfully acknowledges valuable discussion with Adam Wasserman, Daniel Jensen, and Daniel Whitenack.

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## Fragment-Based Time-Dependent Density Functional Theory

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(Received 25 March 2013; published 9 July 2013)

Using the Runge-Gross theorem that establishes the foundation of time-dependent density functional theory, we prove that for a given electronic Hamiltonian, choice of initial state, and choice of fragmentation, there is a unique single-particle potential (dubbed time-dependent partition potential) which, when added to each of the preselected fragment potentials, forces the fragment densities to evolve in such a way that their sum equals the exact molecular density at all times. This uniqueness theorem suggests new ways of computing the time-dependent properties of electronic systems via fragment-time-dependent density functional theory calculations. We derive a formally exact relationship between the partition potential and the total density, and illustrate our approach on a simple model system for binary fragmentation in a laser field.

DOI: [10.1103/PhysRevLett.111.023001](https://doi.org/10.1103/PhysRevLett.111.023001)

PACS numbers: 31.15.E-, 71.15.Mb

Time-dependent density functional theory (TDDFT) [1,2] allows one to predict, in principle, the evolution of the nonrelativistic density  $n(\mathbf{r}t)$  of a system of interacting electrons subject to a time-dependent external potential  $v(\mathbf{r}t)$ . Given an initial wave function, the time-dependent electron density determines the external potential up to a time-dependent constant (Runge-Gross theorem [1]) and the density may be found by solving the time-dependent Kohn-Sham (TDKS) equations. These equations make it possible to perform practical calculations to propagate the electronic density and its related quantities such as linear-response functions. Because of its wide range of applications, TDDFT is expected to continue being a workhorse in the coming years for chemistry, physics, and materials engineering [3].

Although the computational cost of TDKS calculations is low compared to that of other many-body techniques, new ideas are needed to enable the study of larger systems with improved efficiency and accuracy. For the ground-state problem, “divide-and-conquer” fragmentation techniques have been developed [4] and applied successfully through the use of readily available parallel computers. Related strategies have also been developed recently for the time-dependent problem within TDDFT [5]. For example, Casida and Wesolowski [6] introduced a methodology to perform time-dependent calculations within frozen-density embedding theory. It has been shown that this method yields better results than “supermolecular” techniques to estimate excitation shifts of molecules due to complexation [7,8]. Other extensions include linear-response TDDFT for molecules in solvents [9] and TDDFT for interacting chromophores [10]. Additionally, time-dependent calculations within subsystem DFT have been reported, proving it useful for excitation energy transfer and chromophore absorption (see Ref. [11] and references therein). Neugebauer formulated this theory within

linear response in the frequency domain and showed that it yields results consistent with conventional TDDFT [12]. Another method available is fragment-molecular-orbital TDDFT [13], which combines wave-function methods for each individual fragment and calculates the excitations of each of them using linear-response TDDFT. This method shows agreement with supermolecular TDDFT approximations and also was used to predict the first excitation energy of a yellow protein accurately. For the case of dissipative dynamics, Zhou *et al.* [14] showed how the Runge-Gross theorem can be applied and Kohn-Sham equations developed for open systems, given an initial state, memory kernel, and system-bath correlation.

Among density-based ground-state fragmentation techniques, partition density functional theory (PDFT) [15] is a reformulation of density functional theory that allows one to find the solution to the KS equations without solving the total molecular problem directly. The idea is to partition the external potential into an arbitrary number of fragment potentials. The total energy of the isolated systems is minimized under the constraint that the fragment densities sum to the correct molecular density. The Lagrange multiplier associated with the constraint (i.e., the partition potential) can be found by inversion if the total density is known [16] or via the self-consistent procedure of Ref. [15] if it is not. Every fragment is subject to the same partition potential. In contrast with quantum mechanical embedding theories (except for the latest version of quantum embedding [17]) and with subsystem DFT, this potential is global and unique [18]. The set of fragment densities obtained for a given choice of external-potential partitioning is also unique. As Pavanello [19] recently suggested, this uniqueness feature of PDFT makes it a suitable candidate to simplify the formulation of subsystem DFT. This Letter reports on foundational work for such developments. We extend PDFT to the time-dependent regime and show how

the time-dependent external field can be partitioned. A new potential termed the time-dependent partition potential is introduced in the formalism in order to represent the exact time-dependent electronic density.

To extend PDFT to the time-dependent domain, we recall that there is no minimum principle from which the TDKS equations can be derived [20,21]. In view of this, we follow a deductive approach to define our TDKS equations. Our goal is to provide a fragment-based solution to the Liouville equation (we use atomic units throughout)

$$i \frac{\partial \hat{\Gamma}(t)}{\partial t} = [\hat{H}_v(t), \hat{\Gamma}(t)]. \quad (1)$$

If  $\hat{\Gamma}$  is a pure density matrix, then Eq. (1) is equivalent to the time-dependent Schrödinger equation. We suppose that the initial state  $\hat{\Gamma}(t_0)$  is given. In standard DFT notation, the Hamiltonian is given by  $\hat{H}_v(t) = \hat{T} + \hat{V}_{ee} + \int d^3\mathbf{r} v(\mathbf{r}t) \hat{n}(\mathbf{r})$ . It is convenient to express the external potential  $v(\mathbf{r}t)$  as the sum of the potential  $\tilde{v}(\mathbf{r})$  due to the  $M$  nuclei  $\tilde{v}(\mathbf{r}) = -\sum_{\alpha}^M Z_{\alpha}/|\mathbf{r} - \mathbf{R}_{\alpha}|$ , which is not explicitly time dependent, and an additional potential  $v_E(\mathbf{r}t)$  containing all of the explicit time dependence due to external fields:

$$v(\mathbf{r}t) = \tilde{v}(\mathbf{r}) + v_E(\mathbf{r}t). \quad (2)$$

Our task is to divide the quantum system into  $N_f$  fragments of interacting electrons. This is done by assigning an external potential  $v_{\alpha}(\mathbf{r}t)$ , Hamiltonian  $\hat{H}_{\alpha}(t)$ , and initial state  $\hat{\Gamma}_{\alpha}(t_0)$  to each fragment. Out of the infinitely many ways to choose the fragment potentials, there are at least two cases that are physically relevant. (i) Direct partitioning of the time-dependent external potential in analogy to ground-state PDFT:  $v(\mathbf{r}t) = \sum_{\alpha}^{N_f} v_{\alpha}(\mathbf{r}t)$ . For example, if  $N_f = M$ , there are cases of interest where we could define  $v_{\alpha}(\mathbf{r}t) = -Z_{\alpha}/|\mathbf{r} - \mathbf{R}_{\alpha}(t)|$ . In such cases, the electronic density of fragment  $\alpha$  would be an output variable of the dynamics of nucleus  $\alpha$ . (ii) If the system is driven by an electric field or other global potential [22], we find it more convenient to fragment only the static electron-nuclei interaction potential

$$\tilde{v}(\mathbf{r}) = \sum_{\alpha} \tilde{v}_{\alpha}(\mathbf{r}) \quad (3)$$

because partitioning of the external perturbation is avoided. We define the time-dependent fragment potential  $v_{\alpha}(\mathbf{r}t)$  by adding the total time-dependent potential  $v_E(\mathbf{r}t)$  to each of the  $\tilde{v}_{\alpha}(\mathbf{r})$ 's:

$$v_{\alpha}(\mathbf{r}t) = \tilde{v}_{\alpha}(\mathbf{r}) + v_E(\mathbf{r}t). \quad (4)$$

Now, define the many-electron fragment- $\alpha$  Hamiltonian as

$$\hat{H}_{\alpha}(t) = \hat{T} + \hat{V}_{ee} + \int d^3\mathbf{r} [v_{\alpha}(\mathbf{r}t) + v_p(\mathbf{r}t)] \hat{n}(\mathbf{r}). \quad (5)$$

The evolution of the state of this particular fragment is governed by the Liouville equation

$$i \frac{\partial}{\partial t} \hat{\Gamma}_{\alpha}(t) = [\hat{H}_{\alpha}(t), \hat{\Gamma}_{\alpha}(t)]. \quad (6)$$

The time-dependent electronic density of fragment  $\alpha$  is given by  $n_{\alpha}(\mathbf{r}t) = \text{Tr}[\hat{\Gamma}_{\alpha}(t) \hat{n}(\mathbf{r})]$ , and the time-dependent partition potential  $v_p(\mathbf{r}t)$  of Eq. (5) is defined by requiring that the sum of fragment densities reproduces the total molecular density at all times:

$$\sum_{\alpha=1}^{N_f} n_{\alpha}(\mathbf{r}t) = n(\mathbf{r}t). \quad (7)$$

Just like traditional TDDFT is based on a one-to-one mapping between the Kohn-Sham potential  $v_s(\mathbf{r}t)$  and the electronic density  $n(\mathbf{r}t)$ , we now prove an analogous one-to-one mapping between  $n(\mathbf{r}t)$  and  $v_p(\mathbf{r}t)$ . The latter is therefore sharply defined by Eqs. (1)–(7).

*Theorem 1.*—For a given set of initial states  $\{\hat{\Gamma}_{\alpha}(t_0)\}$ , the map between the density and the partition potential is invertible up to a time-dependent constant in the potential.

*Proof.*—The proof uses the Runge-Gross theorem [1] and is analogous to it. Suppose there is a minimum integer  $k \geq 0$  such that

$$\frac{\partial^m}{\partial t^m} [v'_p(\mathbf{r}t) - v_p(\mathbf{r}t)]|_{t=t_0} \begin{cases} = \text{const} & m < k \\ \neq \text{const} & m = k. \end{cases} \quad (8)$$

Also assume that  $v_p$  and  $v'_p$  correspondingly have the associated densities  $\{n_{\alpha}\}$  and  $\{n'_{\alpha}\}$ . Suppose  $\hat{H}_{\alpha}(t)$  and  $\hat{H}'_{\alpha}(t)$  are the Hamiltonians of fragment  $\alpha$  that correspond to  $v_p$  and  $v'_p$ , respectively. The key for the proof is the continuity equation

$$\frac{\partial n_{\alpha}(\mathbf{r}t)}{\partial t} = -\nabla \cdot \mathbf{j}_{\alpha}(\mathbf{r}t) \quad (9)$$

and the Liouville equation for the fragment current densities

$$i \frac{\partial \mathbf{j}_{\alpha}(\mathbf{r}t)}{\partial t} = \text{Tr}\{\hat{\Gamma}_{\alpha}(t) [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}_{\alpha}(t)]\}. \quad (10)$$

Define

$$w_{p,k}(\mathbf{r}) = \frac{\partial^k}{\partial t^k} [v'_p(\mathbf{r}t) - v_p(\mathbf{r}t)]|_{t=t_0}. \quad (11)$$

In virtue of the Runge-Gross theorem [1] and its generalization to ensembles [23], it is easy to show that

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [n'_{\alpha}(\mathbf{r}t) - n_{\alpha}(\mathbf{r}t)]|_{t=t_0} = -\nabla \cdot [n_{\alpha}(\mathbf{r}t_0) \nabla w_{p,k}(\mathbf{r})]. \quad (12)$$

Summing over all fragments gives

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [n'(\mathbf{r}t) - n(\mathbf{r}t)]|_{t=t_0} = -\nabla \cdot [n(\mathbf{r}t_0) \nabla w_{p,k}(\mathbf{r})]. \quad (13)$$

Now, we show that the right-hand side of this equation cannot be zero. Assume  $\nabla \cdot [n(\mathbf{r}t_0) \nabla w_{p,k}(\mathbf{r})] = 0$  and  $\nabla w_{p,k} \neq 0$ . Now, invoke Green's identity to find



$$\begin{aligned}
& \int d^3\mathbf{r} w_{p,k}(\mathbf{r}) \nabla[n(\mathbf{r}t_0) \nabla w_{p,k}(\mathbf{r})] \\
&= - \int d^3\mathbf{r} n(\mathbf{r}t_0) [\nabla w_{p,k}(\mathbf{r})]^2 \\
&+ \frac{1}{2} \oint d\mathbf{S} \cdot n(\mathbf{r}t_0) \nabla(w_{p,k})^2(\mathbf{r}) = 0. \quad (14)
\end{aligned}$$

If the total electronic density falls off enough to make the surface term negligible, then  $\nabla w_{p,k}(\mathbf{r}) = 0$ , which is a contradiction. Therefore, the right-hand side of Eq. (13) cannot be zero. This leads to the conclusion that if  $v'_p$  and  $v_p$  differ by more than a time-dependent constant, then they cannot yield the same density in time.

The above theorem shows that if  $\{\hat{\Gamma}_\alpha(t_0)\}$  and  $v_p(\mathbf{r}t)$  are given, then one obtains a unique set of fragment densities  $\{n_\alpha(\mathbf{r}t)\}$  and total density  $n(\mathbf{r}t)$ . The fragment density  $n_\alpha(\mathbf{r}t)$  can be assumed to be noninteracting  $v$  representable in time. Then, we can associate a TDKS potential  $v_{s,\alpha}(\mathbf{r}t)$  and initial state  $\hat{\Gamma}_{s,\alpha}(t_0)$  to describe the evolution of  $n_\alpha(\mathbf{r}t)$  by means of the TDKS equations

$$i \frac{\partial}{\partial t} \varphi_{i\alpha}(\mathbf{r}t) = \left[ -\frac{1}{2} \nabla^2 + v_{s,\alpha}(\mathbf{r}t) \right] \varphi_{i\alpha}(\mathbf{r}t), \quad (15)$$

where

$$n(\mathbf{r}t) = \sum_\alpha n_\alpha(\mathbf{r}t) = \sum_{i\alpha} f_{i\alpha} |\varphi_{i\alpha}(\mathbf{r}t)|^2. \quad (16)$$

The fragments are allowed to have noninteger average electron numbers that are set by the initial state [18]. Since the Hamiltonians are particle conserving, the occupation numbers  $f_{i\alpha}$  remain fixed during the propagation.

In analogy with PDFT, we define the exchange-correlation (xc) potential by means of

$$\begin{aligned}
& v_{xc,\alpha}[n_\alpha, \hat{\Gamma}_\alpha(t_0), \hat{\Gamma}_{s,\alpha}(t_0)](\mathbf{r}t) \\
&= v_{s,\alpha}[n_\alpha, \hat{\Gamma}_{s,\alpha}(t_0)](\mathbf{r}t) - v_\alpha[n_\alpha, \hat{\Gamma}_\alpha(t_0)](\mathbf{r}t) \\
&- v_H[n_\alpha](\mathbf{r}t) - v_p[n, \{\hat{\Gamma}_\alpha(t_0)\}](\mathbf{r}t), \quad (17)
\end{aligned}$$

where  $v_H(\mathbf{r}t)$  is the time-dependent Hartree potential. By comparing the fragment continuity equations for the interacting and noninteracting (Kohn-Sham) systems, we find that the above definition of the xc potential is consistent with (for example, see Ref. [24])

$$\begin{aligned}
& \nabla \cdot \left\{ n_\alpha(\mathbf{r}t) \nabla \left[ \int d^3\mathbf{r}' \frac{n_\alpha(\mathbf{r}'t)}{|\mathbf{r}' - \mathbf{r}|} + v_{xc,\alpha}(\mathbf{r}t) \right] \right\} \\
&= \nabla \cdot [\mathbf{Q}_\alpha(\mathbf{r}t) - \mathbf{Q}_{s,\alpha}(\mathbf{r}t)], \quad (18)
\end{aligned}$$

where the right-hand sides are hydrodynamical terms given by  $\mathbf{Q}_{s,\alpha}(\mathbf{r}t) = -i\text{Tr}\{\Gamma_{s,\alpha}(t)[\hat{\mathbf{j}}(\mathbf{r}), \hat{T}]\}$  and  $\mathbf{Q}_\alpha(\mathbf{r}t) = -i\text{Tr}\{\Gamma_\alpha(t)[\hat{\mathbf{j}}(\mathbf{r}), \hat{T} + \hat{V}_{ee}]\}$ . This indicates that the conventional xc potential of TDDFT and family of approximations can be used for the fragments' TDKS equations, a direct consequence of van Leeuwen's theorem [25].

Furthermore, from the continuity equations for the total current and fragment current densities, and from Eq. (18), we find a formally exact relationship between the time-dependent partition potential and the total density:

$$\begin{aligned}
\nabla \cdot [n(\mathbf{r}t) \nabla v_p(\mathbf{r}t)] &= \frac{\partial^2 n(\mathbf{r}t)}{\partial t^2} + \sum_\alpha (\nabla \cdot \mathbf{Q}_{s,\alpha}[v_p](\mathbf{r}t) \\
&- \nabla \cdot \{n_\alpha[v_p](\mathbf{r}t) \nabla \bar{v}_{s,\alpha}[v_p](\mathbf{r}t)\}), \quad (19)
\end{aligned}$$

where  $\bar{v}_{s,\alpha}[v_p] = v_{Hxc,\alpha}[v_p] + v_\alpha$ . In principle, evaluation of Eq. (19) at  $t = t_0$  yields a Sturm-Liouville linear differential equation where  $v_p(\mathbf{r}, t = t_0)$  is the unknown variable. If we assume that the density is Taylor expandable at  $t = t_0$ , then it is easy to show that consecutive differentiation of Eq. (19) and evaluation at  $t = t_0$  leads to a family of equations from which the Taylor coefficients of  $v_p(\mathbf{r}t)$  can be constructed in increasing order. This suggests that a given density is  $v_p$ -representable as long as the conditions of the Sturm-Liouville theory are met.

To illustrate our fragmentation approach, consider the simplest nontrivial model system consisting of a one-dimensional "electron," two fragments, and an oscillating electric field of fixed frequency. For the frozen part of the external potential, we choose a sum of soft-Coulomb potentials of equal strength  $V_0$ , a distance  $l$  apart:

$$\bar{v}(x) = V_0 \left( \frac{1}{\sqrt{(x+l/2)^2 + a}} + \frac{1}{\sqrt{(x-l/2)^2 + a}} \right). \quad (20)$$

For the laser field, we choose  $v_E(x, t) = xE \sin(\omega t)$ , with  $E = 0.1$  and  $\omega = 0.3$ .

We partition the system by defining  $v_1(x, t) = V_0/\sqrt{(x+l/2)^2 + a} + v_E(x, t)$  and  $v_2(x, t) = V_0/\sqrt{(x-l/2)^2 + a} + v_E(x, t)$ . The time-dependent fragment equations are (for  $\alpha = 1, 2$ )

$$i \frac{\partial}{\partial t} \varphi_\alpha(xt) = \left( -\frac{1}{2} \frac{d^2}{dx^2} + v_\alpha(xt) + v_p(xt) \right) \varphi_\alpha(xt). \quad (21)$$

The initial states of the fragments are obtained by solving the ground-state PDFT equations as prescribed in Ref. [22]. This procedure generates the initial fragment Kohn-Sham orbitals needed to solve Eq. (21). The distance between the wells was chosen to allow for a significant overlap between the initial fragments' densities.

Even though the principle to construct  $v_p(\mathbf{r}t)$  is simple, note that Eq. (19) can also be written as  $v_p = \mathcal{F}v_p$ , where the operator  $\mathcal{F}$  computes the right-hand side of the equation, solves the differential equation, and finally outputs  $v_p(\mathbf{r}t)$ . One could employ this formula recursively, i.e.,  $v_p^{k+1} = \mathcal{F}v_p^k$ . We observed in our example that the term  $\mathbf{Q}_{s,\alpha}$  becomes noisy even after short times if the simulation box is discretized with large spatial steps. This noise is received by the partition potential during the propagation,

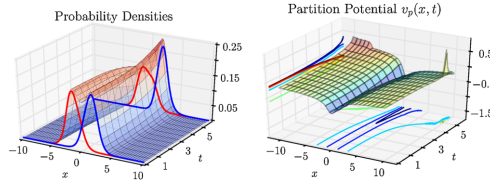


FIG. 1 (color online). Left: Fragment densities at times  $t = 0$  and  $t \approx T/4$  along with the total molecular density. Right: Exact partition potential  $v_p(x, t)$ . Parameters:  $l = 4$ ,  $a = 1$ ,  $V_0 = -1$ ,  $E = 0.1$ , and  $\omega = 0.3$ . A box of length 20 with 401 points was used.

and then it is received again by  $\mathbf{Q}_{s,\alpha}$ . This feedback process turns the algorithm unstable. The problem is reminiscent to what happens in traditional TDDFT when one wants to find the exchange-correlation potential corresponding to a given density, even for only two electrons [26]. To solve this problem in TDDFT, Ref. [27] recently suggested an algorithm to control the feedback. They obtained encouraging results for a periodic system, but the methodology has not been tested for nonperiodic systems.

Instead, we found the exact time-dependent partition potential by using the following optimization procedure: The density and current density of the total system are found at each time step using the Crank-Nicolson propagator. (Other propagation methods may also be used.) A guess is made for the partition potential at the next unknown time, and the fragment wave functions are propagated forward in time using this guess. (For small time steps, the value of the partition potential at the previous time step works well.) The fragment densities  $\{n_\alpha\}$ ,  $\{j_\alpha\}$  are found using these fragment wave functions and added together to form an approximation to the total densities  $(n, j)$ . The errors  $n_{\text{err}} = n - n_{\text{exact}}$  and  $j_{\text{err}} = j - j_{\text{exact}}$  are computed and the residual  $\text{norm}(n_{\text{err}}/n_{\text{exact}}) + \text{norm}(j_{\text{err}}/j_{\text{exact}})$  is used in the optimizer of Ref. [28],

with the  $L^2$  norm. The division by  $n_{\text{exact}}$  and  $j_{\text{exact}}$  weights the error in the asymptotic regions to help increase the convergence rate, similar to the weighting used in Ref. [29].

The right panel of Fig. 1 displays the resulting partition potential. The left panel shows the corresponding fragment densities at the initial time and at 1/4 of a period. The importance of memory effects [30] is evident from Fig. 2, where the dash-dotted lines labeled “Instantaneous” show the fragment densities obtained by solving the ground-state PDFDFT equations for the instantaneous  $v(\mathbf{r}t)$  at 1/4 of a period. Clearly, the correct partition potential is needed. Only when the electric field strength is reduced by a factor of  $10^3$  (keeping all other parameters fixed) does the instantaneous partition potential produce a molecular density that is visibly indistinguishable from the exact molecular density at time  $t \approx T/4$ . Interestingly, the approximation  $v_p(\mathbf{r}t) \approx v_p(\mathbf{r}t_0)$  (labeled “Frozen” in Fig. 2) works qualitatively well for short times, certainly much better than the instantaneous approximation. The inset on the right panel of Fig. 2 shows how the frozen- $v_p$  approximation reproduces the correct dipole for short times. Charge transfer is interpreted in our theory as spreading of the donor density, where a portion of it displaces toward the acceptor. This requires introducing an imaginary boundary around the donor and acceptor fragments. In our example, if we imagine a line dividing the left and right fragments, we note that after one fourth of a period, some charge has been transferred from left to right.

In practice, successful application of our approach to large systems will ultimately rely on the quality of approximations to the time-dependent partition potential. The frozen approximation might be useful for short times. Furthermore, for problems whose physics is best described by invoking fragments (such as charge-transfer excitations), we believe that physically meaningful approximations of  $v_p(\mathbf{r}t)$  will be simpler to construct than approximations of the highly nonlocal exchange-correlation potential and

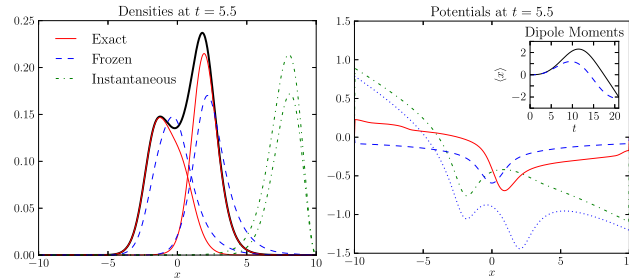


FIG. 2 (color online). Left: Fragment densities at time  $t \approx T/4$  along with the total molecular density (thick solid line) calculated: with the exact  $v_p(xt)$  (thin solid line), frozen  $v_p(xt) = v_p(xt_0)$  (dashed line), and instantaneous  $v_p(xt) = v_p^{\text{PDFDFT}}[n(xt)]$  (dash-dotted line). Right: Corresponding partition potentials and external potential (dotted line) at  $t \approx T/4$ . Parameters:  $l = 4$ ,  $a = 1$ ,  $V_0 = -1$ ,  $E = 0.1$ , and  $\omega = 0.3$ . The inset compares the dipole moment obtained from the exact (solid line) and frozen approximation to  $v_p(xt)$  (dotted line).



kernel of TDDFT. Work along these lines, as well as on the linear-response formalism, is ongoing.

We acknowledge discussions with Jonathan Nafziger. This work was supported by the National Science Foundation CAREER program under Grant No. CHE-1149968.

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## Current density partitioning in time-dependent current density functional theory

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(Received 7 December 2013; accepted 14 February 2014; published online 19 March 2014)

We adapt time-dependent current density functional theory to allow for a fragment-based solution of the many-electron problem of molecules in the presence of time-dependent electric and magnetic fields. Regarding a molecule as a set of non-interacting subsystems that individually evolve under the influence of an auxiliary external electromagnetic vector-scalar potential pair, the *partition* 4-potential, we show that there are one-to-one mappings between this auxiliary potential, a sharply-defined set of fragment current densities, and the total current density of the system. The partition electromagnetic (EM) 4-potential is expressed in terms of the real EM 4-potential of the system and a *gluing* EM 4-potential that accounts for exchange-correlation effects and mutual interaction forces between fragments that are required to yield the correct electron dynamics. We prove the zero-force theorem for the fragmented system, establish a variational formulation in terms of action functionals, and provide a simple illustration for a charged particle in a ring. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867003>]

### I. INTRODUCTION

Time-dependent current density functional theory (TDCDFT)<sup>1–3</sup> provides a formally exact method to calculate the electronic properties of molecules, clusters, and solids in time-dependent electric and magnetic fields. By using the current density as the main variable, TDCDFT is amenable to non-adiabatic local approximations to the exchange-correlation (XC) potential, a feature that is difficult to achieve using the time-dependent density as the main variable.<sup>3–5</sup>

TDCDFT relies on a one-to-one mapping between time-dependent vector potentials and time-dependent current densities, up to a gauge transformation in the potentials. This mapping was first discussed by Xu and Rajagopal,<sup>6</sup> Ghosh and Dhara,<sup>1</sup> and then further explored by Vignale.<sup>2</sup> An extension of TDCDFT to open quantum systems was more recently developed by Yuen-Zhou, Rodriguez-Rosario, and Aspuru-Guzik.<sup>7</sup>

The first rigorous approximation to the XC vector potential was developed by Vignale and Kohn<sup>8</sup> (VK) under the condition that the density and the frequency-dependent perturbation applied to the system are slowly varying in space. Further developments to the XC vector potential benefit from approximations to the stress tensor,<sup>9,10</sup> which can be found by means of quantum continuum mechanics.<sup>11,12</sup> TDCDFT has been useful in the linear-response regime to calculate the optical spectra of semiconductors,<sup>13–17</sup> atomic and molecular excitation energies,<sup>18</sup> polarizabilities of  $\pi$ -conjugated molecular chains,<sup>14</sup> electronic properties of quantum dots,<sup>19</sup> and nanoscale electronic transport.<sup>20</sup>

It is often the case that the magnetic properties of a complex molecule or material can be best described qualitatively

by considering that it is composed of fragments or subdomains, each of which can sustain well-localized current densities. The existing framework of TDCDFT, however, employs the current density of the entire system (or paramagnetic current density in the case of current-DFT<sup>21</sup>), without exploiting the fragmented nature of the problem. Something analogous is true for DFT, which targets the full ground-state density of the system even when this density can be seen as composed of smaller fragment densities. How to best define those fragments in such a way that the sum of their properties *exactly* reproduces the properties of the full system is a challenging problem. The partition theory (PT) proposed in Ref. 22 achieves this for the ground state density. When merged with Kohn-Sham DFT,<sup>23</sup> PT leads to partition density functional theory (PDFT), a method to solve the Kohn-Sham equations via self-consistent calculations on isolated fragments. PDFT has been adapted to allow for external electric and magnetic fields,<sup>24</sup> and has also been extended to the time-dependent regime.<sup>25</sup>

By analogy with PDFT and its time-dependent extension, in this paper we adapt TDCDFT to allow for the partitioning of a system into isolated subsystems, preserving the correct *current density*. The resulting framework can be used to make quantitative something that is qualitatively obvious: The total current density is “made of” of fragment current densities. The method is amenable to parallel implementations to simulate large systems, and it is also useful for finding new conditions that the XC potentials of TDCDFT should satisfy.

First, the necessary background on TDCDFT is provided in Sec. II. We then show in Sec. III that there exists an electromagnetic 4-potential that can be used to represent the total current of the system. Section IV discusses formal aspects of the theory and introduces new potentials that do the job of gluing the fragments in just the right way to achieve the

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additivity we seek for the currents. A zero-force theorem satisfied by the fragments is also derived in the same section. A variational formulation of our theory is then derived in Sec. V by using the Keldysh space technique of van Leeuwen,<sup>26</sup> and we end in Sec. VI by providing a simple illustration for a charged particle in a ring.

## II. BACKGROUND

In preparation for the new developments of Sec. III, we first review the required formalism to describe the non-relativistic electron dynamics of molecules with fixed nuclei when the electrons interact with classical electromagnetic fields. We use second-quantized notation and atomic units throughout.

The Hamiltonian representing the molecule has the form

$$\hat{H}(t) = \hat{T}_A(t) + \hat{W} + \int d^3\mathbf{r} \hat{n}(\mathbf{r})[v(\mathbf{r}) - \phi(\mathbf{r})], \quad (1)$$

where  $\mathbf{A}$  and  $\phi$  are the vector and scalar potentials, respectively. We refer to the pair  $\mathbf{A}, \phi$  as the 4-potential. The operator  $\hat{W}$  represents the electron-electron interaction, and  $\hat{T}_A(t)$  is defined as

$$\hat{T}_A(t) = \frac{1}{2} \int d^3\mathbf{r} \hat{\psi}^\dagger(\mathbf{r})(-\mathbf{i}\nabla + \mathbf{A}(\mathbf{r}))^2 \hat{\psi}(\mathbf{r}). \quad (2)$$

Define the paramagnetic current operator

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i}(\hat{\psi}^\dagger(\mathbf{r})\nabla\hat{\psi}(\mathbf{r}) - \nabla\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})), \quad (3)$$

and the total current operator

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{n}(\mathbf{r})\mathbf{A}(\mathbf{r}). \quad (4)$$

Here we can regard the Hamiltonian as a functional of  $\mathbf{A}, \phi$ . These potentials are related to the electromagnetic field  $\mathbf{E}, \mathbf{B}$  by the following equations:  $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) - \partial_t\mathbf{A}(\mathbf{r})$  and  $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ .

Let us define the average of an operator  $\hat{O}(\mathbf{r})$  as:  $O(\mathbf{r}) = \text{Tr}\{\hat{\Gamma}(t)\hat{O}(\mathbf{r})\}$ , where  $\hat{\Gamma}$  is the density matrix of the

system, which is the solution of the Liouville equation

$$i\partial_t\hat{\Gamma}(t) = [\hat{H}(t), \hat{\Gamma}(t)]. \quad (5)$$

The density matrix  $\hat{\Gamma}(t)$  in general represents a mixed state in the Fermionic Liouville space. This ensures that states with any number of particles, including positive real numbers, are considered in our formalism. The initial state is of the form:  $\hat{\Gamma}(t_0) = \sum_{M,k} w_{M,k} |\psi_{M,k}\rangle\langle\psi_{M,k}|$ , where  $\{M, k\}$  refers to the  $k$ th level of the system with  $M$  electrons.

The density of the system satisfies the continuity equation:  $\partial_t n(\mathbf{r}) = -\nabla \cdot \mathbf{j}(\mathbf{r})$ , which is valid for states with a real number of particles. The current density can be shown to satisfy the hydrodynamical-like equation<sup>2</sup>

$$\partial_t \mathbf{j}(\mathbf{r}) = -\mathbf{q}(\mathbf{r}) - n(\mathbf{r})[\mathbf{E}(\mathbf{r}) + \nabla v(\mathbf{r})] - \mathbf{j}(\mathbf{r}) \times \mathbf{B}(\mathbf{r}), \quad (6)$$

with  $\mathbf{q}(\mathbf{r})$  defined as:  $\mathbf{q}(\mathbf{r}) = -i\text{Tr}\{\hat{\Gamma}(t)[\hat{T} + \hat{W}, \hat{\mathbf{j}}_p(\mathbf{r})]\}$ . This quantity can also be expressed as the gradient of the stress tensor, which causes the non-classical behavior of the current.

Ghosh and Dhara<sup>1</sup> proved that there is a one-to-one mapping, up to a gauge transformation, between 4-potentials and current-densities. Their proof is analogous to that of Runge and Gross.<sup>4</sup> First assume that the 4-potential  $\mathbf{A}, \phi$  can be written as a power series around the initial time  $t = t_0$ . Suppose that there is another analytic 4-potential  $\mathbf{A}', \phi'$ , which differs from  $\mathbf{A}, \phi$  by more than a gauge transformation and yields the current density  $\mathbf{j}'(\mathbf{r})$ . Additionally, the initial conditions demand that  $\mathbf{A}'(\mathbf{r}t_0) = \mathbf{A}(\mathbf{r}t_0)$ . The proof requires that the power series exists. However, we just need to find the lowest numbers  $l$  and  $k$  such that

$$\partial_t^n (\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r}))|_{t=t_0} \neq \text{Const}, \quad n \geq l, \quad (7)$$

$$\partial_t^n (\phi(\mathbf{r}) - \phi'(\mathbf{r}))|_{t=t_0} \neq \text{Const}, \quad n \geq k. \quad (8)$$

Ghosh and Dhara<sup>1</sup> showed that if the above holds then

$$i^n \partial_t^n [\mathbf{j}(\mathbf{r}) - \mathbf{j}'(\mathbf{r})]|_{t=t_0} = \begin{cases} n(\mathbf{r}t_0)\nabla[i^k \partial_t^k (\phi(\mathbf{r}) - \phi'(\mathbf{r}))|_{t=t_0}], & n = k+1, l > k+1 \\ n(\mathbf{r}t_0)i^l \partial_t^l (\mathbf{A}(\mathbf{r}) - \mathbf{A}'(\mathbf{r}))|_{t=t_0}, & n = l, l < k+1 \\ -n(\mathbf{r}t_0)i^{k+1} \partial_t^k (\mathbf{E}(\mathbf{r}) - \mathbf{E}'(\mathbf{r}))|_{t=t_0}, & n = k+1, l = k+1. \end{cases} \quad (9)$$

It follows from Eq. (9) that if the power series of the 4-potentials differs by more than a TD constant, then they cannot yield the same current density for  $t > t_0$ . This result provides solid ground for using the current density as the fundamental variable in TDCDFT. It is also valid for extended systems because it only requires that the current-densities of the unprimed and primed systems differ locally. This is a useful feature for applications in solid state theory and periodic systems in general. However, the electron-

electron interaction makes the solution of Eq. (6) very difficult. Vignale<sup>27</sup> found that the van Leeuwen theorem<sup>28</sup> can be extended to the case of TDCDFT. The theorem states that the current density of a system described by  $\mathbf{A}, \phi$  with particle interaction  $\hat{W}$  and initial state  $\hat{\Gamma}(t_0)$  can be reproduced exactly by another system under the influence of  $\mathbf{A}', \phi'$ , where the particle interaction is described by another operator  $\hat{W}'$  and the initial state is  $\hat{\Gamma}'(t_0)$ . Again, the 4-potential must vary from the original 4-potential by more than a gauge

transformation. The van Leeuwen theorem also requires the initial state of the alternative system to have the correct initial current.

The van Leeuwen theorem is particularly useful when applied to the non-interacting case, i.e., setting  $\hat{W}' = 0$ . For the sake of simplicity, it is convenient to choose a gauge in which the scalar field is set to zero.

Denoting by  $\mathbf{A}_s$  the Kohn-Sham 4-potential that yields the current density  $\mathbf{j}$ , then its evolution is given by

$$\partial_t \mathbf{j}(\mathbf{r}) = -\mathbf{q}_s(\mathbf{r}) - n(\mathbf{r}) \left[ -\frac{\partial \mathbf{A}_s}{\partial t}(\mathbf{r}) + \nabla v(\mathbf{r}) \right] - \mathbf{j}(\mathbf{r}) \times \nabla \times \mathbf{A}_s(\mathbf{r}), \quad (10)$$

where  $\mathbf{q}(\mathbf{r}) = -i\text{Tr}[\hat{\Gamma}(t)[\hat{T}, \hat{\mathbf{j}}_p(\mathbf{r})]]$ . Now decompose  $\mathbf{A}_s$  in the usual Kohn-Sham manner:  $\mathbf{A}_s = \mathbf{A} + \mathbf{A}_H + \mathbf{A}_{XC}$ , where

$$\partial_t \mathbf{A}_H(\mathbf{r}) = -\nabla \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (11)$$

Subtracting Eqs. (6) from (10) and employing the above definition, we find that

$$n(\mathbf{r})\partial_t \mathbf{A}_{HXC}(\mathbf{r}) - \mathbf{j}(\mathbf{r}) \times \nabla \times \mathbf{A}_{HXC}(\mathbf{r}) = \mathbf{q}_s(\mathbf{r}) - \mathbf{q}(\mathbf{r}), \quad (12)$$

where  $\mathbf{A}_{HXC} = \mathbf{A}_{XC} + \mathbf{A}_H$ . The solution of Eq. (12) determines the XC vector potential as a functional of the current density (note that the right-hand-side terms are functionals of  $\mathbf{j}$ ). If the HXC vector potential is expanded as a Taylor series then Eq. (12) can be used recursively to calculate the expansion coefficients.<sup>27</sup>

### III. PARTITIONING THE CURRENT DENSITY

As in PDFT,<sup>23</sup> we fragment the external potential  $v(\mathbf{r})$  due to the nuclei into  $N_f$  fragment potentials  $\{v_\alpha(\mathbf{r})\}$  such that  $v(\mathbf{r}) = \sum_\alpha v_\alpha(\mathbf{r})$ . Our task is to associate a fragment current density  $\mathbf{j}_\alpha(\mathbf{r})$  to each of the  $v_\alpha(\mathbf{r})$  in such a way that

$$\sum_\alpha \mathbf{j}_\alpha(\mathbf{r}) = \mathbf{j}(\mathbf{r}), \quad (13)$$

where  $\mathbf{j}(\mathbf{r})$  is the correct current density of the total molecular system.

Considering that: (i) a fragment that is infinitely far from the molecule is not affected by the other fragments, (ii) the current density around such isolated fragment is determined only by its interaction with the external 4-potential, and (iii) the current density remains localized around the fragment as long as the system is not ionized by the 4-potential; we propose to emulate these properties for *finite* separations between fragments by defining the fragment current densities  $\mathbf{j}_\alpha(\mathbf{r})$  as

$$\mathbf{j}_\alpha(\mathbf{r}) = \text{Tr}[\hat{\Gamma}_\alpha(t)\hat{\mathbf{j}}(\mathbf{r})], \quad (14)$$

where the fragment density matrix  $\hat{\Gamma}_\alpha(t)$  satisfies the Liouville equation

$$i\partial_t \hat{\Gamma}_\alpha(t) = [\hat{H}_\alpha(t), \hat{\Gamma}_\alpha(t)], \quad (15)$$

and the  $\alpha$ -fragment Hamiltonian  $\hat{H}_\alpha$  is given by

$$\hat{H}_\alpha(t) = \hat{T} + \hat{W} + \int d^3\mathbf{r} \left( \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}_p(\mathbf{r}) + \hat{n}(\mathbf{r}) \left[ v_\alpha(\mathbf{r}) - \phi_p(\mathbf{r}) + \frac{1}{2} \mathbf{A}_p^2(\mathbf{r}) \right] \right). \quad (16)$$

Here,  $\mathbf{A}_p, \phi_p$  is the *partition* 4-potential whose purpose, in analogy to the partition potentials of static DFT<sup>22</sup> and TDDFT,<sup>23</sup> is to ensure satisfaction of Eq. (13).

The equation of motion for the  $\alpha$ -fragment current density satisfies

$$\partial_t \mathbf{j}_\alpha(\mathbf{r}) = -\mathbf{q}_\alpha(\mathbf{r}) - n_\alpha(\mathbf{r})[\mathbf{E}_p(\mathbf{r}) + \nabla v_\alpha(\mathbf{r})] - \mathbf{j}_\alpha(\mathbf{r}) \times \mathbf{B}_p(\mathbf{r}), \quad (17)$$

where

$$\mathbf{q}_\alpha(\mathbf{r}) = -i\text{Tr}[\hat{\Gamma}_\alpha(t)[\hat{T} + \hat{W}, \hat{\mathbf{j}}_p(\mathbf{r})]]. \quad (18)$$

(Note: the subindex “ $p$ ” for the paramagnetic current in Eqs. (16) and (18) should not be confused with the subindex “ $P$ ” labeling the partition fields). All quantities that appear in the definition of a fragment are similar to those that define a quantum system in the proof of Ghosh and Dhara.<sup>1</sup> The only difference is that the physical 4-potential has been replaced by the partition field. Therefore, each  $\mathbf{j}_\alpha$  uniquely determines the partition field up to a gauge transformation. Note also that the equations of motion for the current-densities can be added to yield

$$\partial_t \mathbf{j}(\mathbf{r}) = -\sum_\alpha [\mathbf{q}_\alpha(\mathbf{r}) + n_\alpha(\mathbf{r})\nabla v_\alpha(\mathbf{r})] - [n(\mathbf{r})\mathbf{E}_p(\mathbf{r}) + \mathbf{j}(\mathbf{r}) \times \mathbf{B}_p(\mathbf{r})]. \quad (19)$$

Again, we find that the present formulation is analogous to that of Ghosh and Dhara.<sup>1</sup> Hence, there is a 1-1 correspondence between  $\mathbf{j}$  and the partition electromagnetic (EM) field, up to a gauge transformation. The properties of this map are determined by those of the  $\mathbf{j}_\alpha \leftrightarrow \mathbf{A}_p, \phi_p$  maps.

It is also straightforward to show that the van Leeuwen theorem applies in this case: The current density of a fragmented molecule defined by  $\hat{W}, \mathbf{A}_p, \phi$  can be represented by an alternative system with  $\hat{W}', \mathbf{A}_p', \phi'$ . The initial state of the real system and the set of  $N_f$  fragment potentials are fixed, so the proof follows the same steps shown by Vignale<sup>27</sup> applied to the equation of motion for the current density.

### IV. EXTENDED OPERATORS AND THE PARTITION 4-POTENTIAL

The partitioned molecule can be thought of as a single object. One then says that the density matrix of a fragment belongs to the Liouville space  $\mathcal{L}$ , and that it operates on the Fermionic Fock space of the fragment. We define the space of the partitioned molecule as

$$\mathcal{L}_f = \underbrace{\mathcal{L} \otimes \mathcal{L} \otimes \cdots \otimes \mathcal{L}}_{N_f \text{ times}}. \quad (20)$$

The density matrix

$$\hat{\Gamma}_t(t) = \bigotimes_{\alpha=1}^{N_f} \hat{\Gamma}_\alpha(t) \quad (21)$$

represents the state of a partitioned molecule with  $N_f$  fragments and contains all the information required to calculate the total current density of the system. The Hamiltonian for such molecule is given by

$$\hat{H}_t(t) = \hat{H}_1(t) \oplus \hat{H}_2(t) \oplus \cdots \oplus \hat{H}_{N_f}(t), \quad (22)$$

where  $\hat{H}_\alpha(t)$  is the Hamiltonian of fragment  $\alpha$ . For example, for a system with two fragments the operation  $\hat{H}_t(t)\hat{\Gamma}_t(t)$  yields

$$\hat{H}_t(t)\hat{\Gamma}_t(t) = [\hat{H}_1(t)\hat{\Gamma}_1(t)] \otimes \hat{\Gamma}_2(t) + \hat{\Gamma}_1(t) \otimes [\hat{H}_2(t)\hat{\Gamma}_2(t)]. \quad (23)$$

The role of the direct summation and product employed in our definition is to ensure that the energy of the system remains always additive. Other quantities as the density and current are also additive, e.g.,

$$\hat{n}_t(\mathbf{r}) = \bigoplus_{\alpha} \hat{n}_\alpha(\mathbf{r}), \quad \hat{\mathbf{j}}_t(\mathbf{r}) = \bigoplus_{\alpha} \hat{\mathbf{j}}_\alpha(\mathbf{r}), \quad (24)$$

where  $\hat{n}_\alpha(\mathbf{r})$  is the density operator applying on fragment  $\alpha$ , and  $\hat{\mathbf{j}}_\alpha(\mathbf{r}) = \hat{\mathbf{j}}_{p,\alpha}(\mathbf{r}) + \hat{n}_\alpha(\mathbf{r})\mathbf{A}_p(\mathbf{r})$ , being  $\hat{\mathbf{j}}_{p,\alpha}$  the current density operator for fragment  $\alpha$ . These definitions allow us to write

$$\mathbf{j}(\mathbf{r}) = \text{Tr}\{\hat{\Gamma}_t(t)\hat{\mathbf{j}}_t(\mathbf{r})\} = \sum_{\alpha} \mathbf{j}_\alpha(\mathbf{r}). \quad (25)$$

The evolution of the system is thus described by the Liouville equation

$$i\partial_t \hat{\Gamma}_t(t) = [\hat{H}_t(t), \hat{\Gamma}_t(t)]. \quad (26)$$

Now, note that the Hamiltonian has the form

$$\begin{aligned} \hat{H}_t(t) = & \hat{T}_t + \hat{W}_t + \int d^3\mathbf{r} \left[ \hat{\mathbf{j}}_{p,t}(\mathbf{r}) \cdot \mathbf{A}_p(\mathbf{r}) \right. \\ & \left. + \hat{n}_t(\mathbf{r}) \left( v(\mathbf{r}) - \phi_p(\mathbf{r}) - \frac{1}{2} \mathbf{A}_p^2(\mathbf{r}) \right) \right], \quad (27) \end{aligned}$$

where  $\hat{T}_t = \bigoplus_{\alpha} \hat{T}_\alpha$  and  $\hat{W}_t = \bigoplus_{\alpha} \hat{W}_\alpha$ , and  $\hat{\mathbf{j}}_{p,t}$  is the paramagnetic current density operator of the fragmented molecule. The operators  $\hat{T}_\alpha$  and  $\hat{W}_\alpha$  only apply to the Fermionic Fock space of fragment  $\alpha$ .

Equation (26) has the same form of the Liouville equation of the real system, Eq. (5). Differentiation of  $\text{Tr}\{\hat{\mathbf{j}}_t(\mathbf{r})\hat{\Gamma}_t(t)\}$  with respect to time gives rise to the evolution equation of the partitioned molecule as a whole. The evolution equation is the same as that shown in Eq. (19), where the term in the summation over the fragments,  $\sum_{\alpha} \mathbf{q}_{\alpha} + n_{\alpha} \nabla v_{\alpha}$ , is simply  $-i\text{Tr}\{\hat{\Gamma}_t(t)[\hat{H}_t^0, \hat{\mathbf{j}}_{p,t}(\mathbf{r})]\}$ ;  $\hat{H}_t^0$  is the Hamiltonian of the partitioned molecule in the absence of electromagnetic fields. The previous commutator and the commutator  $-i\text{Tr}\{[\hat{T} + \hat{W}, \hat{\mathbf{j}}_p(\mathbf{r})]\hat{\Gamma}_t(t)\}$  are analogous: They are both free of the EM field and they are determined by the initial state. This analogy is what allows us to extend the proof of Ghosh and Dhara<sup>1</sup> to fragmented molecules in the presence of partition EM fields.

Let us define the partition Kohn-Sham Hamiltonian  $\hat{H}_{t,s}(t)$  of the fragmented molecule as follows:

$$\begin{aligned} \hat{H}_{t,s}(t) = & \bigoplus_{\alpha} \left( \int d^3\mathbf{r} \hat{\psi}_{\alpha}^{\dagger}(\mathbf{r}) [-i\nabla + \mathbf{A}_{s,\alpha}(\mathbf{r})]^2 \hat{\psi}_{\alpha}(\mathbf{r}) \right. \\ & \left. + \int d^3\mathbf{r} \hat{n}_{\alpha}(\mathbf{r}) v_{\alpha}(\mathbf{r}) \right), \quad (28) \end{aligned}$$

where

$$\mathbf{A}_{s,\alpha} = \mathbf{A}_p + \mathbf{A}_{H,\alpha} + \mathbf{A}_{XC,\alpha} \quad (29)$$

and

$$\partial_t \mathbf{A}_{H,\alpha}(\mathbf{r}) = -\nabla \int d^3\mathbf{r}' \frac{n_{\alpha}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (30)$$

The state of the partition KS system evolves according to

$$i\partial_t \hat{\Gamma}_{t,s}(t) = [\hat{H}_{t,s}(t), \hat{\Gamma}_{t,s}(t)]. \quad (31)$$

The initial state is chosen such that:

$$\text{Tr}\{\hat{\Gamma}_{s,\alpha}(t_0)\hat{\mathbf{j}}_{\alpha}(\mathbf{r}t_0)\} = \mathbf{j}_{\alpha}(\mathbf{r}t_0). \quad (32)$$

The XC potential is obtained by setting

$$\text{Tr}\{\hat{\Gamma}_{s,\alpha}(t)\partial_t \hat{\mathbf{j}}(\mathbf{r})\} = \text{Tr}\{\hat{\Gamma}_{\alpha}(t)\partial_t \hat{\mathbf{j}}(\mathbf{r})\}. \quad (33)$$

This yields

$$\begin{aligned} n_{\alpha}(\mathbf{r})\partial_t \mathbf{A}_{HXC,\alpha}(\mathbf{r}) - \mathbf{j}_{\alpha}(\mathbf{r}) \times \nabla \times \mathbf{A}_{HXC,\alpha}(\mathbf{r}) \\ = \mathbf{q}_{s,\alpha}(\mathbf{r}) - \mathbf{q}_{\alpha}(\mathbf{r}), \quad (34) \end{aligned}$$

where  $\mathbf{q}_{s,\alpha} = -i\text{Tr}\{\hat{\Gamma}_{s,\alpha}(t)[\hat{T}_{\alpha}, \hat{\mathbf{j}}_{\alpha}]\}$ . The above is the conventional HXC vector potential of TDCDFT and is a functional of  $\mathbf{j}_{\alpha}$ ,  $\hat{\Gamma}_{\alpha}(t_0)$ , and  $\hat{\Gamma}_{s,\alpha}(t_0)$ . Now we can derive the equivalent of the zero-force theorem.<sup>29</sup> Our objective is to represent the evolution of the current density, Eq. (10), by means of the current density shown in Eq. (19). As a consequence, the total momentum  $\mathbf{P}(t) = \int d^3\mathbf{r} \mathbf{j}(\mathbf{r})$  is represented by the partitioned molecule as well. Suppose that the current density  $\mathbf{j}$  is given and that we choose the proper partition field,  $\phi$ ,  $\mathbf{A}_p$ , that yields  $\mathbf{j}$ , and the EM field of the real system is  $\mathbf{E}$  and  $\mathbf{B}$ . Because the hydrodynamic-like quantities  $\mathbf{q}$  and  $\{\mathbf{q}_{\alpha}\}$  do not exert a net external force on the system, comparison of the total momentum obtained from Eqs. (10) and (19) leads to the following exact condition for the partition potential:

$$\begin{aligned} & \int d^3\mathbf{r} (n(\mathbf{r})\mathbf{E}_p(\mathbf{r}) + \mathbf{j}(\mathbf{r}) \times \mathbf{B}_p(\mathbf{r})) \\ & = \int d^3\mathbf{r} (n(\mathbf{r})\mathbf{E}(\mathbf{r}) + \mathbf{j}(\mathbf{r}) \times \mathbf{B}(\mathbf{r}) + n(\mathbf{r})\nabla v(\mathbf{r}) \\ & \quad - \sum_{\alpha} n_{\alpha}(\mathbf{r})\nabla v_{\alpha}(\mathbf{r})). \quad (35) \end{aligned}$$

This last equation suggests that the partition potential must have two types of contributions: one ensuring that the system is subject to the right external forces due to the EM field, and another introducing the correct nuclear forces correcting for the fact that the system is partitioned. Other contributions to the partition field come from the internal forces, i.e., the difference between the stress tensor of the real and partitioned molecule. These internal forces do not contribute

to Eq. (35) but are essential to reproduce the dynamics of the real molecule.

Our simple extension of the proof of Ghosh and Dhara<sup>1</sup> allows us to regard the partition 4-potential as a functional of the current for a given set of fragment potentials  $\{v_\alpha\}$ . The EM field of the real system in Eq. (35) can then be eliminated if the partition field is split as follows:

$$\begin{aligned} &(\mathbf{A}_P, \phi_P)[\mathbf{j}; \hat{\Gamma}_f(t_0), \{v_\alpha\}] \\ &= (\mathbf{A}, \phi)[\mathbf{j}; \hat{\Gamma}_f(t_0), v] + (\mathbf{A}_G, \phi_G)[\mathbf{j}; \hat{\Gamma}_f(t_0), \hat{\Gamma}_f(t_0), v, \{v_\alpha\}]. \end{aligned} \quad (36)$$

The “gluing” 4-potential  $(\mathbf{A}_G, \phi_G)$  accounts for the TD correlation between the fragments and is a major component of the partition 4-potential  $(\mathbf{A}_P, \phi_P)$ . It depends on the current density, where the initial states and external potentials of the real and partitioned system are given. If we evaluate the 4-potential at the current density  $\mathbf{j}$  and plug it into Eq. (35) we obtain the condition

$$\begin{aligned} &\int d^3\mathbf{r} (n(\mathbf{r}t)\mathbf{E}_G(\mathbf{r}t) + \mathbf{j}(\mathbf{r}t) \times \mathbf{B}_G(\mathbf{r}t)) \\ &= \int d^3\mathbf{r} \left( n(\mathbf{r}t)\nabla v(\mathbf{r}t) - n_\alpha(\mathbf{r}t) \sum_\alpha \nabla v_\alpha(\mathbf{r}t) \right). \end{aligned} \quad (37)$$

This equation can be regarded as a generalization of the zero-force theorem of TDCDFT. In fact, if we only had one fragment and eliminated the electron-electron repulsion from the only fragment Hamiltonian we would obtain that the gluing vector potential, in the Weyl Gauge, becomes precisely the HXC-vector potential, and Eq. (37) becomes the zero-force theorem.

The initial density matrix  $\hat{\Gamma}_f(t_0)$  is chosen to represent the initial current density of the system  $\mathbf{j}_0 = \mathbf{j}(\mathbf{r}t_0)$ . We assumed it is given and found the properties that the partition field must satisfy. There are several methods to find the initial state. If the molecule is initially in a stationary state (no current density), then PDFT can be used to find the initial state, which only needs to represent the density. In such a case, we perform the operation

$$E_f[n(t_0)] = \min \{ \hat{\Gamma}_f \in \mathcal{L}_f : \text{Tr}[\hat{\Gamma}_f \hat{H}_f^0] | \hat{\Gamma}_f \rightarrow n(\mathbf{r}t_0) \}, \quad (38)$$

which requires only the introduction of the scalar partition potential  $\phi_P$  (or a longitudinal partition vector potential). On the other hand, if the system has an initial current density  $\mathbf{j}_0$  then we replace the density  $n(\mathbf{r}, t_0)$  by the current density  $\mathbf{j}(\mathbf{r}t_0)$  as the constraint in Eq. (38). The density matrix that minimizes the right-hand-side of Eq. (38) can then be used as the initial state. In a similar fashion, we obtain the initial Kohn-Sham state for each fragment. We simply need to apply the same procedure to each fragment Hamiltonian. In each minimization the constraint to satisfy is that the Kohn-Sham system must yield the initial fragment current density  $\mathbf{j}_\alpha(\mathbf{r}t_0)$  (or density  $n_\alpha(\mathbf{r}t_0)$  if there is no current density).

## V. VARIATIONAL FORMULATION

It is convenient to use the formalism of van Leeuwen<sup>26</sup> to express the partition and gluing fields as functional derivatives of suitable action functionals. Let us consider the Keldysh

space, which is defined by a pseudo-time  $z$ , a vector of the form  $(t, \sigma)$ , where  $\sigma$  only takes on the values  $+$  or  $-$ . We denote  $z$  as  $r'$ . For convenience, we employ the Weyl gauge (or temporal gauge, i.e.,  $\phi_G = 0$ ). The Hamiltonian of the fragmented molecule  $\hat{H}_f$  is a functional of the partition vector potential  $\mathbf{A}_P$ . These two objects,  $\hat{H}_f$  and  $\mathbf{A}_P$ , now depend on the pseudo-time  $z$ . In general, we assume that  $\mathbf{A}_P(\mathbf{r}t^+) \neq \mathbf{A}_P(\mathbf{r}t^-)$ . Now define the action functional

$$F_P[\mathbf{A}] = i \ln \text{Tr}[\hat{\Gamma}_f(t_0) \hat{V}_f[\mathbf{A}_P](z_f, z_i)], \quad (39)$$

where  $z_i = t_0^+$  and  $z_f = t_0^-$  and

$$\hat{V}_f[\mathbf{A}_P](z_f, z_i) = \hat{\mathcal{T}}_K \exp \left( -i \int_{z_i}^{z_f} dz \hat{H}[\mathbf{A}_P](z) \right), \quad (40)$$

where the integration in Eq. (40) over the  $\mathcal{K}$  space is defined as

$$\begin{aligned} &\int_{z_i}^{z_f} dz' \hat{H}[\mathbf{A}_P](z') \\ &:= \begin{cases} \int_{t_0}^{t_1} dt' \hat{H}_f[\mathbf{A}_P](t'^+) & z = t^+ \\ \int_{t_1}^{t_2} dt' \hat{H}_f[\mathbf{A}_P](t'^-) & z = t^- \end{cases} \end{aligned} \quad (41)$$

Here  $t_1 > t_0$  is the upper limit of the propagation in real time.  $\hat{\mathcal{T}}_K$  is the path-ordering operator in the Keldysh space. If  $z_2$  is later than  $z_1$  in the contour, then  $\hat{\mathcal{T}}_K[\hat{A}(z_1)\hat{A}(z_2)] = \hat{A}(z_2)\hat{A}(z_1)$ .  $z_2 = (t_2, \sigma_2)$  is later than  $z_1 = (t_1, \sigma_1)$  if: (i)  $t_2 > t_1$  and  $\sigma_2 = \sigma_1 = +$ , or (ii)  $t_2 < t_1$  and  $\sigma_2 = \sigma_1 = -$ , or (iii)  $\sigma_2 = -$  and  $\sigma_1 = +$  (regardless of the value of  $t_2$  and  $t_1$ ).

It can be shown that

$$\frac{\delta F_P}{\delta \mathbf{A}_P(\mathbf{r}z)} = \tilde{\mathbf{j}}(\mathbf{r}z), \quad (42)$$

where  $\tilde{\mathbf{j}}$  is the pseudo-current

$$\tilde{\mathbf{j}}(\mathbf{r}z) = \frac{\text{Tr}[\hat{\Gamma}_f(t_0) \hat{V}_f(z_f, z) \hat{\mathbf{j}}_{P,f}(\mathbf{r}) + \hat{h}_f(\mathbf{r}) \mathbf{A}_P(\mathbf{r}z) \hat{V}_f(z, z_i)]}{\text{Tr}[\hat{\Gamma}_f(t_0) \hat{V}_f(z_f, z_i)]}. \quad (43)$$

The pseudo-current becomes the physical current of the fragmented molecule when  $\mathbf{A}_P(\mathbf{r}t^+) = \mathbf{A}_P(\mathbf{r}t^-)$ .

To relate the vector potentials of the fragmented and real molecule, define the action of the real system as

$$F[\mathbf{A}] = i \ln \text{Tr}[\hat{\Gamma}_f(t_0) \hat{V}[\mathbf{A}](z_f, z_i)], \quad (44)$$

where  $\hat{V}$  has the same form as  $\hat{V}_f$ , and  $\hat{H}_f$  is replaced by the Hamiltonian  $\hat{H}$  in Eq. (40). We now carry out the following Legendre-transformation

$$L[\tilde{\mathbf{j}}] = -F[\mathbf{A}] + \int d^3\mathbf{r} d\tilde{\mathbf{j}}(\mathbf{r}z) \cdot \mathbf{A}(\mathbf{r}z). \quad (45)$$

The same transformation applied to the functional  $F_P$  yields the current density-functional  $L_P[\tilde{\mathbf{j}}]$ . Finally, let  $L_G[\tilde{\mathbf{j}}]$  be the gluing functional:

$$L_G[\tilde{\mathbf{j}}] = L_P[\tilde{\mathbf{j}}] - L[\tilde{\mathbf{j}}]. \quad (46)$$

Functional differentiation, and insertion of Eq. (36), yields

$$\frac{\delta L_G}{\delta \tilde{\mathbf{j}}(\mathbf{r}z)} = \mathbf{A}_G[\tilde{\mathbf{j}}](\mathbf{r}z). \quad (47)$$

This last equation relates the gluing vector potential with its action functional (the dependency on the initial conditions is



the same). The  $L_G$  action accounts for the interactions that take place between the fragments without considering the external perturbation  $\mathbf{A}$ . The last step to obtain the gluing vector potential of the physical system is to evaluate it at the physical current of the system, that is when  $\tilde{\mathbf{j}}(\mathbf{r}t^+) = \tilde{\mathbf{j}}(\mathbf{r}t^-)$ .

Further differentiation of Eq. (45) and evaluation at the physical regime leads to the interesting relation

$$\chi_{\mu\nu}^{-1}(\mathbf{r}t, \mathbf{r}'t') = \chi_{\mu\nu,P}^{-1}(\mathbf{r}t, \mathbf{r}'t') - \chi_{\mu\nu,G}^{-1}(\mathbf{r}t, \mathbf{r}'t'), \quad (48)$$

where  $\chi_{\mu\nu}^{-1}$  is the inverse first-order response tensor of the super molecule, where

$$\chi_{\mu\nu}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta A_\mu(\mathbf{r}t)}{\delta j_\nu(\mathbf{r}'t')}. \quad (49)$$

Similar equations define  $\chi_{\mu\nu,P}$  and  $\chi_{\mu\nu,G}$ , but of course  $\mathbf{A}$  has to be replaced by  $\mathbf{A}_P$  and  $\mathbf{A}_G$ , respectively. Equation (48) can be recast in the form

$$\underline{\chi} = \underline{\chi}_P + \underline{\chi}_P \underline{\chi}_G^{-1} \underline{\chi}, \quad (50)$$

where  $\underline{\chi}$  refers to the matrix form of the tensor(s). This equation can be used within the linear response regime to obtain the excitation energies of the super molecule. An important property of  $\chi_P^{-1}$  is that it is additive

$$\underline{\chi}_P^{-1} = \sum_\alpha \underline{\chi}_{P,\alpha}^{-1}, \quad (51)$$

where  $\chi_{P,\alpha}^{-1} = \delta \mathbf{j}_\alpha / \delta \mathbf{A}_P$ . However, in Eq. (50), the gluing linear response function must correct  $\underline{\chi}_P$  so that the poles (excitation frequencies) of the super molecule are recovered.

## VI. CHARGED PARTICLE IN A RING

To illustrate the existence of the partition field, consider the case of a charged particle in a ring under a time-independent external periodic potential. The particle is prepared in a linear combination of its ground state and second excited state. We propagate the particle's state in time and find the partition field by solving the inverse problem (we first find the current density and then the partition field giving rise to it). The Hamiltonian of the system is

$$\hat{H} = \frac{1}{2mR^2} \hat{L}_z^2 + V(\varphi), \quad (52)$$

with the external potential chosen as

$$V(\varphi) = -V_0 \cos(2\varphi - \pi). \quad (53)$$

Define two fragments, left (L) and right (R), described by

$$\hat{H}_\alpha[\lambda](t) = \frac{1}{2mR^2} (\hat{L}_z - \lambda(\varphi, t)\Theta(t))^2 + V_\alpha(\varphi) + v_P(\varphi), \quad (54)$$

where  $\alpha = L, R$ ,  $\hat{L}_z = i\partial/\partial\varphi$ . The function  $\Theta(t)$  is the Heaviside function

$$\Theta(t) = \begin{cases} 1 & \text{if } t > 0 \\ 0 & \text{otherwise.} \end{cases} \quad (55)$$

The function  $\lambda$  is defined as

$$\lambda(\varphi, t) = B_{P,z}(\varphi, t) \frac{R^2}{2}, \quad (56)$$

where  $B_{P,z}$  is the  $z$  component of the partition magnetic field. We only need this component because the system is one-dimensional. The potentials defining the partition are

$$V_L(\varphi) = \begin{cases} V(\varphi), & 0 \leq \varphi < \pi \\ 0, & \text{otherwise,} \end{cases} \quad (57)$$

and  $V_R(\varphi) = V_L(\varphi - \pi)$ ,  $0 \leq \varphi \leq 2\pi$ .

Since there are no external time-dependent perturbations in this case, the partition and gluing fields are the same, and the time-dependency of the partition field is due only to the hydrodynamical-like effects and forces between fragments that follow from comparing Eqs. (6) and (19). The objective is to represent a TD current that is initially zero everywhere. For this reason  $\lambda(\varphi, 0) = 0$ . We begin by finding the eigenvalues of the Hamiltonian shown in Eq. (52), that is,  $\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle$ . We wish to represent the initial density and the TD current density that are produced by the following linear combination of states:

$$|\psi(t)\rangle = c_0|\psi_0\rangle e^{-i\epsilon_0 t} + c_2|\psi_2\rangle e^{-i\epsilon_2 t}, \quad (58)$$

where  $c_0 = \sqrt{0.98}$  and  $c_2 = \sqrt{0.02}$ . First, we find the potential  $v_P$  that represents the initial density of the system using ground-state PDFT. The density  $n^{\text{ref}}(\varphi, t=0) = |\psi(\varphi, t=0)|^2$  is used as a reference to minimize the error,

$$e^2[v_P, v_L, v_R] = \|n^{\text{ref}}(t=0) - n_0[v_P, v_L, v_R]\|_2^2 + (E_L[v_P] - E_R[v_P])^2, \quad (59)$$

with respect to the partition potential  $v_P$ , which is represented in a spline basis set. The density as functional of the partition potential and occupation numbers is

$$n_0[v_P, v_L, v_R](\varphi) = v_L|\tilde{\psi}_L[v_P]|^2(\varphi) + v_R|\tilde{\psi}_R[v_P]|^2(\varphi), \quad (60)$$

where  $v_L, v_R$  are the occupation numbers of the right and left fragment, respectively; these numbers satisfy  $v_L + v_R = 1$ . The wave-functions  $\tilde{\psi}_L$  and  $\tilde{\psi}_R$  are ground states, and functionals of the partition potential. These wave-functions are obtained by solving the eigenvalue problem  $\hat{H}_\alpha(t=0)[v_P]|\tilde{\psi}_\alpha[v_P]\rangle = E_\alpha[v_P]|\tilde{\psi}_\alpha[v_P]\rangle$ . The energies  $E_R$  and  $E_L$  are the ground-state energies of the left and right fragment, respectively. The term  $(E_R - E_L)^2$  in Eq. (60) ensures that the chemical potential equalization is satisfied, leading to a unique partition potential.<sup>30</sup> In Eq. (59),  $\|f\|_2$  is the norm

$$\|f\|_2 = \left( \int_0^{2\pi} d\varphi f^2(\varphi) \right)^{1/2}, \quad (61)$$

which is approximated with the trapezoidal rule. The error functional  $e$  is minimized using sequential least-squares quadratic programming. The wavefunctions  $\psi_L$  and  $\psi_R$  are propagated by solving the Schrödinger equation  $i\partial_t \psi_\alpha[\lambda](\varphi, t) = \hat{H}_\alpha[\lambda](t)\psi_\alpha[\lambda](\varphi, t)$  with the Crank-Nicholson method, where  $|\psi_\alpha(t=0)\rangle = |\tilde{\psi}_\alpha\rangle$ . At each time step the following error functional is minimized:

$$\bar{e}^2[\lambda](t) = \|j^{\text{ref}}(t) - j[\lambda](t)\|_2^2. \quad (62)$$

To reproduce the TD current density of the system,  $j^{\text{ref}} = \text{Re}(i^{-1}\psi^* \partial_\varphi \psi)$ , the above functional was minimized using the MINPACK routine `lder`, an implementation of the

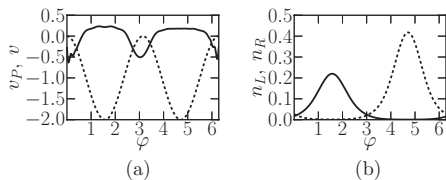


FIG. 1. (a) Partition potential (solid line) and time-independent external potential (dashed line) as function of the angle  $\varphi$ . (b) Initial density of left (solid line) and right (dashed line) fragment vs. angle  $\varphi$ . The mass and radius are set as  $m = 1$ ,  $R = 1$ .

Marquardt-Levenberg method. The potential  $\lambda$  is also expressed using a spline basis set at each time step. The TD total density of the fragmented system is  $n[\lambda](\varphi, t) = v_L|\psi_L[\lambda](\varphi, t)|^2 + v_R|\psi_R[\lambda](\varphi, t)|^2$  and the current is  $j[\lambda](\varphi, t) = v_L j_L[\lambda](\varphi, t) + v_R j_R[\lambda](\varphi, t)$ , where  $j_\alpha = \text{Re}(i^{-1}\psi_\alpha^* \partial_\varphi \psi_\alpha)$ ,  $\alpha = L, R$ . The occupation numbers  $v_L$  and  $v_R$  are the optimal ones obtained from the minimization of  $e^2$  in Eq. (59).

Even though the current density is nearly constant, the  $\lambda$  field varies significantly. An advantage of employing  $\lambda$  to reproduce the current is the explicit dependence of  $j$  on  $\lambda$ ,

$$j(\varphi, t) = j_P(\varphi, t) + n(\varphi, t)\lambda(\varphi, t). \quad (63)$$

Fig. 1(a) shows the external potential of the system and the partition potential required to represent the initial density of the system. The partition potential has two wells, one around  $\varphi = \pi/2$  and another at the boundaries. The partitioning scheme we chose localizes the current-densities of the fragments. The left fragment is isolated from the right fragment. Therefore, the partition potential must allow for some spreading of the left fragment density into the right. The depth of the partition potential depends on the height of the barrier separating the fragment potentials: The higher this barrier, the deeper the partition potential should be. Fig. 1(b) shows the initial electronic densities for both fragments. In this case, the addition of the second excited state adds extra charge to the right fragment density.

The *unique* partition magnetic field is shown in Fig. 2(a). It is initially zero because the scalar partition potential was used to represent the initial density and there is no initial current density; the initial wave function  $\psi(t=0)$  is real-valued. The current densities shown in Fig. 2(b) are also unique, and in this case they are localized around their respective fragments. Each fragment's current density is in a 1-1 correspondence with the partition potential. However, in practice, the map between the total current density and the partition magnetic field (or the partition 4-potential in general) is more useful because if the current density of a fragment is localized around that fragment, then it is largely insensitive to variations of the 4-potential far from it, while the total-current density may not be.

## VII. CONCLUDING REMARKS

We presented a technique to partition, formally, the total current density of a molecule into contributions that can

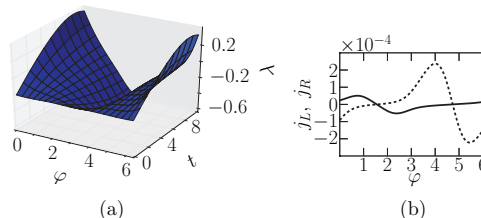


FIG. 2. (a)  $z$  component of the partition magnetic field as function of angle and time. (b) Snapshot of the current densities at  $t = 2.0$  for the left (solid line) and right (dashed line) fragments.

be assigned to user-defined fragments of the molecule. To represent the current density of the real system, a fictitious partition 4-potential was defined. The partition 4-potential accounts for the fragment correlation effects that are ignored when the molecule is partitioned. It also satisfies a balance-of-forces theorem stating that the 4-potential must eliminate the fictitious forces on the system and add the correct force to the fragmented molecule. The balance-of-forces theorem is further simplified by the definition of a gluing field which depends on kinetic, XC, and change-in-external-potential effects.

Our framework offers a new fragment-based approach to study how the molecule responds to electromagnetic fields, or how it responds to scalar potentials as well. It should be particularly useful for application to materials whose magnetic properties arise from a collection of relatively well-localized and weakly-overlapping currents. The method is applicable to both solids and molecules. However, the workhorse of TDCDFT, the VK functional,<sup>8</sup> is especially suitable for solids and long-chained polymers. New functionals are required within TDCDFT to account for memory effects in molecules, for example, using Lagrangian frames of Refs. 5 and 31. We expect the formal theorems derived here will assist on the development of such functionals for  $A_{XC}$ . For practical simulations, they should go hand-in-hand with approximate expressions for the gluing and partition 4-potentials, a topic for future research. Alternatively, for many-electron systems, one may apply the present theory within wave-function schemes where one approximates the fully interacting fragment-Hamiltonians using Hartree-Fock theory<sup>32,33</sup> (or its refinements), and adding the corresponding partition 4-potential. Estimation and identification of the gluing 4-potential can be then carried out by solving inversion problems (given the current-density, or other observable of interest, and partition scheme, find the gluing field), which can help for the development of functional approximations to the gluing 4-potential. This will be subject of future work.

## ACKNOWLEDGMENTS

This work is supported by the Office of Basics Energy Sciences, U.S. Department of Energy, under Grant No. DE-FG02-10ER16196. A.W. also acknowledges support from an Alfred P. Sloan Foundation Research Fellowship.



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# Integer discontinuity of density functional theory

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(Received 12 February 2014; published 12 May 2014)

Density functional approximations to the exchange-correlation energy of the Kohn-Sham theory, such as the local density approximation and generalized gradient approximations, lack the well-known integer discontinuity, a feature that is critical to describe molecular dissociation correctly. Moreover, standard approximations to the exchange-correlation energy also fail to yield the correct linear dependence of the ground-state energy on the number of electrons when this is a noninteger number obtained from the grand canonical ensemble statistics. We present a formal framework to restore the integer discontinuity of any density functional approximation. Our formalism derives from a formula for the exact energy functional and a constrained search functional that recovers the linear dependence of the energy on the number of electrons.

DOI: 10.1103/PhysRevA.89.052506

PACS number(s): 31.15.E—

## I. INTRODUCTION

Density functional theory (DFT) [1,2] is a useful formulation of ground-state quantum mechanics that offers a simple approach to estimate the electronic properties of molecules and solids [3]. Perdew *et al.* [4] (PPLB) considered Mermin's extension [5] of DFT to systems that adiabatically exchange electrons with a distant reservoir at zero temperature. In this framework, the energy as a function of the electron number is a series of straight lines interpolating the energies corresponding to those of closed systems with integer numbers of electrons. PPLB found that the exchange-correlation (XC) potential displays a derivative discontinuity (DD) that, when added to the Kohn-Sham (KS) band gap, yields the fundamental band gap of the system (also see Ref. [6]). The DD is present in molecular dissociation: When two atoms are separated far apart they take on integer numbers of electrons to neutralize their charges, and the total energy of the system, which is nearly additive, tends to display a DD with respect to a change in the number of electrons when one atom transfers its electron to the other.

The DD of the XC energy functional and the linear dependency between discrete intervals is required to improve the physics of density functionals. The missing integer discontinuity causes problems in the estimation of ground-state properties like binding energies [7] and reaction barriers [8]. In time-dependent density functional theory, the missing integer discontinuity is also required to improve the accuracy of density functional approximations (DFA's) [9–14], especially to describe bond-stretching processes. A strong delocalization error [15] occurs due to the lack of piecewise linear dependency of the resulting fragment energies with the number of electrons. This nonlinearity is pervasive and affects all calculations that use continuous XC energy functionals such as the local density approximation (LDA) [16]. These known problems point to the need to develop new functionals with the correct piecewise linearity, capable of describing bond stretching without resorting to symmetry breaking. Long-range and nonlocal corrections are usually added to the XC energy functional [17] to solve these problems. In most cases, the corrections improve the results without completely

recovering the linear behavior of the XC energy between integers and its DD.

Nonempirical functionals such as the LDA and generalized gradient approximations work well for atoms with integer numbers of electrons. Kraisler and Kronik [18] explored the properties of a simple ensemble average of XC energies of pure states. They showed that the piecewise linearity is almost restored by their approach using the optimized effective potential method. Their results illustrate the plausibility of recovering the integer discontinuity of most functionals of discrete-electron states that are apparently continuous in terms of the density.

In this work we propose a formalism to restore *completely* the linear dependency on the electron number between integers. We use the fact that most density functional approximations have been developed for closed systems with integer numbers of electrons. Ensemble- $v$  representability is the central concept employed in this study; we assume that for a given ensemble density there is a corresponding external potential giving rise to such density. This assumption implies that one can extract density matrices, which are density functionals, that allow us to carry out an expansion of the ensemble XC energy functional in terms of XC and KS kinetic energies evaluated at closed, fully interacting discrete-electron densities that sum to the correct ensemble ground-state density. We then connect the resulting expression for the ensemble XC energy to an expansion of the KS kinetic energy evaluated at noninteracting discrete-electron densities that yield the same ensemble ground-state density. For density functional approximations, a constrained search is proposed to replace the Levy-Lieb search that requires the electron-electron repulsion operator. This search assumes noninteracting  $v$  representability of the discrete-state densities and permits one to recover strictly the piecewise-defined linearity for approximate XC energy functionals and their concomitant integer discontinuities.

## II. THEORY

The PPLB density functional is defined as

$$E_v[n] = F[n] + \int d\mathbf{r} n(\mathbf{r})v(\mathbf{r}), \quad (1)$$

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where  $F[n]$  is the constrained-search functional:

$$F[n] = \inf_{\hat{D} \rightarrow n} \text{Tr}[(\hat{T} + \hat{W})\hat{D}]. \quad (2)$$

$\hat{T}$  is the kinetic energy operator,  $\hat{W}$  is the electron-electron repulsion operator, and  $\hat{D}$  is the density matrix operator in Fock space. The notation “ $\hat{D} \rightarrow n$ ” indicates that the search for the infimum is performed over all density matrices satisfying  $\text{Tr}\{\hat{D}\hat{n}(\mathbf{r})\} = n(\mathbf{r})$ . In order to carry out an equivalent search without requiring this density constraint, we introduce the Lagrange multiplier  $u[n]$  as indicated below. The generalized energy  $\mathcal{E}_N[u]$ , now a functional of  $u[n]$ , involves a search over all density matrices corresponding to  $N$  electrons ( $N$  is in general noninteger):

$$\mathcal{E}_N[u] = \inf_{\hat{D} \rightarrow N} \text{Tr}[(\hat{T} + \hat{W} + \int d\mathbf{r} u(\mathbf{r})\hat{n}(\mathbf{r}))\hat{D}]. \quad (3)$$

Here,  $N$  is a real number between  $J$  and  $J+1$ , where  $J$  is a positive integer. If the convexity assumption holds, i.e.,  $\mathcal{E}_{J-1}[u] - \mathcal{E}_J[u] \geq \mathcal{E}_J[u] - \mathcal{E}_{J+1}[u]$  for any  $J$ , then

$$\mathcal{E}_N[u] = (1 - \omega)\mathcal{E}_J[u] + \omega\mathcal{E}_{J+1}[u], \quad (4)$$

where  $\omega[n] = \int d\mathbf{r} n(\mathbf{r}) - J$ . We assume that  $0 < \omega < 1$ . The search for the infimum in Eq. (3) yields a density matrix  $\hat{D}[n]$  that is also a linear interpolation of integer-number density matrices,  $\hat{D}_J$  and  $\hat{D}_{J+1}$ . For example, if the bordering systems are pure ground states then  $\hat{D}_M = |\psi_M\rangle\langle\psi_M|$ ,  $M = J, J+1$ . The densities of the pure states, that is,  $n_M[u](\mathbf{r}) = \text{Tr}\{\hat{D}_M[u]\hat{n}(\mathbf{r})\}$ ,  $M = J, J+1$ , satisfy the restriction:

$$n(\mathbf{r}) = (1 - \omega)n_J[u](\mathbf{r}) + \omega n_{J+1}[u](\mathbf{r}). \quad (5)$$

Because  $u$  is a functional of the density, so are the densities  $n_J$  and  $n_{J+1}$ . Inserting the minimizing density matrix  $\hat{D}[n]$  into  $F[n]$  we find that

$$F[n] = (1 - \omega[n])F[n_J] + \omega[n]F[n_{J+1}]. \quad (6)$$

For notational convenience, we introduce the average function:

$$y(x) = \begin{cases} 1 & x = 0, \\ 1 - x & 0 < x < 1, \\ 1 + x & -1 < x < 0, \\ 0 & \text{otherwise,} \end{cases} \quad (7)$$

which allows us to express  $F$  (as well as the energy, density, etc.) as

$$F[n] = \sum_M y(N - M)F[n_M], \quad (8)$$

where  $N = \int n$  is, of course, a density functional as well, and  $M$  runs over non-negative integer numbers. The functional  $F[n]$  is split in the usual Kohn-Sham manner:

$$F[n] = T_s[n] + E_{\text{HXC}}[n], \quad (9)$$

where  $T_s[n] = \inf\{\text{Tr}[\hat{T}\hat{D}_s]\hat{D}_s \rightarrow n\}$ , and  $E_{\text{HXC}}[n] = E_{\text{H}}[n] + E_{\text{XC}}[n]$ , the Hartree and exchange-correlation energy functionals.

The ground-state energy for the auxiliary system of non-interacting electrons,  $\mathcal{E}_{s,N}$  can be thought of as a functional

of  $u_s(\mathbf{r})$ , an analog of  $u(\mathbf{r})$  introduced to carry out the noninteracting search version of Eq. (3):

$$\mathcal{E}_{s,N}[u_s] = \inf_{\hat{D}_s \rightarrow N} \text{Tr}\left\{\left(\hat{T} + \int d\mathbf{r} u_s(\mathbf{r})\hat{n}(\mathbf{r})\right)\hat{D}_s\right\}. \quad (10)$$

As in the case of  $F[n]$ ,  $T_s[n]$  returns two densities  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  that, when added together with the weight factor  $y(N - M)$ , yield the density  $n(\mathbf{r})$  of the interacting system. In what follows, we will refer to  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  as the noninteracting bordering-integer densities. We emphasize that even employing the *exact* exchange-correlation functional, the noninteracting integer density  $n_{s,M}(\mathbf{r})$  is *not* equal to the  $M$ -electron density of the interacting system [see the next section for a model system we describe later on]. Rather than being the ground-state density of  $M$  interacting electrons in  $v(\mathbf{r})$  [or  $M$  noninteracting electrons in  $v_s(\mathbf{r})$ ], it is the ground-state density of  $M$  noninteracting electrons in  $u_s(\mathbf{r})$ , a potential that differs from  $v_s(\mathbf{r})$  for noninteger  $M$ , as illustrated in Fig. 2(b). For example,  $n_{s,J}(\mathbf{r}) = \sum_{i=1}^J |\phi_i(\mathbf{r})|^2$ , and  $n_{s,J+1}(\mathbf{r}) = n_{s,J}(\mathbf{r}) + |\phi_{J+1}(\mathbf{r})|^2$ , where  $\{\phi_i\}(\mathbf{r})$  are single-particle orbitals that satisfy

$$\left(\hat{T} + \int d\mathbf{r} u_s(\mathbf{r})\hat{n}(\mathbf{r})\right)|\phi_i\rangle = \epsilon_i|\phi_i\rangle, \quad (11)$$

and by definition  $\sum_M y(N - M)n_{s,M}(\mathbf{r}) = n(\mathbf{r})$ . The noninteracting bordering-integer densities  $n_{s,J}(\mathbf{r})$  and  $n_{s,J+1}(\mathbf{r})$  are density functionals as well. Inserting Eq. (9) on both sides of Eq. (8) and expanding  $T_s[n]$  as  $\sum_M y(N - M)T_s[n_M]$ , we obtain the most important result of this paper:

$$E_{\text{HXC}}[n] = \sum_M y(N - M)\{(T_s[n_M] - T_s[n_{s,M}]) + E_{\text{HXC}}[n_M]\}, \quad (12)$$

an exact relation for  $E_{\text{HXC}}[n]$  in terms of quantities that describe pure quantum states, with  $T_s$  evaluated at both, the interacting and noninteracting bordering-integer densities. Equation (12) is trivially true when  $n(\mathbf{r})$  integrates to an integer number, but it is a useful identity when  $J < N < J+1$  in the context of *approximate* DFT, as we show next.

In order to perform an ensemble-ground-state calculation, the external potential and noninteger number of electrons are required, one then needs to average two ground-state energies corresponding to states with integer numbers of electrons, provided the convexity assumption holds. These pure ground-state densities are combined to produce the ensemble density and, through a density-inversion procedure (as illustrated in the next section), one obtains ensemble KS potentials, which formally also come from Eq. (12) by means of functional differentiation. By approaching an integer number of electrons from above, one then observes the discontinuity in the XC potential. An alternative way of performing the calculation is by employing a suitable approximation to the functionals appearing on the right-hand side of Eq. (12) and estimating the KS ensemble potential through the optimized effective potential method or variations of it (see, for example, Ref. [18]).

Let us denote as  $E_{\text{HXC}}^{\text{app}}[n_M]$  an approximation for  $M = 1, 2, \dots$ . Inserting this functional into Eq. (12) yields  $E_{\text{HXC}}^{\text{app}}[n]$ , a useful approximation to the ensemble functional. The densities  $\{n_M\}$  can in principle be obtained from the search in  $F[n]$ , a functional we do not know. But we can circumvent the use of

$F[n]$  by defining

$$G_s[n] = \inf_{\{\tilde{n}_M\} \rightarrow n} \sum_M y(N-M) G_s[\tilde{n}_M], \quad (13)$$

where

$$G_s[\tilde{n}_M] = \inf_{\tilde{D}_s \rightarrow \tilde{n}_M} \text{Tr} \left\{ \left( \hat{T} + \int d\mathbf{r} v_{\text{HXC}}^{\text{app}}[\tilde{n}_M](\mathbf{r}) \hat{n}(\mathbf{r}) \right) \hat{D}_s \right\}. \quad (14)$$

By  $\{\tilde{n}_M\} \rightarrow n$  we refer to the constraint  $\sum_M y(N-M)\tilde{n}_M(\mathbf{r}) = n(\mathbf{r})$ . If  $J < N < J+1$ , the optimal densities  $\{n_M\}$  that minimize the right-hand side of Eq. (13) are obtained from solving two sets of KS equations self-consistently: one with KS potential  $\tilde{v}_s[\tilde{n}_J] = v_{\text{HXC}}^{\text{app}}[\tilde{n}_J] + \tilde{u}$  and another with  $\tilde{v}_s[\tilde{n}_{J+1}] = v_{\text{HXC}}^{\text{app}}[\tilde{n}_{J+1}] + \tilde{u}$ . The orbitals arising from the KS equations with  $\tilde{v}_s[\tilde{n}_J]$  and  $\tilde{v}_s[\tilde{n}_{J+1}]$  are complex squared and added together to yield the densities  $\tilde{n}_J$  and  $\tilde{n}_{J+1}$ . The external potential  $\tilde{u}$  is a Lagrange multiplier arising from the constraint  $\{\tilde{n}_M\} \rightarrow n$  and is to be varied until the constraint is satisfied. If  $\tilde{u}$  is set as the external potential of the system  $v$ , then one obtains an approximation to the ensemble ground-state density. The functional in Eq. (13) reformulates the noninteracting  $v$ -representability problem for an approximate XC potential. When the *exact* XC potential is used, then setting  $\tilde{u} = v$  and solving the two sets of KS equations produces the orbitals needed to build the exact ground-state densities  $n_J$  and  $n_{J+1}$ .

The total energy of the system is

$$E_v^{\text{app}}[n] = \sum_M y(N-M) \left( T_s[n_M] + E_{\text{HXC}}^{\text{app}}[n_M] + \int d\mathbf{r} v(\mathbf{r}) n_M(\mathbf{r}) \right). \quad (15)$$

The approximated ground-state energy is found by setting  $E_N^{\text{app}}[v] = \inf_{n \rightarrow N} E_v^{\text{app}}[n]$ . If the convexity assumption holds for our system of interest, then

$$E_N^{\text{app}}[v] = \sum_M y(N-M) E_M^{\text{app}}[v], \quad (16)$$

where

$$E_M^{\text{app}}[v] = \inf_{n_M} T_{s,M}[n_M] + E_{\text{HXC},M}^{\text{app}}[n_M] + \int d\mathbf{r} v(\mathbf{r}) n_M(\mathbf{r}). \quad (17)$$

Equation (16) shows that it is possible to recover the piecewise linear dependence of the approximated energy. Using the analog of Eq. (5) for  $J-1 < N < J$  and the KS equations, it can be shown that (see Appendix)

$$\frac{\delta E_{\text{HXC}}^{\text{app}}}{\delta n(\mathbf{r})} = E_J^{\text{app}} - E_{J-1}^{\text{app}} - \epsilon_J^{\text{app}} + v_{\text{HXC}}^{\text{app}}(\mathbf{r}) + \sum_M y(N-M) \int d\mathbf{r}' \left( \frac{\delta E_{v,M}^{\text{app}}}{\delta n_M(\mathbf{r}')} \right) \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})}. \quad (18)$$

The term  $\delta E_{v,M}^{\text{app}}/\delta n_M(\mathbf{r}')$  is a constant at the minimum and  $\int d\mathbf{r}' \delta n_M(\mathbf{r}')/\delta n(\mathbf{r}) = 0$ , which leads to (dropping the Hartree contribution)

$$\frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} = -I^{\text{app}} - \epsilon_J^{\text{app}} + v_{\text{XC}}^{\text{app}}(\mathbf{r}). \quad (19)$$

Since  $v_{\text{XC}}^{\text{app}} = \delta E_{\text{XC}}^{\text{app}}/\delta n$ , by definition, we obtain the Janak's theorem [19]  $\epsilon_J^{\text{app}} = -I^{\text{app}}$ , where  $I^{\text{app}} = E_{J-1}^{\text{app}}[u] - E_J^{\text{app}}[u]$  is the ionization energy of the system, and  $J-1 < N < J$ . We can also write Eq. (19) as

$$\frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} = -I^{\text{app}} - \frac{\delta T_s}{\delta n(\mathbf{r})} - u(\mathbf{r}). \quad (20)$$

This result allows us to calculate the XC DD as<sup>1</sup>

$$\begin{aligned} \Delta_{\text{XC}} &= \lim_{\Delta N \rightarrow 0^+} \left. \frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} \right|_{J+\Delta N} - \left. \frac{\delta E_{\text{XC}}^{\text{app}}}{\delta n(\mathbf{r})} \right|_{J-\Delta N} \\ &= I^{\text{app}} - A^{\text{app}} - (\epsilon_{\text{L}}^{\text{app}} - \epsilon_{\text{H}}^{\text{app}}), \end{aligned} \quad (21)$$

where  $A^{\text{app}} = E_J^{\text{app}}[u] - E_{J+1}^{\text{app}}[u]$  is the electron affinity of the  $J$ -electron system and  $\epsilon_{\text{H}}^{\text{app}}$  and  $\epsilon_{\text{L}}^{\text{app}}$  are the HOMO and LUMO orbital energies of the  $J$ -electron system. The XC DD turns out to be the difference between the fundamental gap of the real system and the KS gap. However, the approximated XC DD serves the same purpose: to correct the KS particle band gap.

For an ensemble DFA the Janak's theorem is valid but the ionization theorem is not, in general. For example, for a system with *strictly*  $J$  electrons it is known that the LDA HOMO energy does not match the ionization predicted by LDA, i.e., when  $N = J$ ,  $\epsilon_J^{\text{LDA}} \neq -I^{\text{LDA}}$ . To satisfy the Janak's theorem, a constant must be added to the approximate XC potential to replace the HOMO orbital by the DFA ionization. When  $J-1 < N < J$ , this constant is  $-I - \epsilon_{\text{H}}(N = J)$ . At  $N = J$ , however, there is no need for such correction since the functional derivative with respect to the density at this point is not defined uniquely. On the other hand, using the XC energy functional, the ionization theorem for Coulombic systems leads to the well-known expression for the DD of the XC energy functional:  $-A - \epsilon_{\text{L}}$ .

Equation (12) indicates that the approximation  $\tilde{E}_{\text{XC}}^{\text{app}}[n] = (1-\omega)E_{\text{XC}}^{\text{app}}[n_{s,J-1}] + \omega E_{\text{XC}}^{\text{app}}[n_{s,J}]$  misses the different KS kinetic energy contributions leading to the piecewise linear features of the energy; also observe that  $\tilde{E}_{\text{XC}}^{\text{app}}$  is an average using the densities  $n_{s,M}$  instead of  $n_M$ . (Note that  $\tilde{E}_{\text{XC}}^{\text{app}}$  does hold for the uniform electron gas where the level spacing is negligible. The discrete-state densities returned in that case by the minimization of the kinetic energy are negligibly different from those returned by  $F$  when both are evaluated at the electron-gas density  $n$ , and  $N$  is not an integer). Employing the optimized effective potential method, Kraisler and Kronik [18] showed that the linear dependency on the number of electrons is almost restored using the functional  $\tilde{E}_{\text{XC}}^{\text{app}}$ . With the kinetic energy and density contributions of Eq. (12), it is *completely* restored.

### III. NUMERICAL EXAMPLE

To illustrate our findings, we consider the example of a system of contact-interacting fermions [20,21] described by the energy functional  $E_v[n_M] = T_s[n_M] + E_{\text{H}}[n_M] + E_{\text{X}}[n_M] + \int dx v(x) n_M(x)$ , where  $E_{\text{H}}[n_M] = 1/2 \int dx n_M^2(x)$  and  $E_{\text{X}}[n_M] = -1/4 \int dx n_M^2(x)$ . Suppose that  $n_N^{\text{ref}}(x) =$

<sup>1</sup>This discontinuity is taken along a path of ground-state ensemble densities [27].

$(Na/\pi)\text{sech}(ax)$  is a density of interest with  $N = 2.5$  and  $a = 2$ . To find the potential  $u[n]$ , we minimize the error functional:  $e_N^2[u] = \|\sqrt{n_N}[u] - \sqrt{n_N}^{\text{ref}}\|_2^2$ . The preset density is recovered by solving the KS equations for  $N = 2$  and  $N = 3$  and setting  $n_{2.5}[u](x) = \frac{1}{2}n_2[u](x) + \frac{1}{2}n_3[u](x)$ . Note that the self-consistent procedure has to be applied twice, once for  $v_X[n_2] = -\frac{1}{2}n_2(x)$  and once for  $v_X[n_3] = -\frac{1}{2}n_3(x)$ ; in both cases, the same estimation of  $u$  is used. The finite differences method was employed to solve the Kohn-Sham equations. We represent  $u$  in a spline basis set and  $e_N^2[u]$  is minimized with the Levenberg-Marquardt algorithm [22,23]. This procedure yields the optimal potential  $u[n_{2.5}]$  shown in Fig. 1(a). Now we set that potential as fixed  $v(x) = u(x)$  and calculate the ensemble energy as a function of the number of electrons. Figure 1(b) shows the results. The solid line represents the piecewise ensemble interpolation and the dashed lines result from setting  $E_X[n_N] = -1/4 \int dx n_N^2(x)$  (which lacks the DD) to calculate the energy for any number of electrons. The solid and dashed lines look to the eye very close to each other, but their differences are made clear in Fig. 1(c). This difference is small for the functional chosen. The deviation is more severe for the three-dimensional LDA functional [7].

In Fig. 1(d) we show the estimation of the DD that results from inverting the KS equations for a noninteger number of electrons close to  $N = 2$ . To impose the Janak's theorem we minimize the error functional:

$$\tilde{e}_N^2[u_s] = \|\sqrt{n_N}[u_s] - \sqrt{n_N}^{\text{ref}}\|_2^2 + (\epsilon_{H,N}[u_s] - \epsilon_H^{\text{ref}})^2, \quad (22)$$

where  $n_N^{\text{ref}}$  is the target “exact” ensemble density that corresponds to the external potential shown in Fig. 1(a) and electron number  $N$ .  $\epsilon_H^{\text{ref}}$  is the HOMO eigenvalue of the system with  $N = 3$ , obtained from solving the KS equations with  $v_X = -1/2n_3$  and external potential  $v$ .  $\tilde{e}_N^2$  is minimized using the conjugate-gradient method [24]. Because the ionization theorem is not satisfied, the potential satisfying  $v_X \rightarrow 0$  as

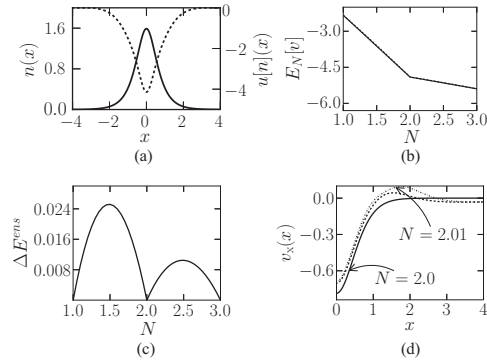


FIG. 1. (a) Preset ensemble density for  $N = 2.5$  (solid line); external potential (dashed line). (b) Energy as a function of  $N$  (solid line); approximated energy (dashed line). (c) Difference between Eq. (16) and the energy calculated using  $E_X[n_N] = -\lambda/4 \int n_N^2$  for any  $N$ . (d) Ensemble exchange potential for  $N = 2.0$  (solid line),  $N = 2.15$  (dashed line), and  $N = 2.01$  (dashed-dotted line).

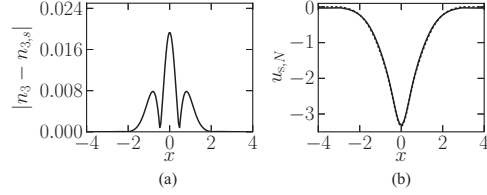


FIG. 2. (a) Difference between  $n_M$  and  $n_{s,M}$  for  $M = 3$ ; these densities are required to yield the density in Figs. 1(a) and 1(b). (b) Kohn-Sham potentials corresponding to  $N = 2.5$  (solid line) and  $N = 2.0$  (dashed line).

$x \rightarrow \pm\infty$  must be shifted by the constant  $-A - \epsilon_H(N = 3)$ . In accordance with Eq. (21), the ensemble exchange potential displays its corresponding derivative discontinuity. In Fig. 1(d), the difference between the curves for  $N = 2.01$  and  $N = 2.0$  is  $-A[v] - \epsilon_L(N = 2.0)$ . If we shifted the solid curve by  $-A[v] - \epsilon_H(N = 2.0)$  ( $A[v] = E_1[v] - E_2[v]$ ) and compared the shifted curve (which is  $\lim_{N \rightarrow 2^-} v_X$ ) with the curve for  $N = 2.01$ , we would observe the discontinuity shown in Eq. (21) around the center of the one-dimensional atom. On the other hand, the KS potential far from the center is given by  $u_s(x) \rightarrow \text{Const.} + 1/(2\phi_2)d^2\phi_2/dx^2$ . When the number of electrons is slightly increased above  $N = 2$ , we are adding a density  $\delta n = \epsilon n_3$  with a slower asymptotic decay than that of the system with two electrons, causing the discontinuity in Fig. 1(d) because  $\delta n(x)$  only affects the potential at distances that are far from the center.

We stress that a functional approximation for discrete states is enough to determine, through Eq. (12), an approximation to the XC functional that is also applicable to ensembles. However, solving the linearity problem in DFA's is not enough to solve the problem of molecular dissociation, which is caused by incorrect electron delocalization. A possible solution is to induce localization by partitioning a molecule into subsystems or a system-bath complex [25]. In such a case, a functional with the correct DD is required since the theory of ensembles provides a rigorous framework for defining energy functionals of open systems. This idea follows the main argument of Ref. [4] pointing to the importance of the XC DD.

#### IV. CONCLUSIONS

We presented a formal framework to extend density functional approximations of pure-state systems to be applicable to densities that integrate to fractional numbers of electrons. The main result, an exact condition, is a recursive formula relating the HXC energy with the KS kinetic energy evaluated at the noninteracting bordering densities, and the HXC and KS energies evaluated at the bordering interacting densities. However, the Hohenberg-Kohn-Mermin theorem expressing the densities  $n_M[u]$  as functionals of  $n(\mathbf{r})$  does not allow us to express  $E_{XC}[n]$  as an explicit functional of  $n(\mathbf{r})$ , not even when using explicit functionals of the discrete-electron densities. Thus, the ensemble  $v_{XC}(\mathbf{r})$  must be accessed through inversion.

## ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences, US Department of Energy, under Grant No. DE-FG02-10ER16196. A.W. also acknowledges support from an Alfred P. Sloan Foundation Research Fellowship.

## APPENDIX: PROOF OF EQ. (18)

Equation (12) is equivalent to

$$E_{\text{HXC}}[n] = -T_s[n] + \sum_M y(N-M)(T_s[n_M] + E_{\text{HXC}}[n_M]).$$

Set  $v = u[n]$  as fixed. We can add  $-\int d\mathbf{r}v(\mathbf{r})n(\mathbf{r}) + \int d\mathbf{r}v(\mathbf{r})n(\mathbf{r})$  to the right-hand side of the above equation to

yield

$$E_{\text{HXC}}[n] = -T_s[n] - \int d\mathbf{r}v(\mathbf{r})n(\mathbf{r}) + \sum_M y(N-M)E_v[n_M].$$

Suppose  $J-1 < N < J$ , and note that  $\delta T_s/\delta n(\mathbf{r}) = \epsilon_J - u_s[n](\mathbf{r})$  [26], where  $u_s[n] = v_{\text{HXC}}[n] + u[n]$ . Using the chain and product rules we get the equation leading to Eq. (18):

$$\begin{aligned} \frac{\delta E_{\text{HXC}}}{\delta n(\mathbf{r})} &= -\epsilon_J + u_s[n](\mathbf{r}) - v(\mathbf{r}) \\ &+ \sum_M \left\{ \frac{\delta N}{\delta n(\mathbf{r})} \frac{\partial y}{\partial x} (N-M) E_v[n_M] \right. \\ &\left. + y(N-M) \int d\mathbf{r}' \frac{\delta E_v[n_M]}{\delta n_M(\mathbf{r}')} \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})} \right\}, \end{aligned}$$

where

$$\frac{\partial y}{\partial x} = \begin{cases} \text{sgn}(-x) & -1 < x < 1 \\ 0 & \text{otherwise,} \end{cases}$$

and  $\delta N/\delta n(\mathbf{r}) = 1$ .

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## NEW VIEWS

### Derivative discontinuities in density functional theory

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(Received 16 July 2014; accepted 18 September 2014)

Fifty years after the original formulation of density functional theory (DFT), subtle consequences of the mathematical mappings underlying its formalism continue to merit new views. In this article, we discuss the origin, the importance, and the challenges associated with finding the derivative discontinuity of the exchange–correlation (XC) energy of DFT at integer–electron numbers. We show how even the energy of a quantum electron gas with finite volume and number of electrons displays such derivative discontinuities, but continuous density functional approximations to the XC functional miss them entirely. We discuss some of the practical problems that arise due to this lack of derivative discontinuities in standard functionals, and explain new ways to recover them.

**Keywords:** density functional theory; fractional number of electrons; exchange–correlation energy; derivative discontinuity; molecular dissociation

#### 1. Introduction

Density functional theory (DFT) has been an invaluable tool in modern physics and chemistry during the last 50 years [1]. DFT introduces a functional of the density for the energy, which upon minimisation becomes the exact ground-state energy of the molecule or solid. Density functional approximations (DFAs) have made the simulation of complex systems possible. Wave-function-based methods, on the other hand, despite their reliability for small molecules, are computationally highly demanding and yield information that is often not used, i.e., the wave-function itself. However, wave-function methods can be used to improve DFAs.

A DFA is usually constructed within Kohn–Sham (KS) DFT [2]. The existence of a system of non-interacting electrons subject to an appropriate external potential (the KS potential) is postulated. The exact KS potential forces the system to reproduce the ground-state density of the real molecule. It is given by the sum of the true external potential, the Hartree potential, and the exchange–correlation (XC) potential, given as the functional derivative of the XC energy functional, the only quantity that needs to be approximated. Approximations to the XC energy functional are either based on first principles or empirical. First-principles functionals are developed by forcing the DFA to satisfy known constraints of the exact functional, while empirical ones are developed to obtain the best estimates of the ground-state energy, and other properties, of a training set of molecules.

For electronic-structure calculations, the types of DFAs commonly used are the local density approximation (LDA) [3,4], generalised gradient approximation (GGA) [5–17], meta-GGA [18], hyper-GGA [19], DFAs based on the random phase approximation [20], and hybrid functionals [21,22]. Two main ideas lead the search for DFAs: (1) the DFA must reduce to the LDA in the electron gas limit, as well as satisfy known exact conditions, or (2) the DFA may not be reduced to the LDA in the electron gas limit or might not have formal properties, but it must be able to predict molecular properties within a certain range of tolerance.

In chemistry, standard DFAs are useful for estimating the ground-state energy of molecules along with their corresponding equilibrium geometries and spectra within the Born–Oppenheimer approximation [23]. However, the estimation of chemical reactivity properties, like formation energies, reaction barriers, etc., is still an active challenge [24]. This requires understanding of exchange and rearrangement processes where electrons are transferred between molecular fragments [25]. For a DFA to be reliable and accurate, it must take into account this highly relevant physical phenomenon. Understanding of quantum open systems is thus necessary [26]. These can be studied using the grand-canonical ensemble (GCE) at 0 K.

The GCE allows for random variations in the number of particles and introduces ground-state densities that integrate to a real number of electrons. An outcome of DFT in the GCE at 0 K is a quantity known as the derivative discontinuity (DD) of the XC energy. This quantity, when added

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to the exact single particle KS gap of a molecule (or solid), yields the exact fundamental gap. Nevertheless, DFAs, like the LDA and GGAs, usually underestimate the gap [27–29] due to the lack of XC DD. It is still imperative to derive functionals that simulate systems of interest in a reasonable amount of time, as well as to derive robust approximations that work for both molecular electronic structure and band-gap estimation.

DFT is exact, its basic theorems are well stated and based on sound quantum mechanical foundations [30]; there is an equivalence between quantum mechanics and DFT. Thus, readers must be advised about the use of language. An explicit form of the exact energy in terms of the density is, if not extremely difficult, impossible, as an exact analytical solution of the Schrödinger equation for all many-electron systems. Therefore, if a calculation fails, it is not DFT to blame, but the particular DFA used in such calculation. So far, there is no single DFA which is able to yield highly reliable results to all known applications. Instead, each functional has its own merits for performing in certain applications [31].

The failure of many DFAs in describing simple dissociation processes in molecules, for example, is due to their lack of integer discontinuity [32]. It has been shown that the lack of XC DD and the failure to describe the molecular dissociation are related [23]. For this reason, we present a review of DFT for open systems at 0 K, and new perspectives on the problem of the DD of the XC energy functional. We approach DFT using only full-body density matrices and derive all the steps that lead to the DD of the XC energy functional. We show that even the quantum electron gas (i.e., the finite electron gas), which is used to construct the paradigmatic model of most DFAs, i.e., the macroscopic electron gas, presents integer discontinuities. We also discuss a formulation we developed in Ref. [33] to relate the XC energy functional of densities that integrate to integer number of electrons with the exact XC energy functional for non-integer number of electrons. This formalism leads to extensions of the LDA, GGAs, and other functionals to the GCE. Our formulation derives from earlier observations made by Casida [34] and Harbola [35] on the problem of KS-DFT for ensembles and Janak’s theorem, and it also extends a recent work by Kraisler and Kronik [36]. This paper is organised as follows: in Section 2, we present basic definitions concerning DFT in the GCE. Several theorems leading to the DD of the XC energy functional are shown in Section 3. The practical relevance of XC DD is then discussed in Section 4. Section 5 presents new developments in the calculation of the integer discontinuities. Finally, future directions are highlighted in Section 6.

## 2. Density functional theory

In this section, we introduce essential aspects and definitions of ground-state DFT, needed for understanding Sec-

tions 3–6. To begin our discussion, let us consider a system of  $J$  electrons under the influence of an external potential  $v(\mathbf{r})$ , which describes the interaction between an electron and the nuclei. For example, if there are  $M_N$  nuclei, then

$$v(\mathbf{r}) = \sum_{I=1}^{M_N} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}, \quad (1)$$

where  $Z_I$  is the charge of the  $I$ th nucleus, and  $\mathbf{R}_I$  is its position vector. The external potential operator for  $J$  electrons is obtained from the potential  $v$  by means of

$$\hat{V}_{\text{ext},J} = \sum_{i=1}^J v(\hat{\mathbf{r}}_i), \quad (2)$$

where  $\hat{\mathbf{r}}_i$  is the position operator for the  $i$ th particle. For states with any number of particles, we employ second quantisation. For example, the non-relativistic Hamiltonian is

$$\hat{H}[v] = \hat{T} + \hat{W} + \hat{V}_{\text{ext}}[v], \quad (3)$$

where  $\hat{T}$  is the kinetic energy operator (expressed in terms of creation,  $\hat{\psi}^\dagger(\mathbf{r})$ , and annihilation,  $\hat{\psi}(\mathbf{r})$ , operators)

$$\hat{T} = \sum_{\sigma} \frac{1}{2} \int d^3\mathbf{r} (\nabla \hat{\psi}_{\sigma}^\dagger(\mathbf{r})) \cdot (\nabla \hat{\psi}_{\sigma}(\mathbf{r})), \quad (4)$$

$\hat{W}$  is the electron–electron repulsion operator:

$$\hat{W} = \sum_{\sigma,\sigma'} \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \hat{\psi}_{\sigma}^\dagger(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}), \quad (5)$$

and  $\hat{V}_{\text{ext}}$  is the external potential operator in second quantisation:

$$\hat{V}_{\text{ext}}[v] = \int d^3\mathbf{r} v(\mathbf{r}) \hat{n}(\mathbf{r}). \quad (6)$$

Here,  $\hat{n}(\mathbf{r})$  is the density operator of the system,  $\hat{n}(\mathbf{r}) = \sum_{\sigma} \hat{\psi}_{\sigma}^\dagger(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r})$ . The last term,  $\hat{V}_{\text{ext}}[v]$ , is a functional of the potential  $v$ .

The state of an electronic system of  $J$  electrons is determined by a wave-function defined in the Hilbert space of  $J$ -electron wave-functions ( $\mathcal{H}_J$ ). The ground-state energy is

$$E_J[v] = \min_{\psi \in \mathcal{H}_J} \langle \psi | \hat{H}[v] | \psi \rangle. \quad (7)$$

Here, the search for the minimum is carried out over all  $J$ -electron functions. The ground-state energy is a functional of the external potential. Now let us denote the ground



state of the system as  $|\psi_J[v]\rangle$ , so the ground-state density is

$$\tilde{n}_J[v](\mathbf{r}) = \langle \psi_J[v] | \hat{n}(\mathbf{r}) | \psi_J[v] \rangle. \quad (8)$$

Equation (7) can be recast in the form:

$$E_J[v] = \langle \psi_J[v] | \hat{T} + \hat{W} | \psi_J[v] \rangle + \int d^3\mathbf{r} \tilde{n}_J[v](\mathbf{r}) v(\mathbf{r}). \quad (9)$$

The last term is simply the integral of the product of two real-valued functions. Equation (8) can be used to generate a map between a space of potentials  $\mathcal{V}$  and a set of  $J$ -particle ground-state densities  $\mathcal{D}_J = \tilde{n}_J[\mathcal{V}]$ . Hohenberg and Kohn [37] (HK) proved that there is a bijection between  $\mathcal{D}_J$  and  $\mathcal{V}$ . Thus, a given density  $n \in \mathcal{D}_J$  determines the potential of the system, and therefore all the observables of the system because the ground-state wave-function is a functional of the external potential. The HK theorem gave birth to DFT as a well-founded theory.

The next step in the HK formulation is the introduction of the functional:

$$F_{\text{HK}}[n] = \langle \psi[n] | \hat{T} + \hat{W} | \psi[n] \rangle \quad (10)$$

and the energy density functional:

$$E_{\text{HK}}[n; v] = F_{\text{HK}}[n] + \int d^3\mathbf{r} n(\mathbf{r}) v(\mathbf{r}), \quad (11)$$

where the external potential is fixed. Thus, the ground-state energy of the system can be obtained as

$$E_J[v] = \min_{n \in \mathcal{D}_J} E_{\text{HK}}[n; v]. \quad (12)$$

A known problem of the functional defined in Equation (11) is its domain: the space  $\mathcal{D}_J$  is restricted only to densities that correspond to ground states. This problem was solved by Levy [38], who introduced the constrained search functional:

$$F_J^*[n_J] = \min_{\psi_J \rightarrow n_J} \langle \psi_J | \hat{T} + \hat{W} | \psi_J \rangle, \quad (13)$$

where the search is again over  $\mathcal{H}_J$ , under the constraint that  $\langle \psi_J | \hat{n}(\mathbf{r}) | \psi_J \rangle = n(\mathbf{r})$ . The domain of  $F_J^*$  is larger than that of  $F_{\text{HK}}$  because now densities that correspond to wave-functions that are not ground states are allowed. Lieb [30] showed that ensemble densities may not be included in the domain of  $F_J^*$ , and that the following functional solves such problem and has a larger domain:

$$F_J[n_J] = \min_{\hat{\Gamma}_J \rightarrow n_J} \text{Tr}\{(\hat{T} + \hat{W})\hat{\Gamma}_J\}, \quad (14)$$

where  $\hat{\Gamma}_J$  is a density matrix including excited states of the system with  $J$  electrons:

$$\hat{\Gamma}_J = \sum_k w_{J,k} |\psi_{J,k}\rangle \langle \psi_{J,k}|, \quad \sum_k w_{J,k} = 1. \quad (15)$$

Here, the index  $k$  runs over all the energy states. Thus, the ground-state energy can be obtained through the minimisation:

$$E_J[v] = \min_n \left\{ F_J[n] + \int d^3\mathbf{r} n(\mathbf{r}) v(\mathbf{r}) \mid \int d^3\mathbf{r} n(\mathbf{r}) = J \right\}. \quad (16)$$

We refer to a functional like  $F_J$  as a discrete-particle-state functional because the number of electrons is an integer and the molecule, or solid, is treated as a closed system.

### 2.1. Search over density matrices

The DFT approach described above only considers densities that integrate to an integer number of electrons. No physically meaningful fluctuations of the number of electrons, or fractional numbers of electrons are taken into account. Now, we want to study densities satisfying

$$\int d^3\mathbf{r} n(\mathbf{r}) \in \mathbb{R}^+ \cup \{0\}. \quad (17)$$

How can one introduce extended functionals that are valid for any number of electrons? The basic principles mentioned in the previous section, which are based purely on quantum mechanics (the theory of discrete numbers of electrons), do not provide a clear path for introducing fractional numbers of electrons. A natural step is to invoke statistical mechanics for open systems at  $0^+ \text{ K}$  [39], i.e., the GCE. We imagine that the molecules of the ensemble are separated from each other, but they can exchange electrons [40] in a macroscopic time scale. Thus, our isolated open molecules can have a mean number of electrons (or time-averaged number) that is controlled by a chemical potential. Alternatively, an equivalent physical picture is this: we place the molecule in contact with a distant metallic lead. Once equilibrium is reached, the statistical population of electrons in the molecule can be controlled again by the chemical potential of the system [41].

To describe the above physical picture, let  $\hat{\Gamma}$  be the grand-canonical density operator:

$$\hat{\Gamma}[v](\beta) = \sum_{M,k} w_{M,k}[v](\beta) |\Psi_{M,k}[v]\rangle \langle \Psi_{M,k}[v]|, \quad (18)$$

where  $|\Psi_{M,k}[v]\rangle$  is the  $k$ th state wave-function of the molecule with  $M$  electrons. The probability of finding a

molecule in the  $M, k$  state is

$$w_{M,k}[v](\beta) = \langle \Psi_{M,k}[v] | \hat{\Gamma}[v](\beta) | \Psi_{M,k}[v] \rangle \\ = \frac{\exp(-\beta(E_{M,k}[v] - \mu M))}{\Xi[v](\beta, \mu)}. \quad (19)$$

Here,  $\Xi$  is the grand-canonical partition function of the molecule:

$$\Xi[v](\beta, \mu) = \text{Tr}\{\exp(-\beta(\hat{H}[v] - \mu \hat{N}))\} \\ = \sum_{M,k} \exp(-\beta(E_{M,k}[v] - \mu M)), \quad (20)$$

where  $\hat{N}$  is the electron-number operator. For a molecule in the ensemble, under the appropriate experimental conditions, it is possible to fix the average number of electrons, which will be denoted as  $N$  and can be calculated as  $N = \text{Tr}[\hat{N}\hat{\Gamma}]$ .

For a system at  $0^+ \text{ K}$ , the average energy of the system ( $E_N[v]$ ) can be calculated by means of

$$E_N[v] = \lim_{\beta \rightarrow \infty} \text{Tr}[\hat{\Gamma}[v](\beta) \hat{H}[v]]. \quad (21)$$

This approach is based on wave-functions, which can be avoided with the following functional defined by Perdew *et al.* [26]<sup>1</sup>:

$$E[n; v] := F[n] + \int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r}), \quad (22)$$

where  $F$  is defined as

$$F[n] := \min_{\hat{\Gamma} \rightarrow n} \text{Tr}\{\hat{\Gamma}(\hat{T} + \hat{W})\}. \quad (23)$$

The search for the minimum is performed over the Liouville space of density matrices that integrate to the density  $n$ . That is,

$$\hat{\Gamma} = \sum_{M,k} w_{M,k} |\psi_{M,k}\rangle \langle \psi_{M,k}|, \quad \sum_{M,k} w_{M,k} = 1. \quad (24)$$

Another functional of interest is the grand-canonical functional

$$\Omega[n; v, \mu] = F[n] + \int d^3\mathbf{r} (v(\mathbf{r}) - \mu)n(\mathbf{r}), \quad (25)$$

where  $\mu$  is the electronic chemical potential. Mermin [42] proved that the grand potential  $\Omega$  is a functional of the density, that there is a density that minimises this functional (with the restriction that it integrates to a given number of electrons), and that the HK principle applies as well.

The minimum of Equation (22) is the minimum of

$$E[v](\{w_M\}) = \sum_M w_M E_M[v], \quad (26)$$

where  $v$  is fixed and the weight coefficients  $\{w_M\}$  are constrained to

$$\sum_{M=1}^{\infty} M w_M = N, \\ \sum_{M=1}^{\infty} w_M = 1. \quad (27)$$

Suppose that  $J-1 < N < J$ , and assume that the ground-state energy is a convex function of the number of electrons, i.e.,

$$I \geq A, \quad (28)$$

for all  $J$ , where  $I$  and  $A$  are the ionisation and affinity, respectively. These quantities are defined as follows:

$$I = E_{J-1} - E_J, \\ A = E_J - E_{J+1}. \quad (29)$$

The result of the minimisation problem is a linear interpolation equation whose end points are the energies of the systems with integer numbers of electrons that are nearest to  $N$ :

$$E_N[v] = (1 - \omega)E_{J-1}[v] + \omega E_J[v]. \quad (30)$$

Here,  $\omega = N - J + 1$ , and  $0 < \omega < 1$ . The equilibrium density of the system is

$$n(\mathbf{r}) = (1 - \omega)n_{J-1}(\mathbf{r}) + \omega n_J(\mathbf{r}). \quad (31)$$

Extending the result for all  $N$ , we find that  $E_N[v]$  as a function of  $N$  is a series of straight lines, as illustrated in Figure 1. Alternatively, we can use Equation (18) to find the graph illustrated in Figure 1. Equation (18) also allows us to find a relationship between the average number of electrons  $N$  and the chemical potential, i.e.,

$$\begin{cases} J-1 < N < J & \text{if } (-\mu) = I \\ N = J & \text{if } A < (-\mu) < I \\ J < N < J+1 & \text{if } (-\mu) = A \end{cases}. \quad (32)$$

Figure 2 illustrates the behaviour of the average number of electrons in terms of the chemical potential. It can be noted that for integer number of electrons there is something similar to a phase transition, with a DD in the energy as function of  $N$  when the number of electrons equals  $J$ , for any integer  $J$ . This important feature of  $E_N[v]$  is the main

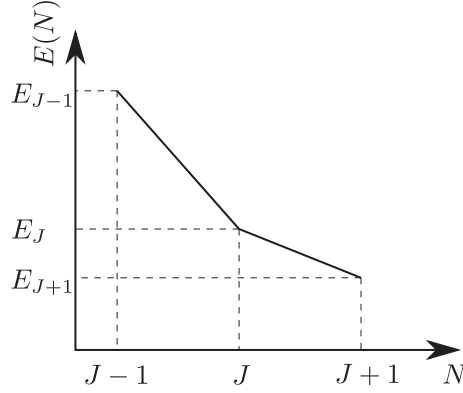


Figure 1. Linear interpolations of ground-state energies.

focus of this work. To approach it, we first need to discuss a purely density-functional framework to determine how the DD in Figures 1 and 2 is related to that of  $E[n; v]$ .

## 2.2. Kohn–Sham DFT

Kohn and Sham [2] defined an auxiliary system of non-interacting electrons to represent the ground-state density. For a system of  $J$  electrons, the ground state of this auxiliary system is given by the Slater determinant  $|\Phi_{J,s}\rangle$  formed by the set of single-particle orbitals  $\{\phi_i\}$ . This is usually denoted as  $|\Phi_{J,s}\rangle = |\phi_1 \dots \phi_J\rangle$ . A given density  $n(\mathbf{r})$  is represented by minimising the kinetic energy:

$$\min_{\Phi_{J,s} \rightarrow n} \sum_{i=1}^J \langle \phi_i | \hat{T} | \phi_i \rangle. \quad (33)$$

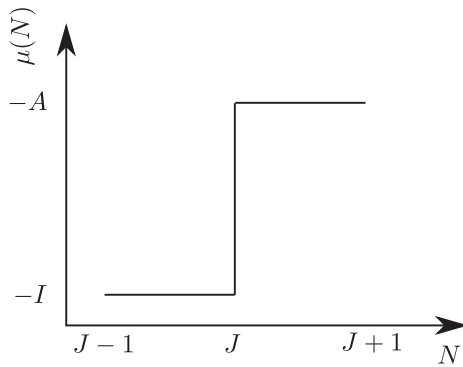


Figure 2. Chemical potential as a function of the number of electrons.

If the density integrates to a non-integer number of electrons, we employ

$$T_s[n] = \min_{\hat{\Gamma}_s \rightarrow n} \text{Tr}\{\hat{T} \hat{\Gamma}_s\}. \quad (34)$$

The density matrix  $\hat{\Gamma}_s$  is defined in a non-particle-conserving Fock space of Slater determinants, which are antisymmetrised products of KS orbitals. These orbitals satisfy the KS equations:

$$\left( \hat{T} + \int d^3\mathbf{r} v_s[n](\mathbf{r}) \hat{n}(\mathbf{r}) \right) |\phi_i[n]\rangle = \epsilon_a[n] |\phi_i[n]\rangle, \quad (35)$$

where  $v_s$  is the KS potential, whose purpose is to enforce that  $\text{Tr}\{\hat{\Gamma}_s \hat{n}(\mathbf{r})\} = n(\mathbf{r})$ .

The energy functional in Equation (22) can then be expressed as

$$E[n; v] = T_s[n] + E_{\text{HXC}}[n] + \int d^3\mathbf{r} n(\mathbf{r}) v(\mathbf{r}), \quad (36)$$

where

$$E_{\text{HXC}}[n] = E_{\text{H}}[n] + E_{\text{XC}}[n]. \quad (37)$$

The Hartree functional is  $E_{\text{H}}[n] = 1/2 \int d^3\mathbf{r} d^3\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ , and  $E_{\text{XC}}[n]$  is the XC energy functional. The minimisation of Equation (36) over  $n(\mathbf{r})$  yields the Euler–Lagrange equation

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu, \quad (38)$$

where

$$v_s(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) + v(\mathbf{r}), \quad (39)$$

and

$$v_{\text{H}}(\mathbf{r}) = \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (40)$$

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})},$$

where the latter is the XC potential.

Using the definitions of  $T_s$  and  $F$  we obtain

$$E_{\text{HXC}}[n] = \min_{\hat{\Gamma} \rightarrow n} \text{Tr}\{(\hat{T} + \hat{W}) \hat{\Gamma}\} - \min_{\hat{\Gamma}_s \rightarrow n} \text{Tr}\{\hat{T} \hat{\Gamma}_s\}. \quad (41)$$

This equation can be written as

$$E_{\text{HXC}}[n] = \int_0^1 d\lambda \frac{d}{d\lambda} \text{Tr}\{(\hat{T} + \lambda \hat{W}) \hat{\Gamma}[n](\lambda)\}, \quad (42)$$

where  $\hat{\Gamma}[n](\lambda)$  is the result of

$$\min_{\hat{\Gamma} \rightarrow n} \text{Tr}\{(\hat{T} + \lambda \hat{W})\hat{\Gamma}\}. \quad (43)$$

From the virial theorem, one obtains that

$$E_{\text{HXC}}[n] = \int_0^1 d\lambda \text{Tr}\{\hat{W}\hat{\Gamma}[n](\lambda)\}. \quad (44)$$

which can further be simplified as

$$E_{\text{HXC}}[n] = \text{Tr}\{\hat{W}\hat{\Gamma}^*[n]\}, \quad (45)$$

with  $\hat{\Gamma}^*[n] = \int_0^1 d\lambda \hat{\Gamma}[n](\lambda)$ . The above expression indicates that the HXC functional is determined by the average electron–electron repulsion, taken over a continuously differentiable path of states connecting the KS state with the fully interacting ground state. Clearly, the functional dependence of the HXC energy on  $n(\mathbf{r})$  is determined by that of the average state  $\hat{\Gamma}^*[n]$ .

### 3. Derivative discontinuities

The DD of the XC energy functional emerges from several fundamental properties of the KS kinetic and potential energies. Here, we present four theorems formally stating such properties.

#### 3.1. Theory

Minimisation of the functional  $E[n; v]$ , Equation (36), subject to the condition  $\int d^3\mathbf{r} n(\mathbf{r}) = N$ , where  $N$  is a positive real number, yields the ground-state energy  $E_N[v]$  and the ground-state density, which we denote as  $n_{v,N}(\mathbf{r})$ . The Hohenberg–Kohn–Mermin (HKM) theorem for ensembles establishes that there is a one-to-one mapping between the density  $n(\mathbf{r})$  and the pair  $v(\mathbf{r}), N$ , up to an arbitrary constant in  $v(\mathbf{r})$ . Throughout this section, we investigate the behaviour of the density-functionals  $E$ ,  $T_s$ , and  $E_{\text{HXC}}$  around the number of electrons  $J$ . If  $0 < \omega < 1$ , the ground-state ensemble densities satisfy:

$$\begin{aligned} n_{v,J+\omega}(\mathbf{r}) &= (1-\omega)n_{v,J}(\mathbf{r}) + \omega n_{v,J+1}(\mathbf{r}), \\ n_{v,J-\omega}(\mathbf{r}) &= (1-\omega)n_{v,J}(\mathbf{r}) + \omega n_{v,J-1}(\mathbf{r}). \end{aligned} \quad (46)$$

This indicates that a density in the ensemble is an average over pure-state densities corresponding to states with integer numbers of electrons.

Minimisation of  $E[n; v]$  subject to  $\int d^3\mathbf{r} n(\mathbf{r}) = N$  leads to the Euler–Lagrange equation:

$$\mu[n_{v,N}] = \left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{n_{v,N}}, \quad (47)$$

where  $\mu[n_{v,N}]$  is the chemical potential of the system. The chemical potential is a functional of the potential and the number of particles. Thus, it is also a functional of the density  $n_{v,N}(\mathbf{r})$ , so we express it as  $\mu[n_{v,N}]$ . Denoting the ionisation and affinity of the system as  $I_{v,J}$  and  $A_{v,J}$ , respectively (now including the dependency on  $v$ ), then, as mentioned in Section 2.1, the chemical potential satisfies

$$\mu[n_{v,N}] = \begin{cases} -I_{v,J} & (J-1 < N < J), \\ -A_{v,J} & (J < N < J+1). \end{cases} \quad (48)$$

The chemical potential  $\mu[n_{v,J}]$  can have any value between  $-I_{v,J}$  and  $-A_{v,J}$ . Although the chemical potential is not uniquely defined at  $J$ , its limits are. Hence, the integer discontinuity along a path of ground-state densities  $n_{v,N}$  is defined as

$$\Delta_{\mu,v}(J) = \lim_{\omega \rightarrow 0^+} \{\mu[n_{v,J+\omega}] - \mu[n_{v,J-\omega}]\} = I_{v,J} - A_{v,J}. \quad (49)$$

An alternative expression for the above quantity is

$$\Delta_{\mu,v}(J) = \lim_{\omega \rightarrow 0^+} \left\{ \left. \frac{\delta E_v}{\delta n(\mathbf{r})} \right|_{n_{v,J+\omega}} - \left. \frac{\delta E_v}{\delta n(\mathbf{r})} \right|_{n_{v,J-\omega}} \right\}. \quad (50)$$

From Equation (22), we note that the term  $\int d^3\mathbf{r} v(\mathbf{r})n(\mathbf{r})$  is continuous. Therefore, the DD of  $E[n; v]$  is the same as that of the functional  $F$  of Equation (23), which is expanded as

$$F[n] = T_s[n] + E_{\text{H}}[n] + E_{\text{XC}}[n]. \quad (51)$$

The functional  $T_s$  represents the kinetic energy of an ensemble of systems with non-interacting electrons. The average density of a member of the ensemble is given by

$$n(\mathbf{r}) = \sum_{\alpha} f(\mu - \epsilon_{\alpha}) |\phi_{\alpha}(\mathbf{r})|^2. \quad (52)$$

The occupation numbers are determined by the Fermi–Dirac distribution:

$$f(\mu - \epsilon_{\alpha}) = \left. \frac{1}{1 + \exp(\beta(\mu - \epsilon_{\alpha}))} \right|_{\beta \rightarrow \infty}. \quad (53)$$

They can be expressed as

$$f(\mu - \epsilon_{\alpha}) = \begin{cases} 1 & (\epsilon_{\alpha} < \mu) \\ \omega & (\epsilon_{\alpha} = \mu) \\ 0 & (\epsilon_{\alpha} > \mu). \end{cases} \quad (54)$$

The restriction in Equation (34) that the sum of squared orbitals yields a prescribed density gives rise to a multiplicative local potential, a Lagrange multiplier. Such multiplier is the well-known KS potential  $v_s(\mathbf{r})$ . As in the case of ensembles of interacting electrons, there is an invertible map

between  $n(\mathbf{r})$  and the pair  $v_s(\mathbf{r})$ ,  $N$ . Let us denote such map as  $\mathcal{D}_s$ . We will also employ the map between potentials and densities that integrate to  $N$  electrons only and their corresponding potentials. Let us denote such map as  $\mathcal{B}_{s,N}$ . This map is useful to define the linear response functions.

We now analyse the discontinuity of the KS kinetic energy potential:

$$\Delta_{s,v}(J) = \lim_{\omega \rightarrow 0^+} \left\{ \left. \frac{\delta T_s}{\delta n(\mathbf{r})} \right|_{n_{v,J+\omega}} - \left. \frac{\delta T_s}{\delta n(\mathbf{r})} \right|_{n_{v,J-\omega}} \right\}, \quad (55)$$

which first requires the following theorem:

**Theorem 3.1:** *Let  $\epsilon_H[n_{v,N}]$  be the highest occupied molecular orbital (HOMO) of the system with  $N$  electrons. Formally, it is defined as*

$$\epsilon_H[n_{v,N}] = \begin{cases} \epsilon_{J+1}[n_{v,N}] & (J < N \leq J+1) \\ \epsilon_J[n_{v,N}] & (J-1 < N \leq J) \end{cases} \quad (56)$$

*If  $N$  is a non-integer number of electrons, then the functional derivative of the KS kinetic energy functional is*

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_{v,N}} = \epsilon_H[n_{v,N}] - v_s[n_{v,N}](\mathbf{r}). \quad (57)$$

**Proof:** This proof follows that of Liu and Ayers [43] for discrete-particle states. Suppose that the density  $n(\mathbf{r})$  integrates to a number of electrons  $J + \omega$ . The KS kinetic energy can be expressed as

$$T_s[n] = \sum_{\alpha=1}^J \langle \phi_\alpha | \hat{T} | \phi_\alpha \rangle + \omega [n] \langle \phi_H | \hat{T} | \phi_H \rangle. \quad (58)$$

Here, the KS orbitals are normalised and are functionals of the density  $n(\mathbf{r})$ . The coefficient  $\omega$  is a functional of the density as well:

$$\omega[n] = \int d^3\mathbf{r} n(\mathbf{r}) - J. \quad (59)$$

Hence, a variation of  $T_s$  around  $J + \omega$  is

$$\delta T_s = \sum_{\alpha=1}^{J+1} f_\alpha \langle \delta \phi_\alpha | \hat{T} | \phi_\alpha \rangle + \text{c.c.} + \delta \omega \langle \phi_H | \hat{T} | \phi_H \rangle, \quad (60)$$

where  $f_\alpha = 1$  if  $\alpha = 1, \dots, J$ , and  $f_{J+1} = \omega$ . Using the KS equations, it is easy to show that

$$\begin{aligned} \delta T_s &= \sum_{\alpha=1}^{J+1} \epsilon_\alpha f_\alpha \langle \delta \phi_\alpha | \phi_\alpha \rangle - \int d^3\mathbf{r} v_s(\mathbf{r}) \left( \sum_{\alpha=1}^{J+1} f_\alpha \delta |\phi_\alpha(\mathbf{r})|^2 \right) \\ &\quad + \epsilon_H \delta \omega - \int d^3\mathbf{r} v_s(\mathbf{r}) \delta \omega |\phi_H(\mathbf{r})|^2. \end{aligned} \quad (61)$$

Because the orbitals are normalised and

$$\delta n(\mathbf{r}) = \sum_{\alpha=1}^{J+1} f_\alpha \delta |\phi_\alpha(\mathbf{r})|^2 + \delta \omega |\phi_H(\mathbf{r})|^2, \quad (62)$$

we obtain

$$\delta T_s = \epsilon_H \delta \omega - \int d^3\mathbf{r} v_s(\mathbf{r}) \delta n(\mathbf{r}). \quad (63)$$

Finally, by noting that  $\delta \omega = \int d^3\mathbf{r} \delta n(\mathbf{r})$  we obtain

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} = \epsilon_H[n] - v_s[n](\mathbf{r}). \quad (64)$$

Evaluation at  $n_{v,N}(\mathbf{r})$  yields Equation (57). It must be remarked that this result is valid for non-integer numbers of electrons.  $\square$

This theorem, applied to Equation (47), leads directly to Janak's theorem [44]:

$$\begin{aligned} \epsilon_H[n_{v,N}] &= \left. \frac{\delta E_v}{\delta n(\mathbf{r})} \right|_{n_{v,N}} \\ &= \mu[n_{v,N}]. \end{aligned} \quad (65)$$

**Theorem 3.2:** *The HOMO of a KS system of non-interacting electrons representing the density  $n_{v,N}(\mathbf{r})$  satisfies*

$$\epsilon_H[n_{v,N}] = \begin{cases} -A_{v,J} & (J < N \leq J+1) \\ -I_{v,J} & (J-1 < N \leq J) \end{cases} \quad (66)$$

A proof of this result can be found in Ref. [35]. The above theorem is valid as long as  $\lim_{r \rightarrow \infty} v_s(\mathbf{r}) = 0$ .

In order to find the discontinuity of the kinetic potential, one has to find the discontinuity of the HOMO energy and the KS potential. However, note that the addition of a constant function  $C_{v,N}$  to the KS potential (or the HOMO energy) does not affect the density. From the KS equations, we note that the quantity  $\epsilon_H[n_{v,N}] - v_s[n_{v,N}](\mathbf{r})$  is not arbitrary by a constant. Therefore, the DD of  $T_s$  is unique.

**Theorem 3.3:** *Let  $N = J + \omega$ . If the density  $n_{v,N}(\mathbf{r})$  can be represented by a system of non-interacting electrons under the potential  $v_s(\mathbf{r}; \omega)$ , then  $v_s(\mathbf{r}; \omega)$  satisfies, as  $\omega \rightarrow 0^+$ ,*

$$\begin{aligned} \delta v_s^+(\mathbf{r}; \omega) &= \omega \int d^3\mathbf{r}' \chi_{s,J}^{-1}(\mathbf{r}, \mathbf{r}') \\ &\quad \times (\Delta n^+(\mathbf{r}) - |\phi_L[n_{v,J}](\mathbf{r}')|^2), \end{aligned} \quad (67)$$

where

$$\chi_{s,J}(\mathbf{r}, \mathbf{r}') = \left( \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} \right)_{N=J} \quad (68)$$

**Proof:** Suppose that the density  $n_{v,J}(\mathbf{r})$  can be represented by a system with KS potential  $v_s[n_{v,J}](\mathbf{r})$ . If the number of electrons is increased by a small quantity  $\omega$  then the density  $n_{v,J+\omega}(\mathbf{r})$  can be expressed as

$$n_{v,J+\omega}(\mathbf{r}) = n_{v,J}(\mathbf{r}) + \delta n_\omega(\mathbf{r}), \quad (69)$$

where

$$\delta n_\omega(\mathbf{r}) = \omega \Delta n^+(\mathbf{r}), \quad (70)$$

and  $\Delta n^+(\mathbf{r}) = n_{v,J+1}(\mathbf{r}) - n_{v,J}(\mathbf{r})$ . The term  $\delta n_\omega(\mathbf{r})$  is a perturbation involving the addition of an electron to the ensemble. Note that the perturbation in the density is in general non-local; it should induce a non-local response in the potential  $\delta v_s(\mathbf{r})$ . Additionally, the perturbed density can be assumed to be of the form  $n_{v,J+\omega}(\mathbf{r}) = \mathcal{D}_s[v_s + \delta v_s^+](J + \omega)$ . Hence, we can write (ignoring higher order responses)

$$\delta n_\omega(\mathbf{r}) = \int d^3\mathbf{r}' \left( \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} \right)_{N=J} \delta v_s^+(\mathbf{r}') + \omega \left( \frac{\partial n(\mathbf{r})}{\partial N} \right)_{v_s, N=J}^+. \quad (71)$$

The functional derivative in Equation (71) is  $\chi_{s,J}(\mathbf{r}, \mathbf{r}')$ , the KS linear response function for the system with  $J$  electrons, Equation (68). To evaluate such quantity one needs the map  $\mathcal{B}_{s,J}$  discussed just before Theorem 1.

The partial derivative in Equation (71) corresponds to the variation of the density when the KS potential is *fixed* at  $v_s(\mathbf{r})$ . The super-index  $+$  denotes the derivative taken on the positive side of  $J$ . If the KS potential is fixed, then the extra electron would occupy the lowest occupied molecular orbital (LUMO) orbital of the molecule with  $J$  electrons. Therefore,

$$\left( \frac{\partial n(\mathbf{r})}{\partial N} \right)_{N=J, v_s}^+ = |\phi_L[n_{v,J}](\mathbf{r})|^2. \quad (72)$$

Using this equation together with Equations (70), we can solve for  $\delta v_s^+$  in Equation (71) by multiplying on both sides by the inverse of  $\chi_{s,J}(\mathbf{r}, \mathbf{r}')$ , obtaining Equation (67). This equation allows us to conclude that  $\delta v_s^+ \rightarrow 0$  as  $\omega \rightarrow 0^+$ . Thus, the potential,

$$v_s(\mathbf{r}; \omega) = v_s[n_{v,J}](\mathbf{r}) + \delta v_s^+(\mathbf{r}; \omega), \quad (73)$$

can be taken as a continuous function of  $\omega$ .  $\square$

It is worthwhile noting that  $\delta v_s^+(\mathbf{r})/\omega$  does not tend to zero as  $\mathbf{r} \rightarrow \infty$ . Therefore, the same analysis applied to the removal of an electron from the  $J$ -electron system shows that  $\delta v_s(\mathbf{r})/\omega$  is discontinuous.

**Theorem 3.4:** *The KS potential  $v_s[n_{v,J+\omega}]$  is a discontinuous function of  $\omega$  satisfying [41]*

$$\lim_{\omega \rightarrow 0^+} (v_s[n_{v,J+\omega}] - v_s[n_{v,J-\omega}]) = C_{XC,v}, \quad (74)$$

where  $C_{XC,v}$  is a constant.

**Proof:** Theorem 3 established that  $n_{v,J+\omega}(\mathbf{r})$  is represented by  $v_s(\mathbf{r}; \omega)$  as  $\omega \rightarrow 0^+$ . Due to the HKM theorem [42], the map  $\mathcal{D}_s$  is one-to-one. Hence, this potential tends to  $v_s[n_{v,J}]$ , which is the potential for which  $\epsilon_J = -I_{v,J}$ . This implies that

$$\lim_{\omega \rightarrow 0^+} \epsilon_{J+1}[v_s(\omega)] = \epsilon_L, \quad (75)$$

is apparent violation of Janak's theorem. The only way to resolve this is by allowing the KS potential, as functional of  $n_{v,J+\omega}$ , to satisfy

$$\lim_{\omega \rightarrow 0^+} v_s[n_{v,J+\omega}] = v_s[n_{v,J}] + C_{XC,v}. \quad (76)$$

This does not violate the HKM theorem because the addition of a constant does not affect the density, but the eigenvalues depend on such constant.  $\square$

Since we demanded that the functional  $v_s[n_{v,N}](\mathbf{r})$  vanish in the asymptotic region, the order in which limits are taken is important. For example, note that

$$\lim_{\omega \rightarrow 0^+} \lim_{|\mathbf{r}| \rightarrow \infty} v_s[n_{v,J+\omega}](\mathbf{r}) = 0, \quad (77)$$

but [41]

$$\lim_{|\mathbf{r}| \rightarrow \infty} \lim_{\omega \rightarrow 0^+} v_s[n_{v,J+\omega}](\mathbf{r}) = C_{XC,v}. \quad (78)$$

As we mentioned before, the DD of  $T_s[n]$  is unique, so it is not affected by a constant in the potential. Now, the map  $\mathcal{D}_s$  evaluated at  $v_s(\mathbf{r}, \omega)$ ,  $J + \omega$  allows us to write

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_{v,J+\omega}} = \epsilon_{J+1}[v_s(\omega)] - v_s(\mathbf{r}; \omega). \quad (79)$$

Given that  $\epsilon_{J+1}[v_s(\mathbf{r}; \omega)] \rightarrow \epsilon_L$ , we conclude that

$$\Delta_{s,v}(J) = \epsilon_L[n_{v,J}] - \epsilon_H[n_{v,J}]. \quad (80)$$

where  $\epsilon_L[n_{v,J}]$  is the LUMO orbital of the molecule with  $J$  electrons.

Finally, since the Hartree functional is continuously differentiable and the external potential  $v(\mathbf{r})$  is fixed, the DD of the XC energy functional is

$$\begin{aligned} \Delta_{XC,v}(J) &= \lim_{\omega \rightarrow 0^+} \left\{ \left. \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \right|_{n_{v,J+\omega}} - \left. \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \right|_{n_{v,J-\omega}} \right\} \\ &= C_{XC,v} = -A_{v,J} - \epsilon_L[n_{v,J}], \end{aligned} \quad (81)$$

in agreement with Theorem 4. This quantity has a special property: when added to the KS gap  $\epsilon_L[n_{v,J}] - \epsilon_H[n_{v,J}]$ , the fundamental gap  $I_{v,J} - A_{v,J}$  is recovered. Continuous functionals like LDA and GGAs lack the DD in Equation (81),

causing serious difficulties in practical calculations such as those discussed next.

#### 4. Practical importance

The absence of XC DD in DFAs is responsible for many problems in applications to molecular and solid-state physics. In this section, we discuss the cases of molecular dissociation and energy gaps.

##### 4.1. Molecular dissociation

The energy changes involved in bond stretching yield the forces that drive the dynamics of chemical reactions, and binding energies for chemical thermodynamics. Let us consider a simple diatomic molecule,  $A - B$ . As the distance between  $A$  and  $B$  is increased, the energy of the molecule tends to be additive, and at infinite separation the molecule becomes a set of two isolated atoms. For instance, suppose that there is a small coupling between the two atoms, forcing them to exchange electrons. Suppose that the only two states available are  $A^- - B^+$  and  $A - B$ . In an ensemble of replicas of these states, the average energy is simply the average of the energies of those two states, weighed by their relative abundances, i.e., using the average charge of atom  $A$ ,  $x_A$ . The average energy, for a large bond length, is a linear function of  $x_A$ . On the other hand, if the system is only in either of the states  $A - B$  or  $A^+ - B^-$ , then the average energy would be a different linear function. When these two linear functions are joined, the energy shows a minimum and a DD at  $x_A = 0$  [26]. This observation is not featured by the LDA (or GGA). For example, if the charge is transferred from one atom to the other, one would observe that the LDA energy derivative is continuous [41] (also see Ref. [45]).

Practice tells us that LDA and GGAs tend to overestimate binding energies [24]. This error is caused by self-repulsion [or self-interaction error (SIE)]: these functionals are derived from the analysis of the homogeneous and nearly homogeneous electron gas, where the number of electrons is large, and where these functionals become exact. A diatomic molecule in its equilibrium distance is in a sense closer to an electron gas than each of its atoms. As the number of electrons increases, the effects of the self-repulsion decrease. However, at dissociation, the effects of self-repulsion are more severe on each atom. Thus, assuming that our DFA works well for the molecule at equilibrium separation, then it might not be so for the individual atoms (or fragments), over-estimating the binding energy.

Cohen *et al.* [46] (also see [47,48]) illustrated the deficiency of the LDA XC functional, which is common to a majority of DFAs, related to the SIE and erroneous electronic delocalisation. The exact XC functional satisfies

$$E_{XC}[n] = -E_H[n]; \quad N = 1 \quad (82)$$

( $E_{HXC}[n] = 0$  when  $N = 1$ ). Additionally, the exact functional  $E[n; v]$  satisfies size consistency. Let us consider an  $H_2^+$  molecule with its protons arranged in a horizontal axis, and let  $v_L$  and  $v_R$  be the electron-nucleus potentials corresponding to the left and right protons, respectively. The density of the  $H_2^+$  molecule, when the distance between the nuclei is large, is quite close to the sum of two ground-state densities, i.e.,  $n_L + n_R$ . The energy of the system satisfies

$$\begin{aligned} E[n_L + n_R; v] &\rightarrow E[n_L; v] + E[n_R; v] \\ &\approx E[n_L; v_L] + E[n_R; v_R]. \end{aligned} \quad (83)$$

The HXC energy functional also tends to be additive, i.e.,  $E_{HXC}[n_L + n_R] \rightarrow E_{HXC}[n_L] + E_{HXC}[n_R]$ . If we write  $n(\mathbf{r}) = \omega_L n_{L,1}(\mathbf{r}) + \omega_R n_{R,1}(\mathbf{r})$ , where  $n_{\alpha,1}(\mathbf{r})$  are densities integrating to one electron, and  $\omega_L$  and  $\omega_R$  are the occupation numbers of each fragment, in this case  $\omega_L = \omega_R = 1/2$ , then we could verify that  $E_{XC}^{LDA}[n] \neq \omega_L E_{XC}^{LDA}[n_{L,1}] + \omega_R E_{XC}^{LDA}[n_{R,1}]$  [49]. (We will also denote  $E[n; v]$  as  $Ev[n]$ ) For the case of a single H atom, the LDA total energy does not satisfy  $E^{LDA}[\omega n_1] = \omega E^{LDA}[n_1]$ ; neither the GGAs nor the LDA functional satisfy size-consistency in this ensemble sense.

The origin of the violation of size consistency in this ensemble sense is the delocalisation error caused by the SIE: because LDA violates Equation (82), it erroneously treats a single electron as a cloud of self-repelling charges, which is more spread out over the  $H_2^+$  molecule than the exact density. In general, if all the nuclei in the chain  $H_{M_p}^{(M_p - N_{tot})+}$  (where  $N_{tot}$  and  $M_p$  are the total number of electrons and protons, respectively, and  $N_{tot} < M_p$ ) are arranged in a lattice where the distance between each other is large, the energy of a single atom in the lattice would correspond to that of an atom with an average fractional charge  $(M_p - N_{tot})/M_p$ . However, the spurious density delocalisation and self-interaction error cause the average-energy-per-atom curve to be convex and deviate from the exact one for this simple case (see Figure 3, recall that  $N$  is the average number of electrons per atom). Further addition of electrons to the chain leads to a curve of average-energy-per-atom vs. average number of electrons that misses the contribution from XC DD at  $N = 1$ . The observations of Cohen *et al.* [46] thus suggest that incorporating the correct piecewise linear dependency on the number of electrons is necessary to avoid the delocalisation error.

In general, the delocalisation/SIE error in DFAs is problematic when distances between atoms are large [50,51], and when the atoms have few electrons. There are many known cases where LDA and/or GGAs fail (for example, see [52–54]). In our opinion, it is easier to diagnose the error in a non-empirical functional than in an empirical one. Alternative approaches treat the delocalisation error as a problem of lack of references instead of lack of piecewise linear dependency on  $N$  (or lack of DD). Works addressing this problem of quasi-degenerate states are reported in the

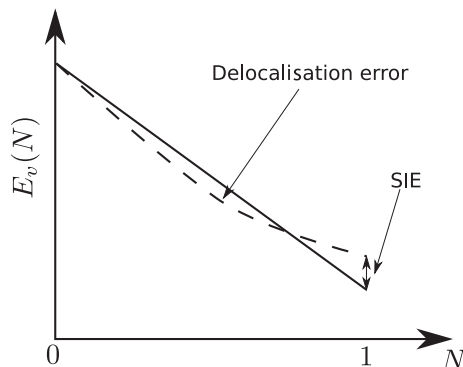


Figure 3. Sketch of the average electronic energy of a hydrogen atom, in the chain  $H_{M_p}^{(M_p-N_{tot})+}$ , as function of its average number of electrons. Solid line, exact; dashed line, LDA.

literature, especially considering multi-references and/or configuration interaction of KS wave-functions [55–64]. However, KS-DFT, as discussed here, is a single reference theory.

#### 4.2. Energy gaps

Consider the example of the previous subsection, the A–B system. The energy of an atom, for example, A, is an average of two states with the nearest number of integer number of electrons. Moreover, in agreement with Section 2.1, the average energy of A is a piecewise linear function of the number of electrons and displays a DD, which constitutes the fundamental gap of the atom. The energy as a function of the number of electrons should be piecewise linear, not piecewise non-linear. The XC energy functional has a DD as well, which replaces the LUMO energy by the affinity of the system (Theorem 4). This discontinuity is missed by continuously differentiable functionals. One can approximate the XC DD using complicated forms in terms of the occupation numbers. However, we remark that piecewise linear dependency is stronger than DD because the former implies the latter, and not the other way around.

Due to the lack of  $\Delta_{XC}$ , roughly speaking, the LDA XC method underestimates the band gap of solids by 40 % [7,65], and LSD over-estimates the electron affinity of atoms even with self-interaction correction [66]. The exact KS band gap ( $\epsilon_L - \epsilon_H$ ) cannot reproduce the fundamental gap of a molecule or the band gap of a solid. Hence, estimating the XC DD is an important goal for the DFT community. For applications in solid-state theory, the XC DD should ideally be an output from a single calculation over the unit cell of the solid with fixed number of electrons. This philosophy of calculation can be applied to isolated molecules as well [67]. One could use the LUMO

orbital density to approximate the density of a molecular anion and its energy. This single-shot estimation idea has been pursued by Gázquez *et al.* [68], who proposed a simple formula using the HOMO and LUMO densities to estimate  $n_{J-1}$  and  $n_J$ , which are input into the XC potential of the corresponding discrete states to estimate the energy gap of the system. They suggest that any functional can be used to estimate the band gap using their approximation and that adding a long-range correction to the functionals improve the calculations. Nevertheless, the addition and relaxation of an electron to the ground state may change the properties of the molecule significantly, probably beyond what a zero-order perturbation correction would predict.

DFA with XC potential discontinuity have been proposed. For example, the functional of Perdew and Zunger [69] corrects partially the self-interaction error and shows an improved estimation of the XC DD. Sham [70] derived an expression for the XC energy functional using Feynman diagrams and the Luttinger–Ward functional (a similar equation has been recently developed within DFT by Yang *et al.* [71]). Sham and Schlüter [72], based on Sham’s equation, derived an integral equation that relates the one-particle many-body Green’s function with the XC potential and the XC self-energy. The Sham–Schlüter equation has been successfully employed to calculate the DD of semi-conductors and insulators [73,74]. Other early estimation of the XC DD for simple-model systems are available [75,76] (see also [77]). Kuisma *et al.* [78] showed that the orbital-dependent functional of Gritsenko *et al.* [79] presents DD, which once averaged over spatial coordinates yields better band-gap prediction for semi-conductors. Other functionals that display DD are the hyper-GGAs and meta-GGAs. In general, as shown in the seminal paper of Krieger *et al.* [80], XC functionals that show dependency on orbitals tend to feature the integer discontinuity.

For the molecular case, Andrade and Aspuru-Guzik [81] proposed a method to correct the asymptotic limit form of the LDA and GGAs XC potentials, and estimate the XC DD. They assumed that there exists a fictitious density that reproduces the XC potential, and proposed a method to correct the asymptotic behaviour of the approximated XC functional using a cut-off criterion for the fictitious density. They further assumed that the LDA (or GGA) averages over the XC DD (see Ref. [65]). Thus, by averaging over space, the difference between their corrected XC potential and the LDA (or GGA) potential, Andrade and Aspuru-Guzik [81] were able to estimate the DD with good accuracy for small molecules.

Seidl *et al.* [82] generalised KS (GKS) DFT by introducing, instead of a system of non-interacting electrons, a system of electrons whose interaction is determined by the user, for example, non-local Hartree–Fock interaction. The screened exchange (sX) LDA method of Bylander and Kleinman [83], which has non-local Fock electron exchange, can also be formalised within the theory of Seidl



*et al.* [82]. The auxiliary electrons of GKS DFT are subject to a local effective potential that guarantees that the density of these electrons corresponds to that of the real system of electrons. The generalised scheme of Seidl *et al.* [82] introduces Schrödinger-like equations with non-local operators whose self-consistent solution yields the generalised single-particle orbitals. Additionally, the sum of the square modulus of the occupied orbitals yields the exact density of the system. Seidl *et al.* [82] showed using perturbation theory and experimental data that the particle gap of sX-LDA is a suitable approximation to the XC DD, making the single-particle band gap closer to the fundamental one. We must remark, however, that the use of exact exchange in standard (i.e., using local potentials) KS-DFT might not improve the KS band gap and make it close to the true band gap [84].

Cohen *et al.* [32] analysed second-order perturbation theory with occupation numbers [34] and obtained discontinuities that improved the band gap over Koopmans' theorem. In fact, they found that the MP2 energy vs. particle number graph is quite closer to the correct linear interpolation form than that of the LDA and HF. Tsuneda *et al.* [85] showed numerically that a series of long-range corrected functionals give close approximations to the ionisation potential when the functionals are implemented within GKS DFT. Tsuneda *et al.* [85] also showed that these long-range corrected functionals, when directly extended to ensembles (that is, using the same functional always) preserve the orbital energies when non-integer number of electrons are considered. They highlighted that this is one of the reasons for the success of long-range corrected functionals.

#### 4.3. Criticisms

The extension to HK DFT by Mermin [42] and Perdew *et al.* [26] has been the subject of criticisms by several authors. Valiev and Fernando [86] suggested that Janak's theorem has no place in DFT because the occupation numbers are not variational parameters. However, as our review shows, using a purely DFT approach within the GCE, one can derive the Janak's theorem. Zahariev and Wang [87] used a thermal regularisation theorem to prove that the XC potential has no derivative discontinuities for integer number of electrons. However, their proof was rejected in Ref. [88] by showing that Zahariev and Wang [87] neglected an order-of-limits problem. Klienman [89,90] pointed out that the Perdew, Parr, Levy, and Balduz (PPLB) result contradicts the result of Levy *et al.* [91] stating that the XC potential tends to zero at large distances. He also argued that the proof of PPLB that the ensemble KS HOMO energy is the negative of the ionisation is incorrect. The discrepancies he found are due to a different choice of occupation numbers he employed. The objections of Klienman were refuted by Perdew and Levy [92], and further studies confirming the DD of the XC potential are reported for the optimised effective potential [34].

Simple practical examples displaying the DD have been reported, for example Sagvolden and Perdew [93] used the exact ground-state densities of  $H^-$  and  $H$  to construct ensemble densities and calculate the XC potential. They showed with this simple example the existence of the discontinuous jump of the XC potential. This was later extended to spin DFT [94] to again find the corresponding jumps in the polarised XC potentials. The DD has also been confirmed by Harbola [95], who extended the differential theorem of Holas and March [96] to the GCE at 0 K and applied it successfully to the helium case.

## 5. Ensemble density-functional approximations

In this section, we present new views on the approximation of the XC energy functional in the GCE.

### 5.1. The LDA and the electron gas

The LDA XC energy functional is exact for the uniform electron gas. It is usually split into exchange and correlation components. The former is

$$E_X^{\text{LDA}}[n] = -C_x \int d^3\mathbf{r} n^{4/3}(\mathbf{r}), \quad (84)$$

where  $C_x$  is given by

$$C_x = \frac{3}{4\pi} (3\pi^2)^{1/3}. \quad (85)$$

For the correlation contribution,

$$E_c^{\text{LDA}}[n] = \int d^3\mathbf{r} n(\mathbf{r}) e_c(n) \Big|_{n=n(\mathbf{r})}. \quad (86)$$

The Perdew–Wang parametrisation of the correlation energy density  $e_c(n)$  [97] is a continuously differentiable function of the density. To derive the LDA functional, one assumes that the density can be approximated as a series of uniform-density bars as

$$n^{\text{approx}}(\mathbf{r}) = \sum_k \chi_k(\mathbf{r}) n_k, \quad (87)$$

where

$$\chi_k(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in k\text{th bar} \\ 0, & \text{otherwise.} \end{cases} \quad (88)$$

Each of the  $n_k$  is a constant that approximates the true density in the corresponding bar (Figure 4). The number  $n_k$  in a large system (e.g., a solid) represents the number of electrons per volume. Experience has proven that the L(S)DA is in many ways a successful approximation for solids. However, strictly speaking, in a small molecule  $n_k$  represents the probability of finding an electron in a volume  $\delta V_k$  times the total number of electrons.

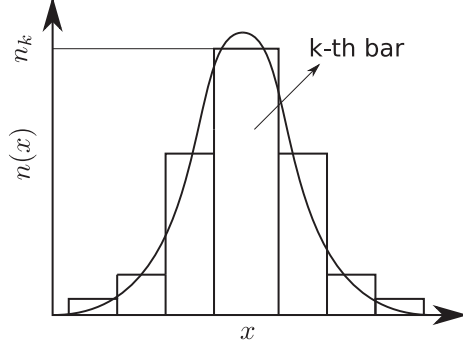


Figure 4. Illustration of the physical concept of the LDA.

As discussed at length before, the LDA XC functional, as well as many others, is unable to reproduce the correct dependency of the energy in terms of the average number of electrons. To investigate the source of this error let us consider a quantum gas with a finite number of electrons, which is the system used to approach the macroscopic electron gas. The quantum electron gas is relevant to study molecules with  $\pi$ -electron clouds, as the electrons can be assumed to lie in a finite box. Let the system be described by the Hamiltonian of Equation (3) with  $\hat{V}_{\text{ext}} = 0$ . The wavefunction of an independent electron is

$$\psi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} \xi_{\sigma} \exp(-i\mathbf{k} \cdot \mathbf{r}), \quad (89)$$

where  $V = L_x L_y L_z$ ,  $\xi_{\sigma}$  is the spin-state, and the momentum quantum number is  $\mathbf{k} = (k_x, k_y, k_z)$ :

$$k_j = \frac{2\pi m_j}{L_j} \quad m_j = 0, \pm 1, \pm 2, \dots \quad j = x, y, z. \quad (90)$$

The single particle energy is

$$\epsilon_{\mathbf{k},\sigma} = 2\hbar^2 \pi^2 \left( \left( \frac{m_x}{L_x} \right)^2 + \left( \frac{m_y}{L_y} \right)^2 + \left( \frac{m_z}{L_z} \right)^2 \right). \quad (91)$$

The thermodynamic properties of an ensemble of these non-interacting, finite electron gases are easily calculated using the grand-canonical partition function

$$\begin{aligned} \Xi(T, V, \mu) &= \sum_{\{n_{\mathbf{k},\sigma}\}} \prod_{\mathbf{q}\sigma} \exp(-\beta n_{\mathbf{q}\sigma} (\epsilon_{\mathbf{q}\sigma} - \mu)) \\ &= \prod_{\mathbf{k}\sigma} [1 + \exp(-\beta(\epsilon_{\mathbf{k}\sigma} - \mu))]. \end{aligned} \quad (92)$$

This function leads to the occupation numbers:

$$f_{\mathbf{k}\sigma}(\beta) = \frac{1}{1 + \exp(\beta(\epsilon_{\mathbf{k}\sigma} - \mu))}, \quad (93)$$

where the total number of electrons is

$$N = \sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}. \quad (94)$$

When the temperature is zero,  $\beta = \infty$ , we obtain a Heaviside function:

$$f(\epsilon_{\mathbf{k}\sigma} - \mu) = f_{\mathbf{k}\sigma}(\beta) \Big|_{\beta=\infty}. \quad (95)$$

Let the HOMO energy be  $\epsilon_{\text{H},\sigma}$  and its occupation number  $f_{\text{H},\sigma} = f(0)$ . Suppose that the average number of electrons is  $N = J + 2\omega$ , where  $0 < \omega < 1$ . Then

$$J + 2\omega = \sum_{\mathbf{k}\sigma} f(\epsilon_{\mathbf{k}\sigma} - \mu) = J + f_{\text{H},\uparrow} + f_{\text{H},\downarrow}. \quad (96)$$

Thus,  $f_{\text{H},\uparrow} + f_{\text{H},\downarrow} = 2\omega$ . If  $f_{\text{H},\uparrow} = f_{\text{H},\downarrow}$ , then  $f_{\text{H},\sigma} = \omega$ . The average energy is

$$\begin{aligned} E^0(N) &= \sum_{\mathbf{k}\sigma} f(\epsilon_{\mathbf{k}\sigma} - \mu) \epsilon_{\mathbf{k}\sigma} = E_J + 2\omega \epsilon_{\text{H}} \\ &= (1 - 2\omega)E_J + 2\omega(E_J + \epsilon_{\text{H}}). \end{aligned} \quad (97)$$

The GCE statistics can be easily adapted to study this microscopic non-degenerate electron gas with full Coulombic interaction between the electrons. In such case, the energy  $E^0(N)$  has to be replaced by the true energy of the system,  $E_v(N)$ . Since this system is a molecule in essence, we expect the energy  $E_v(N)$  to be convex as well, as discussed in Section 2. Thus, we conclude that the energy of the quantum electron gas is a series of first-order spline interpolations (see Figure 5). However, as  $V$  becomes infinitely large,  $E^0(N)$  tends to a continuously differentiable function. In other words, the level spacing between energies tends to zero, allowing us to employ the Euler–McLaurin integration formula to calculate the properties of the electron gas exactly. On the other hand, one can also express the exchange energy as an ensemble average:

$$E_x \approx (1 - \omega)E_x^{\text{LDA}}[n_J] + \omega E_x^{\text{LDA}}[n_{J+1}]. \quad (98)$$

If the level spacing is small enough, we can simply assert that

$$E_x = E_x^{\text{LDA}}[n_{J+\omega}]. \quad (99)$$

Now, we will show that the above two equations are not applicable to molecules.

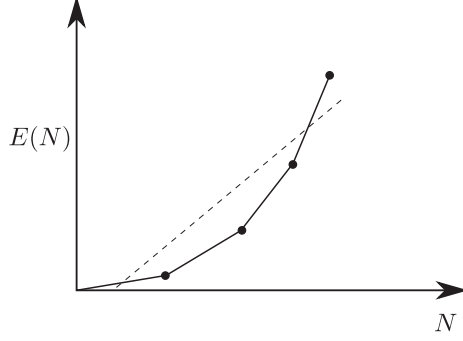


Figure 5. Energy of the quantum electron gas as a function of the number of particles; extreme low densities.

### 5.2. Approximating the HXC ensemble functional

Semi-local functionals are known to perform well at equilibrium geometries when the number of electrons is an integer [98,99]. Casida [34] pointed out that the XC energy functional at non-integer number electrons must be different from the one at integer number electrons. Harbola [35], in order to satisfy Janak's theorem and clarify the debate between Klienman [89,90] and Perdew and Levy [92], conjectured the correct form of the ensemble XC energy. In Ref. [33], we showed how approximated functionals for discrete molecules can be extended to consider ensembles. This extension recovers the linear dependency on the average number of electrons and derivative discontinuities of the approximated XC potential. In light of the observations of Casida and Harbola, we review here the main results of Ref. [33] using the tools that have been outlined in this paper. First, note that the functional  $F$  can be written in terms of discrete-particle-state functionals [100]:

$$F[n] = (1 - \omega[n])F_{J-1}[n_{J-1}] + \omega[n]F_J[n_J], \quad (100)$$

where

$$J - 1 + \omega[n] = \int d^3\mathbf{r} n(\mathbf{r}), \quad (101)$$

and the symbol  $F_M$  ( $M = 1, 2, \dots, J, \dots$ ) refers to the Levy-Lieb search (Equation (14)) over density matrices of systems with  $M$  electrons only. The densities  $n_{J-1}$  and  $n_J$  are density functionals, i.e., functionals of the non-integer density  $n(\mathbf{r})$ . These are determined by minimising the functional:

$$E[n_M; u[n]] = F_M[n_M] + \int d^3\mathbf{r} u[n](\mathbf{r})n_M(\mathbf{r})$$

$$M = 1, 2, \dots, J, \dots, \quad (102)$$

over  $n_M$ ,  $\int n_M(\mathbf{r}) = M$ . Here,  $u[n]$  is that potential that represents  $n(\mathbf{r})$  such that  $n(\mathbf{r}) = (1 - \omega)n_{J-1}(\mathbf{r}) + \omega n_J(\mathbf{r})$ . To generalise our argument, let us introduce the function:

$$y(x) = \begin{cases} 1 & x = 0 \\ 1 - x & 0 < x < 1 \\ 1 + x & -1 < x < 0 \\ 0 & \text{otherwise.} \end{cases} \quad (103)$$

Now we write  $F$  as

$$F[n] = \sum_M y(f n - M) F_M[n_M]. \quad (104)$$

Recall that the  $T_s$  functional is calculated by solving the KS equations. Hence,  $T_s$  is averaged using two non-interacting electron densities  $n_{s,J}(\mathbf{r})$  and  $n_{s,J-1}(\mathbf{r})$ , where

$$n_{s,M}(\mathbf{r}) = \sum_{i=1}^M |\phi_i(\mathbf{r})|^2 \quad (105)$$

(the orbitals  $\phi_i$  come from the KS Equation (35) and they only depend on  $n$ ). Although these densities represent a fictitious system, they sum to the present density  $n(\mathbf{r})$ , i.e.,

$$n(\mathbf{r}) = \sum_M y(f n - M) n_{s,M}(\mathbf{r}) = \sum_i f(\epsilon_i - \mu) |\phi_i(\mathbf{r})|^2. \quad (106)$$

In analogy with the functional  $F$ , we can write  $T_s$  as

$$T_s[n] = \sum_M y(f n - M) T_{s,M}[n_{s,M}], \quad (107)$$

where we define the particle-number-conserving KS energy:

$$T_{s,M}[n_M] = \min_{\hat{\Gamma}_{s,M} \rightarrow n_M} \text{Tr}\{\hat{T} \hat{\Gamma}_{s,M}\}. \quad (108)$$

This search is again performed over states that correspond only to systems with  $M$  electrons. In Equation (107), the KS orbitals obtained to calculate  $T_s[n]$  can also be used to construct the density matrix that results from the search in the functional  $T_{s,M}[n_{s,M}]$ . The functional  $F_M[n_M]$  can be written as usual as

$$F_M[n_M] = T_{s,M}[n_M] + E_{\text{HXC},M}[n_M], \quad (109)$$

where  $E_{\text{HXC},M}$  is the HXC energy functional constrained to densities that integrate to  $M$  electrons. Inserting this expression into Equation (104), we get

$$F[n] = \sum_M y(f n - M) (T_{s,M}[n_M] + E_{\text{HXC},M}[n_M]), \quad (110)$$

where the set of densities  $\{n_M\}$  correspond to interacting-electron systems. Given that  $F[n] = T_s[n] + E_{\text{HXC}}[n]$ , we have

$$E_{\text{HXC}}[n] = -T_s[n] + \sum_M y(f n - M)(T_{s,M}[n_M] + E_{\text{HXC},M}[n_M]). \quad (111)$$

Another way of expressing this result is

$$E_{\text{HXC}}[n] = \sum_M y(f n - M) \left\{ (T_{s,M}[n_M] - T_{s,M}[n_{s,M}]) + E_{\text{HXC},M}[n_M] \right\}. \quad (112)$$

The kinetic energies in the above equation do not cancel each other because they are being evaluated at electronic densities of different kinds. Harbola [35] noted that the thermal averaging of KS kinetic energies yields a different quantity from that given by the ensemble KS kinetic energy (Equation (107)). This observation, and the need to recover Janak's theorem, led Harbola [35] to conjecture the form for the ensemble  $E_{\text{HXC}}$ , which is proven here, Equation (111).

To calculate the interacting densities  $\{n_M\}$ , one would need the functional  $F[n]$ . However, if we were to use  $F$ , then we would not need to use DFT in the first place. On the other hand, the assumption that the densities are ensemble- $v$ -representable is used in this case. Such assumption can be formally expressed as follows:

$$G_s[n] = \min_{\{n_M\} \rightarrow n} \sum_M y(f n - M) G_{s,M}[n_M], \quad (113)$$

where

$$G_{s,M}[n_M] = \min_{\hat{\Gamma}_{s,M} \rightarrow n_M} \text{Tr} \left\{ \left( \hat{T} + \int d^3\mathbf{r} v_{\text{HXC},M}[\mathbf{r}] \times (\mathbf{r}) \hat{n}(\mathbf{r}) \right) \hat{\Gamma}_{s,M} \right\}. \quad (114)$$

In Equation (114),  $\{n_M\} \rightarrow n$  is the requirement that  $\sum_M y(f n - M) n_M(\mathbf{r}) = n(\mathbf{r})$ . This condition requires the introduction of the external potential  $v(\mathbf{r})$  as a Lagrange multiplier, and the self-consistent solution of the KS equations along with their corresponding XC potentials. For example, if  $J < N < J + 1$ , one needs to solve two sets of KS equations, one with  $v_{s,J}(\mathbf{r}) = v_{\text{HXC},J}(\mathbf{r}) + v(\mathbf{r})$  and another with  $v_{s,J+1}(\mathbf{r}) = v_{\text{HXC},J+1}(\mathbf{r}) + v(\mathbf{r})$ . The density  $n(\mathbf{r})$  is then calculated by averaging the densities of the systems with  $J$  and  $J + 1$  electrons.

The discussion so far in this subsection has referred to the exact HXC functional. When an approximate functional  $E_{\text{HXC},M}^A[n_M]$  is known to work well for integer-electron systems, it can then be extended according to

Equation (111) as

$$E_{\text{HXC}}^A[n] = -T_s[n] + \sum_M y(f n - M) \times (T_{s,M}[n_{s,M}] + E_{\text{HXC},M}^A[n_M]). \quad (115)$$

The HXC potentials that solve Equations (113) and (114) now read

$$v_{\text{HXC},M}^A(\mathbf{r}) = \frac{\delta E_{\text{HXC}}^A}{\delta n_M(\mathbf{r})}. \quad (116)$$

This last expression is a derivative over densities that integrate to  $M$  electrons.

The approximated ensemble-averaged energy functional is now:

$$E_v^A[n] = \sum_M y(f n - M) E_{v,M}^A[n_M], \quad (117)$$

where

$$E_{v,M}^A[n_M] = T_{s,M}[n_M] + E_{\text{HXC},M}^A[n_M] + \int d^3\mathbf{r} v(\mathbf{r}) n_M(\mathbf{r}). \quad (118)$$

The energy functional of Equation (117) is minimised first over the pure-state densities and then over the proper occupation number  $\omega$ . This leads to the energy formula:

$$E_N^A[v] = \sum_M y(N - M) E_M^A[v], \quad (119)$$

where

$$E_M^A[v] = \min_{n_M} E_{v,M}^A[n_M]. \quad (120)$$

Note that the functional  $E_N^A[v]$  is a piecewise linear function of  $N$ .

We now show that the above prescription recovers a DD for the ensemble XC potential  $v_{\text{XC}}[n] = \delta E_{\text{XC}}[n]/\delta n$ . The functional derivative of the approximated energy with respect to the density is ( $J - 1 < f n < J$ )

$$\begin{aligned} \frac{\delta E_{\text{HXC}}^A}{\delta n(\mathbf{r})} &= T_{s,J} + E_{\text{HXC},J}^A - T_{s,J-1} - E_{\text{HXC},J-1}^A + v_s(\mathbf{r}) - \epsilon_J^A \\ &+ \sum_M y(f n - M) \int d^3\mathbf{r}' \left( \frac{\delta T_{s,M}}{\delta n_M(\mathbf{r}')} + v_{\text{HXC},M}^A(\mathbf{r}') \right) \\ &\times \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})}. \end{aligned} \quad (121)$$

From Equation (106) we have

$$\frac{\delta n(\mathbf{r}')}{\delta n(\mathbf{r})} = n_J(\mathbf{r}') - n_{J-1}(\mathbf{r}') + (1 - \omega) \frac{\delta n_{J-1}(\mathbf{r}')}{\delta n(\mathbf{r})} + \omega \frac{\delta n_J(\mathbf{r}')}{\delta n(\mathbf{r})}. \quad (122)$$

Using the above result, it can be shown that

$$\begin{aligned} \frac{\delta E_{\text{HXC}}^A}{\delta n(\mathbf{r})} &= E_J^A - E_{J-1}^A + v_{\text{HXC}}^A(\mathbf{r}) - \epsilon_J^A \\ &+ \sum_M y(f n - M) \int d^3 \mathbf{r}' \left( \frac{\delta E_{v,M}^A}{\delta n_M(\mathbf{r}')} \right) \\ &\times \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})}. \end{aligned} \quad (123)$$

The potential  $\delta E_{v,M}^A / \delta n_M(\mathbf{r}')$  is arbitrary by a constant upon minimisation. Therefore,  $\int d^3 \mathbf{r}' \delta n_M(\mathbf{r}') / \delta n(\mathbf{r}) = 0$ , implying

$$\frac{\delta E_{\text{XC}}^A}{\delta n(\mathbf{r})} = -I_v^A - \epsilon_J^A + v_{\text{XC}}^A(\mathbf{r}). \quad (124)$$

By Janak's theorem (Theorem 2) ( $\epsilon_J^A = -I_v^A$ ), we recover  $v_{\text{XC}}^A(\mathbf{r}) = \delta E_{\text{XC}}^A[n] / \delta n(\mathbf{r})$ . Furthermore,

$$\begin{aligned} \frac{\delta E_{\text{HXC}}^A}{\delta n(\mathbf{r})} &= T_{s,J} + E_{\text{HXC},J}^A - T_{s,J-1} - E_{\text{HXC},J-1}^A \\ &+ \sum_M y(f n - M) \int d^3 \mathbf{r}' (\text{const.} - v(\mathbf{r}')) \frac{\delta n_M(\mathbf{r}')}{\delta n(\mathbf{r})} \\ &= -I_v^A - \frac{\delta T_s}{\delta n(\mathbf{r})} - v(\mathbf{r}). \end{aligned} \quad (125)$$

Finally, we arrive at

$$\Delta_{\text{XC},v} = I_v^A - A_v^A - (\epsilon_L^A - \epsilon_H^A). \quad (126)$$

This result is valid for the exact functional and its approximations. In the exact case, the usual expression for the DD,  $-A_v - \epsilon_L$ , is recovered. On the other hand, in the approximate case we cannot assume that the ionisation theorem holds. However, Janak's theorem remains valid. Thus, in the asymptotic region, the XC potential does not decay to 0 but to a constant when  $J - 1 < f n < J$ .

We now rederive a known result due to Perdew and Levy [65]: The continuous LDA/GGA potential averages over the DD [101], implying that

$$\epsilon_H^A \approx -I_v^A + \frac{\Delta_{\text{XC},v}}{2}. \quad (127)$$

Inserting this result into Equation (126) we have

$$\epsilon_L^A \approx -A_v^A - \frac{1}{2} \Delta_{\text{XC},v}. \quad (128)$$

Therefore,

$$\frac{1}{2}(\epsilon_H^A + \epsilon_L^A) \approx -\frac{1}{2}(I_v^A + A_v^A). \quad (129)$$

This implies that the KS electronegativity is close to the 'real' one.

Recently, Kraisler and Kronik [36] considered the ensemble approximation:

$$E_{\text{XC}}[n] = (1 - \omega) E_{\text{XC},J-1}[n_{s,J-1}] + \omega E_{\text{XC},J}[n_{s,J}] \quad (130)$$

which, as shown in the previous subsection, is quite accurate in the electron-gas limit. Using the optimised effective potential method, Kraisler and Kronik [36] applied Equation (130) for the  $\text{H}_2$  molecule and found that the ground-state energy is almost linear. Also, they showed that a DD arises from this approximation.

## 6. Concluding remarks

The motivation of PPLB [26] (discussed at the beginning of Section 4.1) leading to the DDs is shared by partition density functional theory (PDFT) [102–104], which splits the functional  $E[n; v]$  into two contributions: the sum of isolated fragment energies and a partition energy functional. A fragment (or atom) is defined by its external potential and Hamiltonian. The fragments are allowed to exchange electrons with a reservoir. The XC energy functional is thus of the PPLB form and can be approximated as shown in this work. The partition energy functional, when properly approximated, is the piece of the energy responsible for the bonding between fragments. In Ref. [105] it was shown, within PDFT, that the PPLB interpolation of energies and densities combined with an approximation to the partition energy functional solves the static correlation and delocalisation errors of the LDA and GGAs for  $\text{H}_2^+$  and  $\text{H}_2$ .

Equation (115) and its properties can be used to derive DFAs satisfying the conditions of molecular dissociation discussed in Section 4.1. A starting point is the investigation of the functional dependence of  $E_{\text{HXC}}$  on the average density matrix of the system (Equation (45)). This might require functional approximations that satisfy explicitly the ensemble limit of adiabatic separation. Switching functions, which are used by long-range corrected DFAs, can be useful to satisfy the dissociation limit; the overlap connecting functions used in the context of PDFT [105] could be employed as well.

To summarise, we discussed the formal origin of the DD of the total and XC energies of DFT, and their relation

to the adiabatic molecular dissociation problem. The formalism outlined here indicates that the exact HXC energy functional can be constructed from discrete-particle-state functionals. Fragment-based DFT techniques can benefit from approximations to the XC energy functional featuring the XC DD. Moreover, we believe that the dissociation limit can be employed as an additional condition that the exact functional must satisfy. Nevertheless, in a ground-state KS-DFT, addressing problems such as the calculation of ionisations and affinities, elimination of SIE and delocalisation error, and preservation of exact conditions, remains crucial.

### Acknowledgements

We acknowledge support from the National Science Foundation CAREER program [grant number CHE-1149968]. Adam Wasserman also acknowledges support from the Alfred P. Sloan Foundation and the Camille Dreyfus Teacher-Scholar Awards Programs.

### Note

1. We will refer to Ref. [26] as PPLB.

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