

JYU DISSERTATIONS 61

Luis Cort Barrada

Time-Dependent Density-Functional Theory for Strongly Correlated Electrons



UNIVERSITY OF JYVÄSKYLÄ
FACULTY OF MATHEMATICS
AND SCIENCE

JYU DISSERTATIONS 61

Luis Cort Barrada

**Time-Dependent
Density-Functional Theory for
Strongly Correlated Electrons**

Esitetään Jyväskylän yliopiston matemaattis-luonnontieteellisen tiedekunnan suostumuksella
julkisesti tarkastettavaksi yliopiston Ylistönrinteen salissa FYS1
maaliskuun 1. päivänä 2019 kello 12.

Academic dissertation to be publicly discussed, by permission of
the Faculty of Mathematics and Science of the University of Jyväskylä,
in Ylistönrinne, auditorium FYS1, on March 1, 2019 at 12 o'clock noon.



JYVÄSKYLÄN YLIOPISTO
UNIVERSITY OF JYVÄSKYLÄ

JYVÄSKYLÄ 2019

Editors

Robert van Leeuwen

Department of Physics, University of Jyväskylä

Ville Korkiakangas

Open Science Centre, University of Jyväskylä

Copyright © 2019, by University of Jyväskylä

Permanent link to this publication: <http://urn.fi/URN:ISBN:978-951-39-7687-3>

ISBN 978-951-39-7687-3 (PDF)

URN:ISBN:978-951-39-7687-3

ISSN 2489-9003

Preface

The research work of this thesis has been carried out at the Nanoscience Center in the Department of Physics at the University of Jyväskylä during the years 2014 to 2018.

First of all, I would like to express my complete gratitude to my supervisor, Professor Robert van Leeuwen. With you, I have worked with admiration and pleasure. I also want to thank Daniel Karlsson, Ulrika Forsberg, Giovanna Lani, Søren Nielsen, Janne Nevalaita, Riku Tuovinen, Markku Hyrkäs, and Ivan Latella. Without you this work would not have been possible. Finally, I would like to thank my friends and family for their support.

Jyväskylä, March 2019

Luis Cort Barrada

Abstract

One of the most used methods in condensed matter theory and quantum chemistry for the description of matter properties is Time-dependent density-functional theory (TDDFT), an alternative formalism to wave function methods which uses the time-dependent electronic density for the determination of any quantum average of an electronic system. The usual approach in TDDFT is by means a non-interacting system, where all the interaction effects are encoded in an effective one-body potential that exactly reproduces the time-dependent density of any interacting system. The effective potential is called the exchange-correlation (xc) potential. For the calculation of the excited states in TDDFT, one needs the knowledge of the xc potential and its functional derivative with respect to the density, which is known as the xc kernel. For practical applications, both the xc potential and the xc kernel needs to be approximated. In the last years, better approximations for the xc potential and kernel have been constructed, but it turns out that the usual approximations fail for the description of strongly correlated systems. Recently, a new type of density functionals, the strictly correlated electrons (SCE) formalism [1–3] have been constructed with the aim to describe the physics of strongly correlated systems, but not tested so far for the obtaining of excitation energies. One way to gain insight and test the performance of the density functionals is to compare them against exact expressions obtained from exactly solvable systems. In this work, we construct such strongly correlated systems, and we solve them exactly for the subsequent comparison with the predictions provided by the SCE density functionals. The comparison of the results, therefore, will provide insights of the applicability of this kind of density functionals, establishing in this way its range of validity.

- Author** Luis Cort Barrada
Department of Physics
Nanoscience Center
University of Jyväskylä
Jyväskylä, Finland
- Supervisor** Professor Robert van Leeuwen
Department of Physics
Nanoscience Center
University of Jyväskylä
Jyväskylä, Finland
- Reviewers** Dr Oleg Gritsenko
Section Theoretical Chemistry
VU University
Amsterdam, The Netherlands
- Professor Kieron Burke
Departments of Physics and Astronomy
University of California
Irvine, USA
Department of Chemistry
University of California
Irvine, USA
- Opponent** Professor Stefan Kurth
University of the Basque Country UPV/EHU
San Sebastián, Spain
IKERBASQUE, Basque Foundation for Science
Bilbao, Spain.
Donostia International Physics Center (DIPC)
San Sebastián, Spain

List of Publications

- I Luis Cort, Daniel Karlsson, Giovanna Lani, and Robert van Leeuwen, *Time-dependent density-functional theory for strongly interacting electrons*, Phys. Rev. A **95**, 042505 (2017)
- II Luis Cort, Soeren Ersback Bang Nielsen, and Robert van Leeuwen, *Strictly correlated electrons approach to excitation energies of dissociating molecules*, Phys. Rev. A **99**, 022501 (2019)

For the publication **I**, the author developed the theoretical framework, performed the analytical calculations and contributed to the writing of the article.

For the publication **II**, the author developed the theoretical framework, performed the analytical calculations, performed the numerical calculations and wrote the drafts of the article.

Contents

1	Introduction	1
1.1	The electronic many-body system	3
1.2	Energy functional and approximate wave-function method	4
1.3	Reduced density matrices	5
1.3.1	The pair correlation function and the exchange correlation hole	7
1.4	The electronic time-dependent many-body system	9
1.4.1	Continuity equation and local conservation laws	9
2	Density-functional theory	12
2.1	The density-potential mapping: The Hohenberg-Kohn theorem	12
2.2	The Kohn-Sham equations	15
2.3	The coupling constant integration	17
2.4	The exchange-correlation potential	19
2.4.1	Asymptotic properties of the xc potential	19
2.5	Approximate density functionals: Local density approximation and gradient expansion approximations	20
2.6	Dissociation of H_2	21
2.6.1	Wave function description	22
2.6.2	Molecular dissociation in the LDA	23
2.7	The strictly correlated electrons formalism: Ground-state theory	23
3	Time-dependent density functional theory	28
3.1	The time dependent density-potential mapping: The extended Runge-Gross theorem	28
3.2	The time-dependent Kohn-Sham scheme	31
3.3	The exact time-dependent Hxc potential	32
3.3.1	Exact conditions for the time-dependent exchange potential	33
3.3.2	Temporal non-locality and initial state dependence of the time-dependent Hxc potential	33
3.3.3	The adiabatic approximation for the Hxc potential	34
3.4	Linear-response theory	34
3.5	The large frequency limit of the density response function	35
3.6	Linear response function in TDDFT	36
3.6.1	The memory dependence	37
3.7	Local approximations for the Hxc kernel	38
3.7.1	The zero-force theorem and the long-range property	38
3.7.2	Calculation of the excitation energies: The Casida equation	39
3.8	Performance of the ALDA for the calculation of excitation energies of a dissociating H_2 molecule	39
3.9	Strictly correlated electrons in TDDFT	40
3.9.1	The adiabatic SCE functional	40

4	An exactly solvable system	42
4.1	Two interacting electrons on a ring	42
4.2	The strong interaction expansion of the exact solution	44
4.3	Density response of the quantum ring system	47
4.3.1	Exact density response of the quantum ring system	47
4.3.2	Strong interaction expansion of the dynamic density response function	49
4.4	TDDFT in the strong interaction limit	52
4.4.1	The exchange-correlation kernel	52
4.4.2	SCE formalism for the quantum ring	55
4.4.3	The ASCE for the quantum ring system	56
5	A simplified model for describing H₂	58
5.1	The model system	58
5.2	The H ₂ molecular model	58
5.3	Construction of the Hamiltonian and exact solution of the Schrödinger equation	62
5.3.1	The limit of large bond distance: The HL system	63
5.3.2	The limit of large interaction strength: The strongly correlated system	65
5.4	Strictly correlated electrons	72
5.4.1	Kohn-Sham SCE approach	73
5.4.2	Calculation of the excitations in the SCE formalism	75
5.4.3	The excitation energies	77
6	Summary & Outlook	79
	Appendix A: Co-motion functions in one dimension	82
	Appendix B: Functional derivative of the co-motion function in one dimension	83
	Appendix C: The SCE potential in one dimension	84
	Appendix D: The ZPE potential	86
	Appendix E: Functional derivative of the SCE potential	87
	Appendix F: Functional derivative of the ZPE potential	88
	Appendix G: Expansion of the excitation amplitudes	89
	Appendix H: ASCE and AZPE Hxc kernel for the homogeneous QR	92

1 Introduction

In electronic structure theory, the usual approach within the field of quantum chemistry is based on solving the time-dependent Schrödinger equation for the system of interest and calculate the desired observables from the time-dependent wave function. The key difficulty in doing this is that it requires the solution of a problem with many variables. The method is conceptually straightforward, but it becomes practically impossible as soon as the system consists of more than just a few electrons, which is commonly known as "The many-body problem." Consequently, the development of efficient methods to calculate the properties of many-electron systems is of crucial importance for the prediction of material properties within the research areas of theoretical chemistry, nanoscience, and solid-state physics.

(Time-dependent) density-functional theory (TD)DFT [4–10] provides an alternative to traditional wave-function methods. It uses the fact that the time-dependent electronic density contains all the information to determine the properties of any electronic system. The standard procedure used within density-functional theory for obtaining the time-dependent density is the Kohn-Sham (KS) system, a non-interacting system that reproduces the same electronic density as the interacting system of interest. The KS system uses an effective one-body potential that exactly, describes the many-body interactions as a functional of the electronic density. This effective potential is called the exchange-correlation (xc) potential, and the properties of the many body systems are encoded in it. For practical applications, the xc potential must be approximated, a task that has been the focus of intense research over many years, since the type of the approximation used crucially determines the quality of the results. To calculate the excitation energies of a system in TDDFT, it is not enough only the knowledge of xc potential, but also its functional derivative with respect to the density, evaluated at the ground state density [7]. The latter quantity is called the xc kernel, which also needs to be approximated. In recent years progressively better approximate functionals have been constructed leading to more accurate predictions of material properties. Currently, there exist some reliable and useful approximate density functionals that can deal with a wide variety of situations, but there are also well-known failures. In particular, the most commonly used approximate density functionals can not deal with strongly correlated systems. For example, an important situation is the breaking of chemical bonds in molecules, which is a key process in any chemical reaction and therefore of crucial importance in chemistry. The simplest and most commonly used approximation in TDDFT is the adiabatic local-density approximation (ALDA). The adiabatic approximation assumes that the xc potential of a general system at a given time is the same as that of a system having the instantaneous density at its ground state, whereas the local density approximation assumes that spatial variations of the density are small. The ALDA has a number of deficiencies such as, for example, the inability to predict charge transfer excitations [11–14] and Born-Oppenheimer surfaces of excited states in dissociating molecules [15–17]. Some improvements have been made using hybrid functionals, which are non-local in space but still adiabatic, thus lacking the ability to describe complex multi-particle excitations. These methods are not systematic and often system-dependent [18–21]. Other more systematic approaches often rely on perturbative expansions [22–31], which makes them questionable for the description of strongly correlated systems, as the case of molecular dissociation. Thus, it is necessary to develop new functional that can describe the strongly correlated systems.

Recently a new type of density functional which can capture the physics of strongly interacting systems have been developed within the so-called Strictly Correlated Electrons (SCE) [1, 2], and it was found that because of its non-local spatial dependence as a function of the density, it can describe chemical bond breaking well although it fails to describe bond distances [32, 33]. Since the work has been restricted to the ground-state only, for the description of time-dependent processes and excited states, a time-dependent extension of the formalism is needed. The SCE formalism, therefore, has been extended to the time-dependent domain in the adiabatic approximation in [3]. In this work, the formalism was presented, its properties were studied, and it was shown that the xc kernel constructed based on the SCE formalism in the adiabatic approximation could describe the physics that a system with strong correlation shows correctly. The xc kernel was studied for finite one-dimensional systems with density profiles that resemble a molecule in its dissociation process. It was found that due to the spatial non-local dependence of the kernel as a function of the density, the kernel exhibits the right analytical structure to describe dissociation processes accurately.

It is, therefore, the topic of this Ph.D. research project to find improved approximations for the xc kernel that are also reliable in the strong correlation regime. The goal is to extend and apply the SCE formalism within the time-dependent regime to describe excitations in correlated systems such as dissociating molecules and hence, to adequately describe excited state Born-Oppenheimer surfaces. Furthermore, we are interested in describing the electronic response properties of such correlated systems, which are essential for (photo)-chemical reactions and molecular spectroscopy.

This thesis organizes as follows. In Sec. 1.1 and Sec. 1.4 we describe the electronic many-body system and the electronic time-dependent many-body system respectively, we study its exact properties, and we briefly comment the standard methods that are commonly used to find approaches for coping with the many-body problem. In Sec. 2 and Sec. 3 we introduce the foundations of DFT and TDDFT respectively. We review the fundamental theorems that allow using the density as a fundamental variable as a replacement of the electronic wave-function and we summarize the most relevant exact conditions that the xc potential and the xc kernel must obey. We introduce the most used approximations, i.e., local approximations for DFT and adiabatic local approximations for TDDFT, and we explain why these approximations cannot deal with strongly correlated systems like a dissociating molecule. We introduce the ground-state SCE formalism and its extension for the time-domain in the adiabatic approximation, we explain how the ground-state theory performs for the calculation of the energy curve of H_2 in its dissociation process and we point out the insights that are behind the SCE theory in time domain for this functional to successfully describe the excitation energies of the H_2 in its dissociation process. In Sec. 4 we review the work done in [34], which consist on solving an interacting model system in an exact way for any range of the interaction strength, such that it allows obtaining the exact Hartree-xc (Hxc) kernel of TDDFT. With the exact Hxc kernel we develop an asymptotic expansion valid for large values of the interaction strength, and we compare the results with those that are obtained by using the SCE formalism in the adiabatic approximation, finding agreement with the leading order and the next to the leading order of the asymptotic expansion. We, therefore, conclude that the SCE formalism can correctly describe strongly interacting systems. Based on the positive results obtained in [34], in Sec. 5 we summarize the work done in [35]. In this work, we construct a simple interacting model system in a way that it reproduces the main features of a H_2 molecule, and with the purpose to analyze it in its dissociation regime. We solve the model exactly, and we calculate both the wave functions and energy spectrum in the dissociation limit, and in the limit when the interaction strength becomes very large, but for arbitrary but finite bond distance. Additionally, we obtain the excitation energies with the SCE formalism in the adiabatic approximation, and we analyze them in the limit of large bond distances. The goal is to test if such formalism reproduces the excitation energies of a dissociating molecule and hence, establish the range of validity of the SCE formalism.

1.1 The electronic many-body system

Consider a system of N non-relativistic electrons, under the influence of an external potential v , and with a two-body electron-electron interaction w . The interacting N -electron many-body Hamiltonian in the the Born-Oppenheimer approximation is given in atomic units by

$$\widehat{H} = \widehat{T} + \widehat{V} + \widehat{W}, \quad (1.1)$$

where

$$\widehat{T} = \frac{1}{2} \sum_{i=1}^N \widehat{\mathbf{p}}_i^2 \quad (1.2)$$

is the kinetic energy operator and $\widehat{\mathbf{p}}_i$ is the single particle momentum operator, which in position space reads $\widehat{\mathbf{p}} = i\nabla_{\mathbf{r}}$. In turn, the external potential operator which acts on each electron i reads

$$\widehat{V}_e = \sum_{i=1}^N v_e(\mathbf{r}_i), \quad (1.3)$$

and the two-body electron-electron interaction between electrons i and j reads

$$\widehat{W} = \sum_{i<j}^N w(\mathbf{r}_i, \mathbf{r}_j). \quad (1.4)$$

The electron-electron interaction is assumed in general to depend only of the distance between electrons as $w(|\mathbf{r}_i - \mathbf{r}_j|)$, being the fundamental interaction the Coulomb interaction $w(|\mathbf{r}|) = \frac{1}{|\mathbf{r}|}$. It is instructive to write the interacting N -electron many-body Hamiltonian as the sum of the N one-body Hamiltonian acting at each electron plus the sum of interactions between the pairs as

$$H(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N h(\mathbf{r}_i) + \sum_{i<j}^N w(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1.5)$$

where h is defined to be the single-particle Hamiltonian

$$h(\mathbf{r}) = -\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_e(\mathbf{r}). \quad (1.6)$$

The full description of the N electron system is given by the N -electron wave function, which is the solution of the time-independent Schrödinger equation and which in position-spin basis reads

$$H(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N), \quad (1.7)$$

where E is the energy eigenvalue and Ψ the eigenstate and the variable $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ refers to both position and spin. The full N -electron wave-function must be antisymmetric under the simultaneous interchange of space and spin variables. With the information of the interacting N -electron wave function any physical observable is calculated according to

$$O = \langle \Psi | \widehat{O} | \Psi \rangle. \quad (1.8)$$

for a normalized antisymmetric wave function Ψ .

Consider now a non-interacting N -electrons system under the influence of an external potential, and in the absence of the two-body electron-electron interaction. In this particular case, the N -electron Hamiltonian is composed merely by the sum of N single particle Hamiltonians

$$H(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N h(\mathbf{r}_i), \quad (1.9)$$

and consequently, the non-interacting N -particle Schrödinger equation decouples in N identical single-particle Schrödinger equations

$$h(\mathbf{r})\varphi_{n_i}(\mathbf{x}) = \varepsilon_{n_i}\varphi_{n_i}(\mathbf{x}), \quad (1.10)$$

where n_i is the level of the occupied orbital and i its label which runs from 1 to N . The totally antisymmetric non-interacting N -electron wave functions is a Slater determinant where two electrons can occupy each orbital with opposite spins. The eigenenergies of an arbitrary excited-state are simply the sum of the single N -electron eigenenergies for the occupied levels

$$E = \sum_{i=1}^N \varepsilon_{n_i} \quad (1.11)$$

We then see that for the ground-state energy, the occupation numbers are simply $(n_1, \dots, n_N) = (1, \dots, N)$.

When the electron-electron interaction is considered and because the interacting N -electron many-body Hamiltonian is not separable anymore, the single-particle picture is lost. We, therefore, see that once the two-body electron-electron interaction is present, the task of solving the Schrödinger equation becomes hard and thus it is needed to find alternative methods for calculating both the wave functions and the energy spectrum of the N interacting many-body system. Some of these methods we proceed to explain in the following section.

1.2 Energy functional and approximate wave-function method

An important method for the calculation of approximate ground-state wave function and ground-state energy is given by means the Rayleigh-Ritz variational method, whose criteria is based on the variational theorem which states that for a Hamiltonian, the following inequality holds

$$E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (1.12)$$

where E_0 is the ground-state energy and $|\Psi_0\rangle$ represents one element of the set of ground-state wave functions since we are also considering degenerate ground-states. The N -particle many-body Hamiltonian that solves the time-independent Schrödinger equation reads

$$\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle, \quad (1.13)$$

where $i \neq 0$ refers to excited states, ordered according to $E_0 \leq E_1 \leq \dots$. The theorem can be proved by expressing every general state Ψ written as a linear combination of the basis spanned by the Hamiltonian operator \hat{H} , i.e.

$$|\Psi\rangle = \sum_i c_i |\Psi_i\rangle. \quad (1.14)$$

By means the definition of the ground-state energy we have

$$E_0 = \frac{\sum_i |c_i|^2 E_0}{\sum_i |c_i|^2} \leq \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (1.15)$$

which proves the inequality Eq.(1.12). From the variational theorem, therefore, it can be defined a wave-function functional as follows

$$E[\Psi] \equiv \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0, \quad (1.16)$$

whose domain is defined for all normalizable antisymmetric ground-state wave functions Ψ where the minimum is the ground-state energy, and where the equal sign holds only for the elements of the set of the ground-state wave function $\Psi = \Psi_0$. This condition bounds from below the energy functional and we can write the variational property as

$$E_0 = \min_{\Psi} E[\Psi], \quad (1.17)$$

which means that the ground-state wave function is a stationary point of the energy functional. It can be shown that the stationary condition is satisfied when Ψ is an eigenfunction of the Hamiltonian, i.e., when the wave function fulfills the Schrödinger equation.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \quad (1.18)$$

Therefore, the stationary condition provides a criterion and a procedure to calculate approximations for the ground-state energy and ground-state wave function in a systematic way. Given a trial ground-state wave function $\tilde{\Psi}$, the variational theorem states that

$$E_0 \leq \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad (1.19)$$

where the equality holds only for every element of the set of ground-states $\tilde{\Psi} = \Psi_0$ wave functions.

1.3 Reduced density matrices

For the proper introduction of the objects called reduced density matrices, let us express the quantum average of a general k -body operator $\langle \hat{O} \rangle$ in the position-spin basis, being $k \leq N$, and where N is the number of interacting electrons. The expectation of the operator \hat{O} then reads

$$\langle \Psi | \hat{O} | \Psi \rangle = \int dx_1 \dots dx_N dx'_1 \dots dx'_N \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N) O(\mathbf{x}'_1, \dots, \mathbf{x}'_k; \mathbf{x}_1, \dots, \mathbf{x}_k) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N). \quad (1.20)$$

We see that the calculation of a quantum average $\langle \Psi | \hat{O} | \Psi \rangle$ of a general N -body operator ($k = 0$) \hat{O} of a system of N interacting electrons requires from the knowledge of the interacting N -particle wave function. However, from the above expression we notice that for the calculation of the expectation value of a k -body operator it is not needed the full interacting N -particle wave function, since in the evaluation of such expectations, the matrix elements of the operator \hat{O} do not depend on all the position-spin coordinates, but they depend only on k \mathbf{x}' and k \mathbf{x} coordinates. Thus, $N - k$ coordinates of the N -particle wave function have been integrated out, which means that practically (but not fundamentally), limited information of the full N -particle wave function is required. We thus can define conveniently a new object which is called k -particle reduced density matrix, which is defined from the N -particle wave function once having integrated the $N - k$ coordinates \mathbf{x}_i and \mathbf{x}'_i for $i = k + 1, \dots, N$ and whose knowledge determines the knowledge of the desired quantum average completely. For example, and as we will see later in the case of the calculation of the ground-state energy as the expectation average of the Hamiltonian Eq.(1.5), only the 2-particle reduced density matrix is needed.

Let us define the spin summed N -particle density matrix as

$$\Gamma_N(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_N) = \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N), \quad (1.21)$$

and let us also define the spin integrated N -particle density matrix as

$$\Gamma_N(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{r}'_1, \dots, \mathbf{r}'_N) = \sum_{\substack{\sigma_1 \dots \sigma_N \\ \sigma'_1 \dots \sigma'_N}} \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N). \quad (1.22)$$

The k -particle reduced density matrix is obtained from the N -particle density matrix integrating out $N - k$ coordinates as follows

$$\Gamma_k(\mathbf{x}_1, \dots, \mathbf{x}_k; \mathbf{x}'_1, \dots, \mathbf{x}'_k) = \frac{N!}{(N - k)!} \int d\mathbf{x}_{k+1} \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_k, \mathbf{x}_{k+1}, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_k, \mathbf{x}_{k+1}, \dots, \mathbf{x}_N). \quad (1.23)$$

From the definitions Eq.(1.21) and Eq.(1.23) it follows that

$$\Gamma_k(\mathbf{x}_1, \dots, \mathbf{x}_k; \mathbf{x}'_1, \dots, \mathbf{x}'_k) = \frac{1}{(N - K)!} \int d\mathbf{x}_{k+1} \dots d\mathbf{x}_N \Gamma_N(\mathbf{x}_1, \dots, \mathbf{x}_k, \mathbf{x}_{k+1}, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_k, \mathbf{x}_{k+1}, \dots, \mathbf{x}_N) \quad (1.24)$$

and

$$\Gamma_k(\mathbf{x}_1, \dots, \mathbf{x}_k; \mathbf{x}'_1, \dots, \mathbf{x}'_k) = \frac{1}{(N - K)} \int d\mathbf{x}_{k+1} \Gamma_{k+1}(\mathbf{x}_1, \dots, \mathbf{x}_k, \mathbf{x}_{k+1}; \mathbf{x}'_1, \dots, \mathbf{x}'_k, \mathbf{x}_{k+1}). \quad (1.25)$$

Particular interest have the traces of the Γ_1 and Γ_2 that from Eq.(1.23), Eq.(1.24) and Eq.(1.25) they integrate to

$$\int d\mathbf{x} \Gamma_1(\mathbf{x}; \mathbf{x}) = N \quad (1.26)$$

and

$$\int d\mathbf{x}_1 d\mathbf{x}_2 \Gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) = N(N - 1). \quad (1.27)$$

Let us analyze the probability interpretation of the reduced matrices Γ_1 and Γ_2 . The trace of the 1-particle reduced density matrix is the particle density $\Gamma_1(\mathbf{x}; \mathbf{x}) = n(\mathbf{x})$ which integrates to N particles. This means that it gives the probability distribution to find an electron at the point \mathbf{x} with spin σ . The trace of the 2-particle density matrix in turn, integrates to $N(N - 1)$, which is the double of the number of pairs we can form with N electrons and therefore $\Gamma_2(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$ represents the probability distribution of finding one electron at point \mathbf{r} with spin σ and other electron at point \mathbf{r}' with spin σ' .

For the calculation of the ground-state energy of the interacting N -electron system, we average the Hamiltonian Eq.(1.5) with the N -electron ground-state wave function, which can be expressed in terms of the 1 and 2-particle reduced density matrices as

$$E_0 = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (1.28)$$

where

$$\langle \Psi | \hat{H} | \Psi \rangle = \int d\mathbf{r} h(\mathbf{r}) \Gamma_1(\mathbf{r}; \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|) \Gamma_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'). \quad (1.29)$$

From the ground-state energy expression Eq.(1.29) we see that because the part of the Hamiltonian that contains the one-body operator $h(\mathbf{r})$ depends only on one coordinate, it is averaged with the diagonal of the 1-particle reduced density matrix or electronic density. The two-body electron-electron interaction, in turn, it is a two-body operator which depends on two position coordinates $w(|\mathbf{r} - \mathbf{r}'|)$, and hence it is averaged with the pair density. We, therefore, see that for the calculation of the N -electron interacting ground-state energy the full knowledge of the N -particle wave function is not needed provided the complete knowledge of the spin integrated 1 and 2-particle reduced density

matrices are known. We can say more and express the N -electron ground-state energy implicitly as a function of the spin integrated 2-particle reduced density matrix, since we note that by Eq.(1.25) we have the relation

$$\Gamma_1(\mathbf{x}_1; \mathbf{x}'_1) = \frac{1}{(N-1)} \int d\mathbf{x}_2 \Gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}_2) \quad (1.30)$$

and thus, the variational principle Eq.(1.16) can be reformulated as a minimization of a functional of the 2-reduced particle density instead of the wave function as follows

$$E[\Gamma_2] = \inf_{\Psi \rightarrow \Gamma_2} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (1.31)$$

where the minimization consists on searching over all the set of 2-particle reduced density matrices that are obtained from antisymmetric normalized wave functions. Such a domain is called N -representable. To proceed with the minimization, it is needed to know the constraints the 2-particle reduced density matrix has to fulfill. These constraints are known as N -representable constraints for the 2-reduced particle density matrix and they have been known recently [36]. Discussion about this issue is out of the scope of this work and extended discussions about this topic can be found at [36]. Assuming then that the N -representability conditions are known for the 2-particle reduced density matrix, one has the variational property for the ground-state energy

$$E_0 \leq E[\Gamma_2], \quad (1.32)$$

where the equal sign holds only for the 2-particle reduced density matrix obtained from the interacting N -electron ground-state wave function.

1.3.1 The pair correlation function and the exchange correlation hole

Two specific probability distribution functions constructed from the spin integrated 2-reduced particle density matrix are particularly relevant because of its physical meaning. These objects are the pair-correlation function and the exchange-correlation hole.

Let us define a new probability distribution according to the relation

$$g(\mathbf{x}, \mathbf{x}') = \frac{\Gamma_2(\mathbf{x}, \mathbf{x}')}{n(\mathbf{x})n(\mathbf{x}')}. \quad (1.33)$$

This probability distribution function is called the pair-correlation function, and it provides information about the degree of correlation of an N -electron system. When the probability to find an electron at the position \mathbf{r} with spin σ and another at the position \mathbf{r}' with spin σ' are independent events, then the 2-particle reduced density matrix is just the product of the electronic densities $\Gamma_2(\mathbf{x}, \mathbf{x}') = n(\mathbf{x})n(\mathbf{x}')$, and hence the correlation factor is $g(\mathbf{x}, \mathbf{x}') = 1$. We say then that the N -electron system is completely uncorrelated. This situation happens when the system is a non-interacting system, whose correlation function reads

$$g(\mathbf{x}, \mathbf{x}') = 1 - \frac{|\gamma(\mathbf{x}, \mathbf{x}')|^2}{n(\mathbf{x})n(\mathbf{x}')}, \quad (1.34)$$

where the function $\gamma(\mathbf{x}, \mathbf{x}')$ is known as the exchange contribution, originated due to the antisymmetry of the Slater determinant and which it is zero if we have different spins $\sigma \neq \sigma'$. The source of spin correlations are due to the Pauli exclusion principle encoded in the antisymmetry property of the non-interacting N -electron wave function, since the electrons that are in the same position $\mathbf{r} = \mathbf{r}'$ avoid to have the same spin projection and therefore, even if there is not present in the Hamiltonian

a two-body electron-electron interaction, there is still a correlation. These type of correlations are due to the spin interaction, or correlations due to the exchange. The rest of the correlations are due to the two-body electron-electron interaction term.

Let us now re-express the interaction term of the energy expectation value Eq.(1.29) as a function of the spin integrated pair-correlation function, which reads

$$W = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|)n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r}, \mathbf{r}') \quad (1.35)$$

and let us separate the full interaction energy in its classical electrostatic contribution or the so-called Hartree energy and the xc part, which is the contribution with genuine quantum origins, as follows

$$W = W_{xc} + U_H, \quad (1.36)$$

where

$$U_H = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|)n(\mathbf{r})n(\mathbf{r}') \quad (1.37)$$

is the Hartree energy and the xc part of the interaction energy W_{xc} is defined as

$$W_{xc} = \int d\mathbf{r}d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|)n(\mathbf{r})n(\mathbf{r}')[g(\mathbf{r}, \mathbf{r}') - 1], \quad (1.38)$$

where $g(\mathbf{r}, \mathbf{r}')$ is the spin integrated pair-correlation function.

From the 2-particle reduced density matrix we can construct in turn another equivalent probability distribution, which is called the xc hole, and it is defined as

$$n_{xc}^h(\mathbf{x}, \mathbf{x}') = \frac{\Gamma_2(\mathbf{x}; \mathbf{x}')}{n(\mathbf{x}')} - n(\mathbf{x}) = n(\mathbf{x})[g(\mathbf{x}, \mathbf{x}') - 1], \quad (1.39)$$

where the term $\frac{\Gamma_2(\mathbf{x}; \mathbf{x}')}{n(\mathbf{x}')}$ represents the conditional probability to find an electron on the position \mathbf{r} with spin projection σ , provided that a reference electron is at the position \mathbf{r}' with spin projection σ' . By the definition of the pair-correlation function and the normalization of the 2-reduced particle density matrix, we can derive the sum rule for the xc hole, which reads

$$\int d\mathbf{x} n_{xc}^h(\mathbf{x}, \mathbf{x}') = \int d\mathbf{x} n(\mathbf{x})[g(\mathbf{x}, \mathbf{x}') - 1] = -1, \quad (1.40)$$

meaning that the hole is a probability distribution that integrates to -1 electron. Now the physical meaning of the xc hole distribution becomes clear. It represents the probability distribution to find a minus electron at position \mathbf{r} with spin projection σ , given a reference electron at position \mathbf{r}' with spin projection σ' . Since the probability to find an electron near to the reference one is reduced because of both the Pauli exclusion principle and electron-electron interaction, then we say that the presence of correlations create a hole in the electronic density distribution $n(\mathbf{x})$. When the electrons are completely uncorrelated the conditional probability reads $\frac{\Gamma_2(\mathbf{x}; \mathbf{x}')}{n(\mathbf{x}')} = n(\mathbf{x}')$ and therefore, the xc hole distribution function is identically zero.

If we once again express the xc part of the interaction energy as a function of the xc hole distribution function, it reads

$$W_{xc} = \frac{1}{2} \int d\mathbf{x}d\mathbf{x}' n(\mathbf{x})n_{xc}^h(\mathbf{x}, \mathbf{x}')w(|\mathbf{r} - \mathbf{r}'|). \quad (1.41)$$

We see that to calculate the properties of a N -electron interacting system, such as its ground-state energy, it is needed to model the 1 and 2-particle reduced density matrices. Many methods

for coping with this problem have been developed during the years for calculating these objects in an approximate way. Some of them, wave function methods are based on the variational principle previously explained, such as configuration-interaction [37], which for a basis set considering just single and double excitations it is easy to implement, while for larger basis sets it turns out that the method is very expensive to implement computationally for a system of just few electrons. Another method relies on perturbation expansions with respect of the interaction term, and for a detailed discussion we refer to [38], but the method is questionable for describing strongly correlated systems. The method which is the one that we proceed to explain in the next chapters, Sec. 2 and Sec. 3 is density-functional theory, but before it, we briefly review the electronic time-dependent many-body problem.

1.4 The electronic time-dependent many-body system

Consider a system of N non-relativistic electrons, under the influence of a time dependent external potential $v(\mathbf{r}, t)$, and with an electron-electron interaction $w(|\mathbf{r}_i - \mathbf{r}_j|)$ between electrons i and j . The interacting time-dependent Hamiltonian of the N electron system in the Born-Oppenheimer approximation is given in atomic units by

$$\widehat{H}(t) = \widehat{T} + \widehat{V}(t) + \widehat{W}, \quad (1.42)$$

where now the one-body external potential operator which acts on each electron i is time-dependent and reads

$$\widehat{V}_e(t) = \sum_{i=1}^N V_e(\mathbf{r}_i, t). \quad (1.43)$$

The full description of the N electron system is given by the interacting time-dependent N -electron wave function, which is the solution of the time-dependent Schrödinger equation

$$H(\mathbf{r}_1, \dots, \mathbf{r}_N, t)\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t) = i\partial_t\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t), \quad (1.44)$$

which propagates a given initial state $\Psi(t_0) = \Psi_0$ being t_0 the initial time and where in most of the cases is chosen to be the ground-state. The full time dependent N -electron wave function must be antisymmetric under the simultaneous interchange of the space and spin variables. With the information of the interacting N -electron wave function any physical observable is calculated according to

$$O(t) = \langle \Psi(t) | \widehat{O}(t) | \Psi(t) \rangle. \quad (1.45)$$

We can also introduce the time-dependent reduced density matrices, which are defined by means the interacting time-dependent N -electron wave function in the same fashion as we did for the time-independent case, Sec. 1.3, and therefore there is no need for more discussion about them.

Before going through time-dependent density functional theory, it is needed to discuss some exact properties of the time-dependent many body systems.

1.4.1 Continuity equation and local conservation laws

In this section, we discuss the exact relations of the time-dependent many-electron that will be used in the following sections to derive the fundamental theorem time-dependent density-functional theory relies on, which can be found at [6, 7]

First of all, let us define the density operator as

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (1.46)$$

and the current-density operator as

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{i=1}^N [\nabla_i \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i]. \quad (1.47)$$

Let us calculate the time-dependent expectation values of both the density operator and the current density operator. The time-dependent expectation values are given by averaging the operator with the time-dependent wave function $\Psi(t)$ which is the solution of the time-dependent Schrödinger equation as

$$n(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle \quad (1.48)$$

$$\mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle. \quad (1.49)$$

The evolution of the quantum average of any operator is obtained according to

$$\partial_t \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = -i \langle \Psi(t) | [\hat{O}(t), \hat{H}] | \Psi(t) \rangle + \langle \Psi(t) | \partial_t \hat{O}(t) | \Psi(t) \rangle. \quad (1.50)$$

Let us now calculate the evolution equation for the density operator, which reads

$$\partial_t n(\mathbf{r}, t) = -i \langle \Psi(t) | [\hat{n}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle, \quad (1.51)$$

and after working out the commutator, we find the continuity equation

$$\partial_t n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t). \quad (1.52)$$

Analogously, we can take the current-density operator to find its evolution equation as

$$\partial_t \mathbf{j}(\mathbf{r}, t) = -i \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle \quad (1.53)$$

and working out the commutator we arrive at the following equation for the i component of the current

$$\partial_t j_i(\mathbf{r}, t) = -n(\mathbf{r}, t) \partial_i v_e(\mathbf{r}, t) - F_i^{\text{kin}}(\mathbf{r}, t) - F_i^{\text{int}}(\mathbf{r}, t), \quad (1.54)$$

where $i = 1, 2, 3$ are the Cartesian coordinates. The last equation has the meaning of a local force balance equation. The vectors F_i^{kin} and F_i^{int} correspond to the internal forces due to the kinetic and interaction energy respectively. The kinetic force is given by $F_i^{\text{kin}} = \sum_j \partial_i \tau_{ij}$, where the kinetic stress tensor is defined as

$$\tau_{ij}(\mathbf{r}, t) = \frac{1}{2} \left[\lim_{\mathbf{r} \rightarrow \mathbf{r}'} \left(\partial_{r_i} \partial_{r'_j} + \partial_{r_j} \partial_{r'_i} \right) \Gamma(\mathbf{r}, \mathbf{r}', t) - \frac{\delta_{ij}}{2} \nabla^2 n(\mathbf{r}, t) \right], \quad (1.55)$$

and $\Gamma(\mathbf{r}, \mathbf{r}', t)$ is the 1-particle reduced density matrix. In turn, the interaction force density is

$$F_i^{\text{int}}(\mathbf{r}, t) = 2 \int d\mathbf{r}' \Gamma_2(\mathbf{r}, \mathbf{r}', t) \partial_i w(|\mathbf{r} - \mathbf{r}'|), \quad (1.56)$$

where $\Gamma_2(\mathbf{r}, \mathbf{r}', t)$ is the diagonal of the 2-reduced particle density matrix. The interaction force can also be written in the form of a divergence of a tensor as $F_i^{\text{int}} = \sum_j \partial_i w_{ij}$, where the interaction stress tensor is

$$w_{ij}(\mathbf{r}, t) = - \int d\mathbf{r}' \frac{r'_i r'_j}{r'} \int_0^1 d\lambda \Gamma_2(\mathbf{r} + \lambda \mathbf{r}', \mathbf{r} - (1 - \lambda) \mathbf{r}', t). \quad (1.57)$$

Let us now define the total momentum that acts on the many-electron system as

$$\mathbf{P}(t) = \int d\mathbf{r} \mathbf{J}(\mathbf{r}, t). \quad (1.58)$$

Taking the time derivative and using the time evolution equation for the current-density Eq.(1.54) we get

$$\partial_t \mathbf{P}(t) = - \int d\mathbf{r} n(\mathbf{r}, t) \nabla v_e(\mathbf{r}, t), \quad (1.59)$$

where the total kinetic energy force and interaction force do not contribute since they are written in terms of a total divergence, and therefore its integral over the space is zero provided that the stress tensor vanishes sufficiently quick at infinity. The physical reason why these terms vanish is because neither the total kinetic energy nor the two-body electron interaction can provide a change of momentum to the system and therefore, the total kinetic energy term and the interaction term cannot produce a net force. This is nothing but the second Newton's law where the variation of the total momentum of the system is due to the external force, which is caused by the one-body external potential.

Similarly, we can define the total angular momentum as

$$\mathbf{L}(t) = \int d\mathbf{r} \mathbf{r} \times \mathbf{j}(\mathbf{r}, t) \quad (1.60)$$

Proceeding analogously as the total momentum, and taking its time derivative, we also obtain

$$\partial_t \mathbf{L}(t) = - \int d\mathbf{r} n(\mathbf{r}, t) \mathbf{r} \times \nabla v(\mathbf{r}, t), \quad (1.61)$$

which the contributions from the kinetic and the interaction vanish. Also, in this case, the physical meaning is clear since neither kinetic energy force nor the two body electron-electron interaction can provide to the system a change of angular momentum, i.e., they cannot produce a torque in the system since it can only be produced by an external force.

We are now ready for the derivation of the central equation we will use for establishing the density-potential mapping in TDDFT. Taking the divergence of evolution equation for the current-density Eq.(1.54) and using the continuity equation we arrive to

$$\partial_t^2 n(\mathbf{r}, t) = \nabla[n(\mathbf{r}, t) \nabla v_e(\mathbf{r}, t)] + q(\mathbf{r}, t), \quad (1.62)$$

where we have defined q to be

$$q(\mathbf{r}, t) = \nabla \mathbf{F}^{\text{kin}}(\mathbf{r}, t) + \nabla \mathbf{F}^{\text{int}}(\mathbf{r}, t). \quad (1.63)$$

This is the equation that provides a relation between densities and one-body external potential since also q depends implicitly on the density by means the 1 and 2-particle reduced density matrices. The above equation is just a formal equation which shows how the one-body external potential depends on the density and vice versa, but it is not possible to solve for the one-body external potential unless the reduced density matrices are known and which are given via the N -electron time-dependent wave function. The above-derived equations Eq.(1.62) and Eq.(1.63) will be the objects for proving the unique mapping of densities and potentials.

2 Density-functional theory

2.1 The density-potential mapping: The Hohenberg-Kohn theorem

In this section, we introduce the foundations of the density-functional theory. In the previous section and by the variational property, we have shown that the ground-state energy Eq.(1.29) of a N -electron interacting system is completely determined with the knowledge of the 2-particle reduced density matrix. Likewise, we are going to show that the ground-state electronic density completely determines the ground-state energy and every quantum average of any electronic system.

For an N -electron interacting system described by the Hamiltonian Eq.(1.5), the ground-state wave function which for simplicity we assume to be non-degenerate up to a global phase factor, is determined via the solution of the time-independent Schrödinger equation Eq.(1.7). Once the one-body external potential is specified and for a fixed two-body electron-electron interaction, the Schrödinger equation, therefore, defines a map between the set of the external one-body potentials which differ more than a constant, \mathcal{V} and the ground-state wave functions which vary more than a global phase factor, \mathcal{G} . Let us denote the map from \mathcal{V} to \mathcal{G} , A as

$$A : \mathcal{V} \longrightarrow \mathcal{G}. \quad (2.1)$$

The N -electron wave function, in turn, determines the spin integrated ground-state density according to Eq.(1.23) as

$$n_0[v_e](\mathbf{r}) = \langle \Psi[v_e] | \hat{n}(\mathbf{r}) | \Psi[v_e] \rangle = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N |\Psi_0[v_e](\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2, \quad (2.2)$$

where the density operator is Eq.(1.46), and where we wrote $\Psi_0[v_e]$, which indicates that the ground-state wave function is a functional of the external potential, which is obtained via the map A . We have then introduced a second map between the set of ground-state wave functions \mathcal{G} and the set of ground-state densities \mathcal{N} generated by Eq.(2.2), which we call B

$$B : \mathcal{G} \longrightarrow \mathcal{N}. \quad (2.3)$$

We, therefore, can say that the ground-state density is obtained via the composite map $B \circ A$ between the set of one-body external potentials \mathcal{V} to the set of ground-state densities \mathcal{N} as

$$\begin{array}{ccc} \mathcal{V} & \xrightarrow{A} & \mathcal{G} & \xrightarrow{B} & \mathcal{N} \\ & & & \searrow & \\ & & & & \mathcal{N} \\ & & & \nearrow & \\ & & & & \mathcal{V} \end{array}$$

$B \circ A$

and hence, the ground-state density constitutes a functional of the external potential, ie, we write $n_0[v_e]$. We are interested in showing that there exists an inverse map $(B \circ A)^{-1}$ between the set of ground-state densities \mathcal{N} to the set of one-body external potentials \mathcal{V} . For showing it, it is needed to

be proved that the map $B \circ A$ is unique. This proof forms the content of the Hohenberg-Kohn (HK) theorem [39, 40], which we proceed to announce in the following:

Hohenberg-Kohn theorem: For an N -electron interacting system with a fixed electron-electron interaction, there exist a one-to-one correspondence between the external potential v_e and the ground-state density n_0 , i.e., the one-body external potential is a unique functional of the ground-state density $v_e[n_0]$, up to an arbitrary constant.

The proof is given in two steps via *reductio ad absurdum* as follows. In the first part of the proof, it is shown that two potentials that differ more than a constant lead to different ground-state wave functions which differ more than a phase factor. For proving it we assume the contrary, that is, two different one-body external potentials produce the same ground-state wave function, and we write

$$\left(\widehat{T} + \widehat{V}_{e1} + \widehat{W}\right) |\Psi\rangle = E_1 |\Psi\rangle \quad (2.4)$$

$$\left(\widehat{T} + \widehat{V}_{e2} + \widehat{W}\right) |\Psi\rangle = E_2 |\Psi\rangle. \quad (2.5)$$

By subtraction of both equations and writing the resulting one-body operator in position basis one finds

$$\sum_{i=1}^N [v_{e1}(\mathbf{r}_i) - v_{e2}(\mathbf{r}_i)] \Psi = (E_1 - E_2) \Psi. \quad (2.6)$$

Furthermore, assuming that the wave function does not vanish on a set of non-zero measure, ie, wherever $\Psi \neq 0$, we can factorize the wave function, and we get

$$\sum_{i=1}^N [v_{e1}(\mathbf{r}_i) - v_{e2}(\mathbf{r}_i)] = E_1 - E_2, \quad (2.7)$$

which means that both external potentials are related by a constant, thus in contradiction of the initial assumption. Therefore, two different external potentials produce two different ground-state wave functions.

For the second part of the proof, we want to show that two different ground-state wave functions, which are produced by two different one-body external potentials via the solution of the Schrödinger equation, produce two different ground state densities. For proving it we assume the contrary again, that is, two different ground-states, namely Ψ_1 and Ψ_2 , produce the same ground-state density. Applying the Ritz variational theorem, we have that

$$E_1 < \langle \Psi_2 | \widehat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \widehat{H}_2 + \widehat{V}_{e1} - \widehat{V}_{e2} | \Psi_2 \rangle = E_2 + \int d\mathbf{r} n_1(\mathbf{r}) [v_{e2}(\mathbf{r}) - v_{e1}(\mathbf{r})]. \quad (2.8)$$

But we can invert the reasoning and do the change $1 \rightarrow 2$ and $2 \rightarrow 1$ for obtaining

$$E_2 < \langle \Psi_1 | \widehat{H}_2 | \Psi_1 \rangle = \langle \Psi_1 | \widehat{H}_1 + \widehat{V}_{e2} - \widehat{V}_{e1} | \Psi_1 \rangle = E_1 + \int d\mathbf{r} n_{02}(\mathbf{r}) [v_{e1}(\mathbf{r}) - v_{e2}(\mathbf{r})]. \quad (2.9)$$

Summing up the above equations we get the inequality

$$\int d\mathbf{r} [n_{01}(\mathbf{r}) - n_{02}(\mathbf{r})] [v_{e1}(\mathbf{r}) - v_{e2}(\mathbf{r})] > 0, \quad (2.10)$$

but we assumed that two different one-body potentials which differ more than a constant produce the same ground-state density, i.e., $n_{01} = n_{02}$ leading again to a contradiction resulting from Eq.(2.10).

Therefore, we conclude that one ground-state wave function produces one ground-state density. With all together we have shown that the composite map $B \circ A$ is unique and therefore the inverse composite map $(B \circ A)^{-1}$ from the set of ground-state densities \mathcal{N} to the set of one-body external potentials \mathcal{V} , exist, so that, the ground-state density uniquely determines the one-body external potential of an N -particle many-body system. As an important remark, note that for proving the HK theorem it has been needed to write the one-body potential in position basis since in this particular basis it is a diagonal operator, fact that allowed to factorize the ground-state wave function in Eq.(2.7), which it is not guaranteed to follow if the many-body Hamiltonian is written in an arbitrary basis. As an immediate consequence of the HK theorem, we deduce that the N -particle interacting Hamiltonian is also a functional of the ground-state density since the one-body external potential is. Therefore, the many body N -particle ground-state wave function, all the excited-states and the energy spectrum which are solution of the Schrödinger equation are also unique functionals of the ground-density, which we denote by $\Psi_i[n_0]$. Indeed, the Schrödinger equation reads

$$\hat{H}[n_0]|\Psi_i[n_0]\rangle = E_i[n_0]|\Psi_i[n_0]\rangle, \quad (2.11)$$

and therefore any expectation value of a general operator \hat{O} is a functional of the ground-state density

$$O_i[n_0] = \langle \Psi_i[n_0] | \hat{O} | \Psi_i[n_0] \rangle. \quad (2.12)$$

Thus, all the properties of the N -electron interacting system are determined by the ground-state density. Since it has particular interest the ground-state energy of an interacting N -electron system, let us take as a specific case of Eq.(2.12) the Hamiltonian, i.e., $\hat{O} = \hat{H}[v_e]$, which with the "notation $[v_e]$ " we want to emphasize that the Hamiltonian now is fixed by its one-body external potential. By means the variational theorem Eq.(1.12), the following inequality is satisfied

$$E_{v_e}[n_0] = \langle \Psi_0[n_0] | \hat{H}[v_e] | \Psi_0[n_0] \rangle < \langle \Psi[n] | \hat{H}[v_e] | \Psi[n] \rangle \quad \text{for} \quad n \neq n_0, \quad (2.13)$$

where we have considered any normalized antisymmetric wave functions $\Psi_0[n_0]$ that produces the ground-state density n_0 . The set of ground-state densities \mathcal{N} which are produced by a suitable normalized antisymmetric wave-functions are called N -representable densities and it can be shown by explicit construction that one can always find such a wave-function, which in fact, it is a Slater determinant and therefore, $\Psi[n_0]$ can be defined for arbitrary ground-state densities [40, 41].

The variational property of the ground-state energy Eq.(2.13) can also be expressed as follows

$$E_{v_e}[n_0] = \min_n \langle \Psi[n] | \hat{H}[v_e] | \Psi[n] \rangle = \min_n E_{v_e}[n] \quad (2.14)$$

and since by the HK theorem it is proved that the ground-state energy for a non-degenerate system is a unique functional of the ground-state density, we can write the energy functional as

$$E_{v_e}[n] = F[n] + \int d\mathbf{r} v_e(\mathbf{r})n(\mathbf{r}), \quad (2.15)$$

where the functional $F[n]$ is the HK universal functional defined as

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle, \quad (2.16)$$

which is defined by construction for all ground-state densities. Note that despite of the HK theorem has been proved only for non-degenerate ground-state energy, the $F[n]$ functional can also be defined for degenerate ground-states because all of them produce the same ground-state energy, but in general no other expectation value is a functional of the density since not all the ground-state wave functions produce the same ground-state density. We called the HK functional universal in the sense that it

does not depend on the external potential v_e and once the two-body electron-electron interaction is fixed, the functional is the same for all electronic systems.

The minimum condition Eq.(2.14) can also be formulated by means the variational equation as follows

$$\left. \frac{\delta F[n]}{\delta n(\mathbf{r})} \right|_{n_0} + v_e(\mathbf{r}) = \mu, \quad (2.17)$$

where μ ensures the density to integrate to N particles. The above equation Eq.(2.17) is an equation to be solved for the ground-state density n_0 once the universal functional $F[n]$ is known. Of course, the form of the exact HK functional is not known as a functional of the density in a simple way, and for practical applications, it needs to be approximated.

2.2 The Kohn-Sham equations

We have established that the ground-state density of N -electron interacting system, as an alternative of the N -particle wave function contains enough information for the determination of any expectation value. The Kohn-Sham (KS) construction allows to calculate the ground-state density of an N -electron interacting system by means a N -electron non-interacting system which produces the same ground-state density as the interacting one.

For deducing the KS equations, consider first an N -electron non-interacting system, i.e., $\widehat{W} = 0$ such that it produces a given ground-state density n . The single-particle Hamiltonian h_s is given by Eq.(1.9) where we introduced the subindex "s" for making explicit that it stands for "single particle", and where the single particle equations Eq.(1.10) in position-spin basis read

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_s[n](\mathbf{r}) \right] \varphi_i(\mathbf{x}) = \varepsilon_{\sigma i} \varphi_i(\mathbf{x})$$

with

$$n(\mathbf{r}) = \sum_{\sigma, i} |\varphi_i(\mathbf{x})|^2, \quad (2.18)$$

where $v_s[n]$ is the one-body external potential that produces a given non-interacting ground-state density n and where the sum in the ground-state density runs over all occupied orbitals. Note that since the external potential is a functional of the ground-state density, the single-particle orbitals and the energy spectrum are both also functionals of the ground-state density. Let us write the non-interacting energy functional as

$$E_s[n] = T_s[n] + \int d\mathbf{r} v_s(\mathbf{r})n(\mathbf{r}), \quad (2.19)$$

where $T_s[n]$ is the kinetic energy of the N -electron non-interacting system. According to the variational principle, the ground-state density is obtained by solving the variational equation

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_0} + v_s(\mathbf{r}) = \mu_s, \quad (2.20)$$

where the constant μ_s ensures that the density integrates to N particles.

Consider now a N -electron interacting system described by the Hamiltonian Eq.(1.5), with a given one-body external potential v_e such that it produces a ground-state density n_0 . The key point of the KS scheme is that it is assumed that for any electronic N -interacting system with external one-body potential v_{e0} producing a density n_0 , there always exist a non-interacting system with one-body external potential $v_s[v_e, n_0]$ which produces the same density n_0 . The following construction determines by means the non-interacting system the ground-state density of the interacting one, for a given one-body external potential. By writing the N -electron interacting energy functional in the following convenient way

$$E_{v_e}[n] = T_s[n] + \int d\mathbf{r} v_e(\mathbf{r})n(\mathbf{r}) + E_{\text{Hxc}}[n], \quad (2.21)$$

where we have added and subtracted the kinetic energy of the non-interacting system $T_s[n]$, and where the Hxc energy functional is defined as

$$E_{\text{Hxc}}[n] = F[n] - T_s[n], \quad (2.22)$$

then the variational equation that solves for the ground-state density n_0 now reads

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_0} + v_e(\mathbf{r}) + v_{\text{Hxc}}[n_0](\mathbf{r}) = \mu_s, \quad (2.23)$$

where we have defined the Hxc potential as

$$v_{\text{Hxc}}[n](\mathbf{r}) = \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})} \quad (2.24)$$

for all ground-state densities. Now, and by virtue of the HK theorem, we know there exist only one potential producing a given ground-state density and therefore

$$v_s[n_0](\mathbf{r}) = v_e(\mathbf{r}) + v_{\text{Hxc}}[n_0](\mathbf{r}), \quad (2.25)$$

defined for any ground-state density $n = n_0$. The external potential v_s and more specifically, the Hxc potential v_{Hxc} is not known as a functional of the density in a simple way, and for practical purposes, it needs to be approximated. Finding, therefore, good approximations for the Hxc potential has been the task during the last years. It is important to notice that the KS scheme only reproduces the N -particle interacting ground-state density by means the KS ground-state wave function, but being both ground-state wave function and energy spectrum different than the interacting one.

Once the ground-state density of the interacting system is known, the ground-state energy of the N -electron interacting system can be expressed as a function of the ground-state density in the following way. By multiplying the KS equations Eq.(2.18) by the hermitic conjugate KS orbital, we have for the kinetic energy that

$$T_s[n] = \sum_{\sigma,i} \int d\mathbf{x} \varphi_i^*(\mathbf{x}) \left(-\frac{\nabla^2}{2} \right) \varphi_i(\mathbf{x}) = \sum_{\sigma,i} \varepsilon_{\sigma,i} - \int d\mathbf{x} v_s[n](\mathbf{r})n(\mathbf{r}), \quad (2.26)$$

wherein the second step we used the KS equation. Inserting the KS kinetic energy in Eq.(2.19) finally one obtains

$$E_{v_{e0}}[n] = \sum_{\sigma,i} \varepsilon_{\sigma,i} - \int d\mathbf{x} v_{\text{Hxc}}[n](\mathbf{r})n(\mathbf{r}) + E_{\text{Hxc}}[n], \quad (2.27)$$

which is an exact expression for the interacting N -particle ground-state energy as a functional of the ground-state density which depends on both the Hxc energy and Hxc potential.

Let us analyze the compounds of the Hxc energy functional for their subsequent use in the following sections. First of all, we define the two-body expectation value due only to correlation effects in the same fashion as Eq.(2.31), by subtracting the classical electron-electron interaction expectation value as

$$W_{xc}[n] = W[n] - U_H[n]. \quad (2.28)$$

Furthermore, we note that since the interacting and the non-interacting system both produce the same density, by using the variational theorem and the fact that Ψ and Ψ_s produce the same ground-state density, we get the following inequality

$$T_s[n] = \langle \Psi_s[n] | \hat{T} | \Psi_s[n] \rangle < \langle \Psi[n] | \hat{T} | \Psi[n] \rangle = T[n] \quad (2.29)$$

and hence we can define the kinetic energy due to the correlation effects by subtracting the kinetic energy of the non-interacting system as

$$T_{xc}[n] = T[n] - T_s[n] \geq 0. \quad (2.30)$$

Then, we see that the xc energy takes into account the energy due to correlation effects and which is compound of a kinetic and a two-body interaction part as

$$E_{xc}[n] = T_{xc}[n] + W_{xc}[n], \quad (2.31)$$

being the original Hxc energy related with the xc by the addition of the classical electron-electron interaction as

$$E_{Hxc}[n] = E_{xc}[n] + U_H[n] \quad (2.32)$$

The next section is devoted to constructing an alternative expression of the Hxc energy functional which allow for practical approximations.

2.3 The coupling constant integration

In this section we introduce a more general N -electron interacting Hamiltonian as a useful tool which allows deriving relations among density functionals and in particular, it provides a convenient expression for the Hxc/xc energy functional.

Let us introduce the N -electron interacting λ -Hamiltonian as follows

$$\hat{H}_\lambda[n] = \hat{T} + \hat{V}_\lambda[n] + \lambda \hat{W}, \quad (2.33)$$

where \hat{T} is the kinetic energy operator and \hat{W} is the two-body electron-electron interaction operator which are given by the expression Eq.(1.2) and Eq.(1.4) respectively. The electron-electron interaction is now scaled with λ , a non-dimensional, continuous and real parameter. Finally the one-body external potential operator reads

$$\hat{V}_\lambda[n] = \sum_{i=1}^N V_\lambda[n](\mathbf{r}_i). \quad (2.34)$$

The one-body external potential is defined in a way that the ground-state density that it produces is independent of λ and equal to the ground-state density that a given external potential for $\hat{V}_{\lambda=1} \equiv \hat{V}_e$ produces. We can write this condition as follows

$$n(\mathbf{r}) = \langle \Psi_{\lambda,0} | \hat{n}(\mathbf{r}) | \Psi_{\lambda,0} \rangle = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N |\Psi_{\lambda,0}[n](\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2, \quad (2.35)$$

where the density operator was defined at Eq.(1.46) and where $\Psi_{\lambda,0}$ is the ground-state eigenvector of the interacting N -particle many-body Hamiltonian Eq.(2.33) that solves the time-independent Schrödinger equation

$$\widehat{H}_\lambda[n]|\Psi_{\lambda,i}\rangle = E_{\lambda,i}[n]|\Psi_{\lambda,i}\rangle, \quad (2.36)$$

where $E_{\lambda,i}$ and $\Psi_{\lambda,i}$ are its eigenvalue and eigenstates respectively. Therefore, for a given external potential for $\lambda = 1$, \widehat{V}_e , the one-body external potential of the λ -Hamiltonian is an implicit functional of the density which is assumed to exist for all λ , ie, we assume all the densities are v_λ -representable and according to with the HK theorem, if the v_λ exist, it is unique for each λ . Therefore with the λ -Hamiltonian we can describe different scenarios. For example, for $\lambda = 1$ the Hamiltonian Eq.(2.33) describes the system at full coupling constant while for $\lambda = 0$ it describes a non-interacting system producing the same density than the full interacting one $\lambda = 1$, i.e., the KS system.

Having introduced the λ -Hamiltonian, we now derive an expression for the Hxc energy as a function of the pair-correlation distribution function g_λ . We start by considering the ground-state energy obtained by the Hamiltonian Eq.(2.33). Taking its derivative as a function of λ and by Hellman-Feynman theorem we have

$$\frac{dE_\lambda[n]}{d\lambda} = \langle \Psi_\lambda[n] | \frac{d\widehat{H}_\lambda}{d\lambda} | \Psi_\lambda[n] \rangle, \quad (2.37)$$

where we have dropped the "0" of the ground-state eigenstate and energy since none of the excited-states are used. Integrating the above relation back from 0 to λ we get

$$\begin{aligned} E_\lambda[n] - E_0[n] &= \int_0^\lambda \langle \Psi_\alpha[n] | \frac{d\widehat{H}_\alpha}{d\alpha} | \Psi_\alpha[n] \rangle d\alpha = \int_0^\lambda \langle \Psi_\alpha[n] | \frac{d\widehat{V}_\alpha}{d\alpha} + \widehat{W} | \Psi_\alpha[n] \rangle d\alpha \\ &= \int d\mathbf{r} n(\mathbf{r}) [v_\lambda(\mathbf{r}) - v_0(\mathbf{r})] + \int_0^\lambda d\alpha \langle \Psi_\alpha[n] | \widehat{W} | \Psi_\alpha[n] \rangle, \end{aligned} \quad (2.38)$$

wherein the last step, we interchanged the integration in λ and space. We now recognize E_0 as the the KS ground-state energy functional, and therefore we obtain the following expression for E_λ

$$E_\lambda[n] = T_s[n] + \int d\mathbf{r} n(\mathbf{r}) v_\lambda(\mathbf{r}) + \int_0^\lambda d\alpha \langle \Psi_\alpha[n] | \widehat{W} | \Psi_\alpha[n] \rangle. \quad (2.39)$$

Now and because the external one-body potential is uniquely defined, according to the HK theorem we can construct the universal HK functional for all λ defined as

$$F_\lambda[n] = \langle \Psi_\lambda[n] | \widehat{T} + \lambda \widehat{W} | \Psi_\lambda[n] \rangle, \quad (2.40)$$

and then we can define a Hxc energy functional

$$E_{\text{Hxc}}^\lambda[n] = F_\lambda[n] - T_s[n]. \quad (2.41)$$

By comparing with Eq.(2.41), we recognize the last term of Eq.(2.39) to be the Hxc energy functional, i.e.,

$$E_{\text{Hxc}}^\lambda[n] = \int_0^\lambda d\alpha W_\alpha[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') \bar{g}(\mathbf{r}, \mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|), \quad (2.42)$$

and we see that the Hxc energy of one system λ is given by the contribution of all the systems α . We have then obtained an expression for the Hxc energy functional as a function of the coupling constant pair-correlation distribution function g_α , where we have defined the integrated pair-correlation function \bar{g}_λ as,

$$\bar{g}_\lambda(\mathbf{r}, \mathbf{r}') = \int_0^\lambda d\alpha \frac{\Gamma_\alpha(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} = \int_0^\lambda d\alpha g_\alpha(\mathbf{r}, \mathbf{r}'). \quad (2.43)$$

The above expression has been found to be very useful in the construction of approximate density functionals, and it is the expression we will base our future analysis on. Furthermore, since by the variational principle we have that $T_\lambda > T_s$ for all λ , we can define the Hxc kinetic energy T_{Hxc}^λ as the kinetic energy due to correlation effects as

$$T_{\text{Hxc}}^\lambda[n] = T_\lambda[n] - T_s[n], \quad (2.44)$$

and then, we can express the Hxc energy functional as a kinetic plus electron-electron interaction contribution as

$$E_{\text{Hxc}}^\lambda[n] = T_{\text{Hxc}}^\lambda[n] + \lambda W_\lambda[n]. \quad (2.45)$$

As a final remark, we note by means the definition of the Hxc Eq.(2.42) that the kinetic and the electron-electron interaction functionals as a function of the Hxc energy read respectively

$$W_{\text{Hxc}}^\lambda[n] = \frac{dE_{\text{Hxc}}^\lambda[n]}{d\lambda} \quad (2.46)$$

$$T_{\text{Hxc}}^\lambda[n] = E_{\text{Hxc}}^\lambda[n] - \lambda \frac{dE_{\text{Hxc}}^\lambda[n]}{d\lambda}. \quad (2.47)$$

2.4 The exchange-correlation potential

2.4.1 Asymptotic properties of the xc potential

In this section, we briefly discuss the asymptotic properties of the xc potential for Coulomb systems. Since for practical implementation of the KS scheme the xc potential needs to be approximated, the knowledge of the asymptotic behavior of the xc potential is useful for the construction of such approximations.

Consider a neutral atom with $Z = N$, being Z the nuclear charge and N the number of electrons. We are interested in the behavior of the xc potential far away from the density cloud when ($\mathbf{r} \rightarrow \infty$). For doing so, we remove one electron of the system, and we bring it far away from the atom, leaving $N - 1$ electrons. The potential that will experience this electron because of the N positive charges and $N - 1$ negative charges will be that one created by a positive charge. Thus, far away from the density cloud the KS potential behaves as

$$v_s(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} \quad (|\mathbf{r}| \rightarrow \infty). \quad (2.48)$$

We also know that the external potential of the interacting system and the Hartree potential respectively accomplish that

$$v_e(\mathbf{r}) = -\frac{N}{|\mathbf{r}|}, \quad v_H(|\mathbf{r}|) = \frac{N}{|\mathbf{r}|} \quad (|\mathbf{r}| \rightarrow \infty). \quad (2.49)$$

Therefore, the xc potential must have the following asymptotic behavior

$$v_{\text{xc}}(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} \quad (|\mathbf{r}| \rightarrow \infty). \quad (2.50)$$

A rigorous derivation of this result can be found in [42].

2.5 Approximate density functionals: Local density approximation and gradient expansion approximations

The simplest and the most used approximation in DFT is the so-called local density approximation (LDA). The LDA assumes the Hxc energy functional to depend on the density in one single point of the space, i.e., locally. For a practical implementation of the LDA, it is assumed that the system at hand we want to study behaves locally as it would be an homogeneous electron gas (HEG). The reason for taking the HEG as a reference physical system is because the density at one point describes the density everywhere and therefore, the approximation is aimed to work for those inhomogeneous systems that do not deviate so much from homogeneous ones. Doing a local approximation, the Hxc energy functional reads

$$E_{\text{Hxc}}^{\text{LDA}}[n] = \int d\mathbf{r} \ e_{\text{Hxc}}^h(n)|_{n(\mathbf{r})}, \quad (2.51)$$

where $e_{\text{Hxc}}^h(n)$ is the energy density of the HEG which is replaced by the density of the inhomogeneous system $n(\mathbf{r})$. We see that the LDA is an enormous simplification since for an arbitrary inhomogeneous system, the Hxc energy and the Hxc potential have in general a complicated dependence of the density, as it is manifest from the exact expression Eq.(2.41). Thus, the LDA Hxc potential gets the spatial dependence only by means the density at one spatial point. Effectively, taking functional derivatives with respect to the density of the LDA energy functional, the Hxc potential reads

$$v_{\text{Hxc}}^{\text{LDA}}(\mathbf{r})[n] = \left. \frac{de_{\text{Hxc}}^h(n)}{dn} \right|_{n=n(\mathbf{r})}, \quad (2.52)$$

where the homogeneous density is replaced by the density of an inhomogeneous system. For the HEG, and because the exchange pair correlation function can be calculated exactly, the exchange energy density contribution is known exactly and reads

$$\epsilon_x^{\text{hom}} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}, \quad (2.53)$$

where it is defined the Fermi vector $|\mathbf{k}| = (3\pi^2 n)^{1/3}$ as the wave modulus vector which refers to the highest occupied energy level. For the correlation contribution, only the high and low-density limits are known analytically. For the high-density limit or weak interaction limit, the energy density per volume reads [43]

$$e_c^{\text{HEG}} = c_0 \ln r_s - c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots \quad (r_s \rightarrow 0). \quad (2.54)$$

where the Wigner-Seitz radius $r_s = \left(\frac{3}{4\pi n} \right)^{1/3}$ is defined as the radius of a sphere whose volume is equal to the mean volume per atom in a solid. For the low-density limit or the strong interaction limit, the HEG crystallizes in the form of a b.c.c. lattice, which is the so-called Wigner crystal [44, 45]. In the strong or low-density limit, the kinetic energy of the electrons becomes negligible in comparison of the contribution of the electron-electron repulsion. Since when the electron-electron repulsion becomes infinitely strong, the lowest energy configuration is that one that the electrons remain in their equilibrium positions, it is assumed that when the system acquires kinetic energy, their motion is just restricted to perform small oscillations around their equilibrium position. By implementing an expansion around the minimum of the potential, corrections to the leading order of the correlation energy per volume in the strong/low-density limit are obtained, which read

$$e_c^{\text{hom}} = -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \frac{d_2}{r_s^2} + \dots \quad (r_s \rightarrow \infty). \quad (2.55)$$

The energy per particle of the HEG provide a Hxc energy functional and Hxc potential where we insert the density of any arbitrary inhomogeneous system.

One has to consider that although an inhomogeneous system can have a density that does not deviate so much from the uniform density in one point, it can still have rapid variations, i.e., the gradient of the density can be important. Consider a density evaluated at $\mathbf{r} + d\mathbf{r}$. The Hxc potential evaluated in that density reads

$$v_{\text{Hxc}}[n(\mathbf{r} + d\mathbf{r})] = v_{\text{Hxc}}[n(\mathbf{r}) + \nabla n(\mathbf{r})d\mathbf{r}], \quad (2.56)$$

from where we see that if the gradients of the density are negligible in comparison with the density, the evaluation of the Hxc potential at the local density can be a good approximation, but if the gradients of the density are not negligible they must be taken into account. A systematic way to generate semi-local corrections to the LDA is to consider the Hxc energy to depend not only on the local density but also on its gradients, generating like this a semi-local functional. It is in this spirit how the gradient expansions approximations are constructed [46]. For its derivation, it is considered weakly inhomogeneous systems such that the density of the inhomogeneous system vary not so much in comparison with the HEG, and also the gradients of the density are taken into consideration, leading to an energy functional constructed as follows

$$E_{\text{Hxc}}^{\text{GEA}}[n] = \int d\mathbf{r} e_{\text{Hxc}}^h [n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \dots]. \quad (2.57)$$

As a final remark on the local approximations, we point that the LDA can be performed not only in the energy functional but also in other relevant quantities, like the pair-correlation distribution function, or the exchange-correlation hole.

It is needed to comment that there are other systematic approaches to generate Hxc energy functional more than the local and semi-local approximations we explained in this section. An example is what is known as Görling-Levy perturbation theory [47], which is a perturbation expansion that generates a Hxc functional based on the coupling constant integration Hamiltonian Sec. 2.3. The perturbation expansion is performed around the KS Hamiltonian, i.e., for small interaction strength with the constraint that in each order of the perturbation expansion, the ground-state density remains independent of the interaction strength. As we commented in the introduction, it is dubious that these approaches to generating a Hxc energy functional that relies on perturbation expansions for a weak interaction perform well to describe strongly correlated systems.

2.6 Dissociation of H₂

In this section, we review a strongly correlated system which we are interested in describing by density functional methods, namely, the H₂ molecule in the limit of large bond distances or dissociation limit. We first describe the system in terms of its 2-electron wave function in the limit of large bond distances, and we discuss on the basis of the asymptotic wave function the correlations that the system shows. We then study how local approximations of the density perform to describe the physics of this strongly correlated system.

2.6.1 Wave function description

The starting point is the Hamiltonian of the H_2 molecule, which is given by

$$H(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2} (\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2) + v_e(\mathbf{r}_1) + v_e(\mathbf{r}_2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2.58)$$

and where the external one-body potential is

$$v_e(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} - \frac{1}{|\mathbf{r} - \mathbf{R}|}, \quad (2.59)$$

being $|\mathbf{R}|$ the bond distance between the nucleus. For the two electrons system, the ground-state wave function which is the solution of the Schrödinger equation can be written as the product of the spatial times the spin wave function in the following way

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(\sigma_1, \sigma_2). \quad (2.60)$$

Because the ground-state is a singlet, then the spin wave function reads

$$\chi(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} (\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}), \quad (2.61)$$

and since the spin wave function is antisymmetric, it follows that the space wave function must be symmetric under the interchange of space variables, in order the total wave function to be antisymmetric under simultaneous interchange of space and spin variables. We are interested in the description of the system in the large separation limit, when $|\mathbf{R}| \rightarrow \infty$. At large bond distances, the two-body interaction becomes negligible, and the system must become that one of two independent atoms. The wave function that minimizes the energy functional for all two-body interactions is the well-known Heitler-London (HL) wave function, which reads

$$\psi_{\text{HL}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) - \psi_u(\mathbf{r}_1)\psi_u(\mathbf{r}_2)], \quad (2.62)$$

where g and u stands for "gerade" and "ungerade" respectively, and which are given by

$$\psi_g(\mathbf{r}) = \frac{1}{\sqrt{2}} [\varphi_a(|\mathbf{r}|) + \varphi_b(|\mathbf{r} - \mathbf{R}|)] \quad (2.63)$$

$$\psi_u(\mathbf{r}) = \frac{1}{\sqrt{2}} [\varphi_a(|\mathbf{r}|) - \varphi_b(|\mathbf{r} - \mathbf{R}|)], \quad (2.64)$$

where $\varphi_a(\mathbf{r}) = \exp(-|\mathbf{r}|)$ and $\varphi_b(\mathbf{r}) = \exp(-|\mathbf{r} - \mathbf{R}|)$ are the localized orbitals. Without loss of generality, since the Hamiltonian Eq.(2.58) is invariant under a translation of the separation $|\mathbf{R}|$, the atoms have been placed one in $\mathbf{r} = 0$ and the other at $\mathbf{r} = \mathbf{R}$.

Let us look at the probability distributions constructed by the HL wave function Eq.(2.62). The exact conditional probability constructed by the HL ground-state wave function reads

$$\frac{|\psi(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})} = \frac{\varphi_a^2(|\mathbf{r}|)\varphi_b^2(|\mathbf{r}'|) + \varphi_b^2(|\mathbf{r}|)\varphi_a^2(|\mathbf{r}'|)}{\varphi_a^2(|\mathbf{r}|) + \varphi_b^2(|\mathbf{r}|)}. \quad (2.65)$$

If we now suppose that the reference electron is close to the $\mathbf{r} \sim 0$, then the conditional probability in the limit of large bond distances reduces to

$$\frac{|\psi(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})} = \varphi_b^2(|\mathbf{r}'|), \quad \text{for } (|\mathbf{R}| \rightarrow \infty), \quad (2.66)$$

which means that if we put a reference electron close to the atom 1, then the probability to find the second electron somewhere in the space is an exponential probability distribution picked in the center of the atom 2, $|\mathbf{r}| \sim |\mathbf{R}|$, reducing in this way the probability to find it close to the atom 1. It is with this meaning that we can say that the electrons are strongly correlated, since if the reference electron is close to the atom 1, the other electron is around the atom 2 with the probability distribution Eq.(2.66), hence being the electrons strongly correlated.

Once the general features of a H_2 molecule in dissociation are presented, we discuss in the next section how the LDA performs for the description of such correlations.

2.6.2 Molecular dissociation in the LDA

In this section, we review qualitatively the performance of the Hxc potential constructed from LDA for the description of a dissociating molecule [41]. For finite systems like atoms and molecules, the exact density is known to have an exponential decay far away from the electronic cloud as [42]

$$n(\mathbf{r}) \sim e^{-2\sqrt{2I}|\mathbf{r}|}, \quad (|\mathbf{r}| \rightarrow \infty), \quad (2.67)$$

where I is the ionization energy. Since the density decays exponentially, the behavior of the Hxc potential in the LDA approximation is known to have also an exponential decaying far away from the electronic cloud region $|\mathbf{r}| \rightarrow \infty$, which as we explained, it is the wrong asymptotic behavior. Since the asymptotic behavior is not the Coulomb $-1/|\mathbf{r}|$, a direct consequence of this fact is that the KS energy spectrum obtained by means the LDA for atoms and molecules does not reproduce the Rydberg series correctly. One observes that the Hxc potential is too much short range as it must be, and the reason is because it depends on the density in only one point, i.e., the density dependence is too much simple. Since the density behaves exponentially, then all the derivatives of the density also behave exponentially meaning that they are equally important. Therefore, making local approximations, we would have to take into account all the gradients, which already indicates that any functional based on local and semi-local approximations of the density is condemned to fail for this type of systems, in the same way that LDA does.

It is therefore needed to construct new density functionals which can capture the correct non-local dependence of the Hxc functional as a function of the density to describe a strongly correlated system like a molecule under dissociation. It is in this spirit how the strictly correlated electrons functional, a formalism which aims to deal with strongly correlated electrons in DFT framework has been introduced.

2.7 The strictly correlated electrons formalism: Ground-state theory

The strictly correlated electrons (SCE) formalism is a ground-state density-functional theory which can capture the physics of an interacting N -particle system when the interaction between electrons becomes very large. The starting point of the formalism is to define the SCE energy functional as the infimum of the two-body electron interaction

$$V_{\text{SCE}}[n] = \inf_{\Psi \rightarrow n} \langle \Psi | \widehat{W} | \Psi \rangle. \quad (2.68)$$

The form of the minimizer is a spin-integrated distribution function, the so-called the SCE distribution function $|\Psi_{\text{SCE}}|$ and it is searched in a way that it guarantees a given smooth density. The minimizer was already introduced in [1, 2] without proof, and it has recently been proved to be the correct minimizer of the functional Eq.(2.68) [48], which is

$$|\Psi_{\text{SCE}}(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 = \frac{1}{N!} \sum_{\mathcal{P}} \int ds \frac{n(\mathbf{s})}{N} \delta(\mathbf{r}_1 - \mathbf{f}_{\mathcal{P}(1)}(\mathbf{s})) \times \dots \times \delta(\mathbf{r}_N - \mathbf{f}_{\mathcal{P}(N)}(\mathbf{s})), \quad (2.69)$$

wherein Eq.(2.69) the \mathcal{P} denotes a permutation over the label $1\dots N$. The distribution function $|\Psi_{\text{SCE}}|^2$ is zero everywhere except in a subspace of the full space \mathbb{R}^{3N} , which we denote by M and which is defined as

$$M = \{\mathbf{r}, \mathbf{f}_1(\mathbf{s}), \dots, \mathbf{f}_N(\mathbf{s}) \mid \mathbf{s} \in P\}, \quad (2.70)$$

where P is the subspace such that $P \subseteq \mathbb{R}^3$ is the region where the ground-state density is defined. It is in M where the ground-state energy reaches its minimum, which must be degenerate, a required condition to guarantee a smooth density. If the minimum was not degenerate in this subspace, there would be a set of discrete points such that the ground-state energy would reach its minimum, forcing in this way the electrons to collapse in those positions to minimize the energy of the system and producing a non smooth density, in contradiction with the requirement. The physical meaning of the co-motion functions $\mathbf{f}_i(\mathbf{s})$ is that provided the position of a reference electron, namely \mathbf{s} is fixed, the position of all others $N - 1$ electrons are given by means the co-motion functions at the positions $\mathbf{r}_i = \mathbf{f}_i(\mathbf{s})$ for $i = 1, \dots, N$. Because of the electrons are indistinguishable, the position of the reference electron is chosen arbitrarily, and then the co-motion functions must obey the cyclic properties

$$\begin{aligned} \mathbf{f}_i(\mathbf{s}) &= \underbrace{\mathbf{f}(\dots\mathbf{f}(\mathbf{s}))}_{i \text{ times}} \\ \mathbf{s} &= \underbrace{\mathbf{f}(\dots\mathbf{f}(\mathbf{s}))}_{N \text{ times}}. \end{aligned} \quad (2.71)$$

Since the position of the reference electron determines the positions of all the others $N - 1$ electrons, the probability of finding the reference electron in the volume element $d\mathbf{r}$ around the position \mathbf{r} must be the same that the probability of finding the i th electron in the volume element $d\mathbf{f}_i(\mathbf{r})$ around the position $\mathbf{f}_i(\mathbf{r})$. It thus means that the co-motion function must satisfy the following differential equation

$$n(\mathbf{f}_i(\mathbf{s})) d\mathbf{f}_i = n(\mathbf{s}) ds \quad \text{for} \quad i = 2, \dots, N, \quad (2.72)$$

and therefore, they are determined by the ground-state density. For one dimensional systems, the differential equation for the co-motion functions allows for an integrated solution [49], and whose form is shown in the appendix A. After the substitution of the SCE distribution function in Eq.(2.68), the SCE energy functional takes the form

$$V_{\text{SCE}}[n] = \frac{1}{2} \sum_{i < j}^N \int ds \frac{n(\mathbf{r})}{N} w(|\mathbf{f}_i(\mathbf{s}) - \mathbf{f}_j(\mathbf{s})|) = \frac{1}{2} \sum_{i=2}^N \int ds \frac{n(\mathbf{r})}{N} w(|\mathbf{s} - \mathbf{f}_i(\mathbf{s})|), \quad (2.73)$$

and then, the SCE total energy can be written as

$$E_{\text{SCE}}[n] = V_{\text{SCE}}[n] + \int d\mathbf{r} v_{\text{SCE}}(\mathbf{r})n(\mathbf{r}) \quad (2.74)$$

where v_{SCE} is the SCE one-body external potential that guarantees the required smooth density.

Now we establish the connection with the energy functional Eq.(2.40). The SCE energy functional was introduced without proof as the reasonable limit of the HK functional in the strong interaction

limit $\lambda \rightarrow \infty$ of $\frac{F_\lambda[n]}{\lambda}$, since in this limit, by Eq.(2.46) and Eq.(2.47), the kinetic energy becomes negligible in comparison with the two-body interaction contribution, but it was never proved that in the λ infinity limit, the resulting distribution function is that one that minimizes the two-body interaction functional only [48]. The result is the following

$$\lim_{\lambda \rightarrow \infty} \frac{F_\lambda[n]}{\lambda} = V_{\text{SCE}}[n], \quad (2.75)$$

and therefore, the variational equation Eq.(2.17) leads to the definition of the SCE potential as the functional derivative with respect to the density of the SCE energy functional as

$$v_{\text{SCE}}(\mathbf{r}) = -\frac{\delta V_{\text{SCE}}[n]}{\delta n(\mathbf{r})}, \quad (2.76)$$

which it has been proved it can be calculated via the expression [50]

$$\nabla v_{\text{SCE}}[n](\mathbf{s}) = -\sum_{i=2}^N w'(|\mathbf{s} - \mathbf{f}_i(\mathbf{s})|) \frac{\mathbf{s} - \mathbf{f}_i(\mathbf{s})}{|\mathbf{s} - \mathbf{f}_i(\mathbf{s})|}, \quad (2.77)$$

and which has the following physical meaning: The SCE potential acting in one electron i counteracts the two-body electron-electron repulsion between pairs of the others $N - 1$ electrons to keep the prescribed density $n(\mathbf{s})$. As an illustrative example, we compute in the appendix B the functional derivative of the SCE energy functional for two particles systems in one dimension in a straightforward way, obtaining the general result Eq.(2.77).

Because of result Eq.(2.75), the SCE energy functional can be understood as the leading order term of an expansion it is assumed to exist, of the coupling constant $W_\lambda[n]$ energy functional for the large interaction strength $\lambda \rightarrow \infty$. The following step is to introduce a model for giving an expression to the next to the leading order term in the large interaction strengths limit. It then can be thought that since in the SCE limit, the electrons are frozen in their equilibrium position $\mathbf{r}_i = \mathbf{f}_i(\mathbf{s})$ such that the energy functional is minimized while keeping a smooth density, it is, therefore, a plausible assumption that when the coupling constant is large, but not strictly infinity, the electrons are allowed to perform small vibrations around the equilibrium positions $\mathbf{r}_i \sim \mathbf{f}_i$, which for an N -electron system in D dimensions is given by [2]

$$V_{\text{ZPE}}[n] = \frac{1}{2} \sum_{i=4}^{DN-D} \int ds \frac{n(\mathbf{s}) \omega_\mu(\mathbf{s})}{N \frac{2}{2}}, \quad (2.78)$$

where ZPE stands for "zero-point energy", and where ω_i are the frequencies of the local normal modes, which are given by the diagonal elements of the Hessian matrix around the SCE energy minimum. For two electrons systems in one dimension, systems which we are interested in, there is a single frequency which has an explicit expression as a function of the two body interaction and the single co-motion function $f(s)$ as [32]

$$\omega(s) = \sqrt{w''(|s - f(s)|) \left[\frac{n(s)}{n(f(s))} + \frac{n(f(s))}{n(s)} \right]}. \quad (2.79)$$

The harmonic approximation assumption implies that the $DN - D$ frequencies are proportional to the square root of the interaction strength, and it is believed that the remaining terms in the large interaction strength expansion of the functional $W_\lambda[n]$ obey a power expansion in terms of the square root of the interaction strength as

$$W_\lambda[n] = V_{\text{SCE}}[n] + \frac{V_{\text{ZPE}}[n]}{\sqrt{\lambda}} + \mathcal{O}(\lambda^{-3/2}). \quad (2.80)$$

All together amounts for an expression for the Hxc energy functional in terms of powers of the square root of the interaction strength as follows

$$E_{\text{Hxc}}^\lambda[n] = \lambda V_{\text{SCE}}[n] + 2\sqrt{\lambda}V_{\text{ZPE}}[n] + V_3[n] + \mathcal{O}\left(\lambda^{-1/2}\right), \quad (2.81)$$

where we see that the contribution for the Hxc of the zero-point energy is twice the two-body interaction expectation, since $T_{\text{xc}}[n] = W_\lambda[n]$. Assuming then we are allowed to take functional derivatives term-wise, the first order functional derivative with respect to the density gives an expansion for the Hxc potential in orders of $\sqrt{\lambda}$ as

$$v_{\text{Hxc}}^\lambda(\mathbf{r}) = \lambda v_{\text{SCE}}(\mathbf{r}) + \sqrt{\lambda}v_{\text{ZPE}}(\mathbf{r}) + v_3(\mathbf{r}) + \mathcal{O}\left(\lambda^{-1/2}\right). \quad (2.82)$$

For the ZPE potential in the case of 2-electrons systems in one dimension, we refer to the appendix B for a detailed derivation.

The SCE formalism, therefore, proposes a construction of the Hxc energy functional and Hxc potential which encodes in them a non-local ground-state density dependence via the co-motion functions and thus it becomes a good candidate functional to describe strongly correlated systems. The next section is devoted to study the SCE formalism for a strongly correlated system of interest, i.e., the dissociation of molecules.

The KS-SCE equations and the H₂ dissociation

The KS-SCE consists of the use of the large interaction strength expansion of the Hxc potential obtained by the SCE Eq.(2.82) in a KS scheme, and evaluate such expansion in the physical system $\lambda = 1$. The first approximation with this approach is to take the leading term of the large λ expansion which in this case is $v_{\text{Hxc}}(\mathbf{r}) = v_{\text{SCE}}(\mathbf{r})$. The KS-SCE equations then read

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v(\mathbf{r}) + v_{\text{SCE}}[n](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

with

$$\sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 = n(\mathbf{r}). \quad (2.83)$$

The KS-SCE has been tested for reproducing the energy curve of a H₂ in dissociation in [33, 51]. It has been found that the SCE potential indeed dissociates correctly. The reason is that the co-motion function, in the limit of large bond distances, localize each of the electrons exactly where the positions of the nucleus are, depicting in this way the right physics of a dissociation process in the asymptotic region although the SCE electronic wave function is different than the HL wave function. By any manner, the SCE formalism only reproduces the asymptotic region, and the energy gets underestimated when the bond distance approaches to the equilibrium distance, since the KS-SCE energy fulfills

$$T_s[n] + V_{\text{SCE}}[n] \leq F[n], \quad (2.84)$$

which becomes equal only in the asymptotic region. Also, the SCE+ZPE have been used as a Hxc potential, i.e.,

$$v_{\text{Hxc}}(\mathbf{r}) = v_{\text{SCE}}(\mathbf{r}) + v_{\text{ZPE}}(\mathbf{r}), \quad (2.85)$$

producing in this way a much worse result [32]. The reason is because despite the co-motion functions describe the physics of dissociation correctly and therefore the SCE leading order describes

the dissociation limit accurately, there is not an energy contribution due to vibrations around an equilibrium position since the system we want to describe, the dissociating H_2 molecule is not an interacting system with an infinitely strong repulsion, and therefore the ZPE picture does not apply to a dissociating system.

A proof of the fact that the KS-SCE formalism gives the correct ground-state energy in the dissociation limit $R \rightarrow \infty$ can be found in [50]. The theorem proves nothing but the KS-SCE energy of a H_2 molecule gives the energy of 2 separate H atoms in the dissociation limit. This result indicates that the SCE-DFT model correctly describes the H_2 molecule in its dissociating limit and put on solid foundations the KS-SCE scheme.

3 Time-dependent density functional theory

3.1 The time dependent density-potential mapping: The extended Runge-Gross theorem

Consider an interacting time-dependent N -electron system described by the Hamiltonian Eq.(1.42). The time-dependent N -electron wave function is determined by solving the time-dependent Schrödinger equation Eq.(1.44) for a given initial state Ψ_0 . The time-dependent density is calculated according to

$$n[\Psi_0, v_e](\mathbf{r}, t) = \langle \Psi[\Psi_0, v_e](t) | \hat{n}(\mathbf{r}) | \Psi[\Psi_0, v_e](t) \rangle = \sum_{\sigma_1, \dots, \sigma_N} \int d\mathbf{r}_2 \dots \mathbf{r}_N |\Psi[\Psi_0, v_e](\mathbf{x}_1, \dots, \mathbf{x}_N, t)|^2 \quad (3.1)$$

As in the ground-state case, for a fixed two-body interaction, the time-dependent Schrödinger equation defines a map by which each external potential $v(\mathbf{r}, t)$ produces a given time-dependent density, once the initial state is specified. The content of the extended Runge-Gross (RG) theorem shows not only the uniqueness of the map which allows defining the time-dependent density as a fundamental variable, but also shows that the time-dependent density can be produced by another time-dependent potential $v'(\mathbf{r}, t)$. The extended RG theorem contains two statements, which are announced as follows [4, 9, 52, 53]

Extended Runge-Gross theorem:

- The time-dependent density produced by an interacting N -electron time-dependent system described by the Hamiltonian $\hat{H}(t)$, with a two-body electron-electron interaction \widehat{W} and for a given initial state Ψ_0 is a unique functional of the time dependent external potential $v_e(\mathbf{r}, t)$, up to a time-dependent constant.
- The time-dependent density produced by an interacting N -electron time-dependent system described by the Hamiltonian $\hat{H}(t)$ and two-body electron-electron interaction \widehat{W} , for a given initial state Ψ_0 can also be reproduced by another time-dependent system $\hat{H}'(t)$ with two-body electron-electron interaction \widehat{W}' and initial state Ψ'_0 , up to a time-dependent constant. The initial state Ψ'_0 must be chosen in a way that it correctly yields the given density and its time derivative at the initial time.

Let us now prove the theorem. Consider the time-dependent many-body system Eq.(1.42) whose solution of the time-dependent Schrödinger equation is $\Psi(t)$ and its initial state is Ψ_0 . Consider a second many-body system described by the Hamiltonian

$$\hat{H}'(t) = \hat{T} + \hat{V}'(t) + \widehat{W}', \quad (3.2)$$

whose solution of the time-dependent Schrödinger equation is $\Psi'(t)$ and its initial state is Ψ'_0 . Our hypothesis assumption is that the time-dependent wave function solution of the primed system Ψ' with initial state Ψ'_0 produces the same density as the time-dependent wave function of the original system, i.e., we assume that the time-dependent densities of each system are the same for all times, ie, $n(\mathbf{r}, t) = n'(\mathbf{r}, t)$. We further assume that the time-dependent external potential of both systems are analytic in time, i.e., for all times their time derivatives exist

$$v_e(\mathbf{r}, t) = \sum_{k=0}^{\infty} v_k(\mathbf{r})(t - t_0)^k \quad (3.3)$$

$$v'_e(\mathbf{r}, t) = \sum_{k=0}^{\infty} v'_k(\mathbf{r})(t - t_0)^k \quad (3.4)$$

Now we make use of the equation which relates the time-dependent potential with the time-dependent densities. The equation that relates time-dependent densities and time-dependent external potentials Eq.(1.62) for both systems reads

$$\partial_t^2 n(\mathbf{r}, t) = \nabla[n(\mathbf{r}, t)\nabla v_e(\mathbf{r}, t)] + q(\mathbf{r}, t) \quad (3.5)$$

$$\partial_t^2 n(\mathbf{r}, t) = \nabla[n(\mathbf{r}, t)\nabla v'_e(\mathbf{r}, t)] + q'(\mathbf{r}, t) \quad (3.6)$$

where q' is defined in and analogous way as Eq.(1.63) for the primed system. Since the equations Eq.(3.5) and Eq.(3.6) are second order partial differential equations in time domain for the density, we need to impose two initial conditions. The first one is that both initial states of the unprimed and primed systems must yield the same density at the initial time

$$n(\mathbf{r}, t_0) = n'(\mathbf{r}, t_0) \quad (3.7)$$

The second initial condition involves the first derivatives of the density of the unprimed and primed system, which must also be equal

$$\partial_t n(\mathbf{r}, t)|_{t=t_0} = \partial_t n'(\mathbf{r}, t)|_{t=t_0} \quad (3.8)$$

This condition means that the initial state Ψ'_0 must be chosen such that the initial momentum of both systems are the same, and finite, i.e.,

$$\mathbf{P}(t) = \int d\mathbf{r} \mathbf{J}(\mathbf{r}, t) = \int d\mathbf{r} \mathbf{r} \partial_t n(\mathbf{r}, t) < \infty, \quad (3.9)$$

since the momentum depends on the density and no other quantity. Because the densities are the same by assumption for all times and hence its time derivatives, it implies that the momenta are the same for all times, which cannot be satisfied if the momenta of the unprimed and primed systems are different at the initial time, which would require an infinite force to make them equal at an immediate time after the initial time $t > t_0$. By subtracting Eq.(3.5) and Eq.(3.6) we obtain

$$\nabla [n(\mathbf{r}, t)\nabla\omega(\mathbf{r}, t)] = \zeta(\mathbf{r}, t) \quad (3.10)$$

where we defined $\omega = v - v'$ and $\zeta = q' - q$. The above equation does not contain time derivatives any more. It is a Sturm-Liouville equation type, which has a unique solution for ω if n and ζ are given, and if we further specify the boundary conditions for ω such that it vanishes at infinity. Notice also that imposing the boundary conditions at infinity also means that we are fixing the time-dependent gauge $C(t)$ in $v'_e(\mathbf{r}, t)$. Let us now first look at $t = t_0$, where the equation Eq.(3.10) becomes

$$\nabla [n(\mathbf{r}, t_0)\nabla\omega(\mathbf{r}, t_0)] = \zeta(\mathbf{r}, t_0) \quad (3.11)$$

and since $n(\mathbf{r}, t)$ is known for all the times, and ζ_0 can be calculated from the both the initial states of the unprimed and primed system, then there is a unique solution for the zeroth order coefficient of the Taylor expansion

$$v'(\mathbf{r}, t_0) = v(\mathbf{r}, t_0) + \zeta(\mathbf{r}, t_0) \quad (3.12)$$

Proceeding in the same way, we can take the k derivative of the equation Eq.(3.10), which in general yields to

$$\nabla \left[n(\mathbf{r}, t_0) \nabla \omega^{(k)}(\mathbf{r}) \right] = \mathcal{Q}^k(\mathbf{r}) \quad (3.13)$$

where the operator \mathcal{Q}^k is given by

$$\mathcal{Q}^k(\mathbf{r}) = \zeta^k(\mathbf{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \nabla \left[n^{(k-l)}(\mathbf{r}) \nabla \omega^{(l)}(\mathbf{r}) \right] \quad (3.14)$$

and where ζ^k involves commutators between the operator \hat{q} and the Hamiltonians averaged between their respective initial states, and time derivatives of the Hamiltonians. Therefore, the term \mathcal{Q}^k is wholly determined provided we have determined the previous \mathcal{Q}^{k-1} by means the density, the potential of the unprimed system, and the initial states Ψ_0 and Ψ'_0 are known. This procedure, then, determines all the Taylor expansion coefficients systematically and hence, the method provides a complete determination of the primed potential at all times. The meaning of the extended Runge-Gross theorem can be seen schematically in the Fig. 3.1. Since the extended Runge-Gross theorem

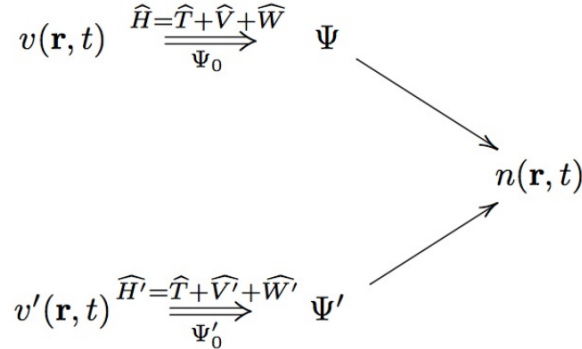


Figure 3.1: Extended Runge-Gross theorem: The time-dependent density produced by $\hat{H}(t)$ and a given initial state Ψ_0 can also be produced by $\hat{H}'(t)$ with an initial state Ψ'_0 .

does not depend on the shape of the primed two-body interaction \widehat{W} , let us now take the particular case that the unprimed system is equal to the primed, i.e., $w = w'$ and $\Psi_0 = \Psi'_0$. Since the unprimed and primed systems and their initial states are the same, it means that the time-dependent density is a unique functional of the external time-dependent potential and the initial state Ψ_0 . Therefore the map of the set of time-dependent densities to the set of time-dependent potentials is invertible, meaning that the time-dependent external potential is a unique functional of the time-dependent density and the initial state and hence, the N interacting time-dependent many body Hamiltonian is a unique functional of the time-dependent density and the initial state, which we write as

$$\hat{H}[n, \Psi_0](t) \Psi[n, \Psi_0](t) = i \partial_t \Psi[n, \Psi_0](t) \quad (3.15)$$

As a consequence, the time-dependent many-body wave function and therefore all the physical observables given by a quantum average are functionals of the time-dependent density and the initial

state, and thus, every quantum average is a functional of the time-dependent density and the initial state as

$$O[\Psi_0, n](t) = \langle \Psi[\Psi_0, n](t) | \widehat{O}(t) | \Psi[\Psi_0, n](t) \rangle, \quad (3.16)$$

which puts on solid foundations the use of the time-dependent density as an alternative variable instead of the time-dependent wave function.

Another case of interest is when the primed system is a non-interacting system, i.e., when $w' = 0$ with the initial state of the non-interacting system $\Psi'_0 = \Phi_0$. According with the extended Runge-Gross theorem there is a unique potential, namely $v_s(\mathbf{r}, t)$ up to a time-dependent constant such that it produces the time-dependent density $n(\mathbf{r}, t)$ for all times $t > t_0$. This justifies the time-dependent KS (TDKS) scheme.

3.2 The time-dependent Kohn-Sham scheme

In the previous section, we have proved the extended Runge-Gross theorem. It not only states that for a given a time-dependent many-body Hamiltonian $\widehat{H}(t)$ given by Eq.(1.42) with a fixed two-body interaction, there is a one-to-one correspondence between time-dependent one-body external potentials and time-dependent ground-state densities for a given initial state Ψ_0 , but also it states that the time-dependent ground-state density can be obtained via another $\widehat{H}'(t)$ for a given initial state Ψ'_0 . In particular, we are interested in the choice of the primed system such that $\widehat{W}' = 0$ which immediately allows for the TDKS construction [6].

Consider a non-interacting system h_s where the single particle equations in position-spin basis are given by

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_s[\Phi_0, n](\mathbf{x}, t) \right] \varphi_i(\mathbf{x}, t) = i \partial_t \varphi_i(\mathbf{x}, t)$$

with

$$n(\mathbf{r}, t) = \sum_{\sigma, i} |\varphi_i(\mathbf{x}, t)|^2 \quad (3.17)$$

where $v_s[\Phi_0, n]$ is the time-dependent one-body external potential that produces a given time-dependent ground-state density $n(t)$, for a given initial state Φ_0 of the non-interacting N -electron many-body wave function, and where the sum in the ground-state density runs over all occupied orbitals. Consider now a N -electron interacting time-dependent system described by the Hamiltonian Eq.(1.42), with a given one-body external potential $v_e(t)$ featuring a time dependent density $n_0(t)$. According to the extended Runge-Gross theorem, we can always find a time-dependent N -electron non-interacting system with a time-dependent one-body external potential $v_{ks}(t)$ featuring the same time-dependent density $n_0(t)$. In this case, the single particle equations in position-spin basis read

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_{ks}[\Psi_0, \Phi_0, v_e, n](\mathbf{r}, t) \right] \varphi_i(\mathbf{x}, t) = \varepsilon_{\sigma i} \varphi_i(\mathbf{x}, t)$$

with

$$n(\mathbf{r}, t) = \sum_{\sigma, i} |\varphi_i(\mathbf{x}, t)|^2 \quad (3.18)$$

where now the single particle one-body potential of the non interacting system is a functional of the one-body potential of the interacting system, the initial states of both the interacting and non-interacting system and the time-dependent density. The one body potential $v_{\text{ks}}[v_{\text{e0}}, n]$ is constructed in the following way

$$v_{\text{ks}}[\Psi_0, \Phi_0, v_e, n](\mathbf{r}, t) = v_e(\mathbf{r}, t) + v_{\text{Hxc}}[\Psi_0, \Phi_0, n](\mathbf{r}, t)$$

with

$$v_{\text{Hxc}}[\Psi_0, \Phi_0, n](\mathbf{r}, t) = v_s[\Phi_0, n](\mathbf{r}, t) - v_e[\Psi_0, n](\mathbf{r}, t) \quad (3.19)$$

Whenever the density $n = n_0$ and according to the extended Runge-Gross theorem, there exist only a unique potential producing a given time-dependent density provided the two-body electron-electron interaction is fixed, and therefore

$$v_e(\mathbf{r}, t) = v_e[\Psi_0, n_0](\mathbf{r}, t) \quad (3.20)$$

and thus

$$v_{\text{ks}}[\Psi_0, \Phi_0, v_e, n](\mathbf{r}, t) = v_s[\Phi_0, n](\mathbf{r}, t) \quad (3.21)$$

for all time-dependent densities $n = n_0$. We therefore see that the set of equations Eq.(3.19) have a solution at the density $n = n_0$ for given initial state Ψ_0 and Φ_0 . From the expression of the KS potential Eq.(3.19) we explicitly see that $v_{\text{Hxc}}[\Psi_0, \Phi_0, n]$ is an object which in general depends on the ground-state density, the initial state of the interacting system and the initial state of the non-interacting system. It is also customary in the TDKS scheme to split the time-dependent Hxc potential in the Hartree potential plus the xc potential.

3.3 The exact time-dependent Hxc potential

The central object of the TDKS scheme is the Hxc or the xc time-dependent potential, where all the effect of the two-body electron interaction are encoded. We dedicate this section to study the most relevant properties of the xc potential that are important for the present work.

From the general expression Eq.(3.6) we can derive the fundamental equation that the xc potential obeys. Particularizing the primed system to be the KS system, ie, $\widehat{W} = 0$, we have that $\omega = -v_{\text{Hxc}}$, which inserted in Eq.(3.11) we obtain for the Hxc potential [54]

$$\nabla [n(\mathbf{r}, t) \nabla v_{\text{Hxc}}(\mathbf{r}, t)] = q(\mathbf{r}, t) - q_s(\mathbf{r}, t) \quad (3.22)$$

where the quantities q and q_s depend on the 1 and 2 time-dependent reduced particle density matrices of the interacting system and the KS system respectively. Equation Eq.(3.22) is a Sturm-Liouville equation for the Hxc potential, which gives a unique solution for given n , Γ , Γ_s , for specified boundary conditions for v_{xc} as it was discussed before in the previous section for the more general case. Expression Eq.(3.22) shows that the Hxc potential has a contribution that comes purely from kinetic origin while there is another part coming from the interaction energy. We therefore see explicitly and not surprisingly that for approximations for the Hxc potential as a function of the density and the initial states one needs to model the time-dependent 1 and 2-particle reduced density matrices as functionals of the density and the initial states of both interacting and non-interacting system.

3.3.1 Exact conditions for the time-dependent exchange potential

As in the static case, a Hxc potential is an unknown object which has to be approximated, and the knowledge of exact properties of the exact Hxc potential can be a guide for the construction of such approximations. In this section, we list some of the exact conditions we will use in the construction of the Hxc potentials. These exact conditions can be found in [7].

The zero-force theorem

Consider the total momentum of the time-dependent interacting system which was defined in Eq.(1.58). Since the total momentum is a quantity that depends only on the time-dependent density and no other quantity, the KS momentum must be the same as the interacting one, and hence

$$\mathbf{P}(t) = \int d\mathbf{r} \mathbf{j}(\mathbf{r}, t) = \int d\mathbf{r} \mathbf{r} \partial_t n(\mathbf{r}, t) = \int d\mathbf{r} \mathbf{j}_s(\mathbf{r}, t) = \mathbf{P}_s(t) \quad (3.23)$$

where the KS current-density \mathbf{J}_s is defined in an analogous way as

$$\mathbf{j}_s(\mathbf{r}, t) = \langle \Phi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle \quad (3.24)$$

Therefore the following identity follows

$$0 = \partial_t [\mathbf{P}(t) - \mathbf{P}_s(t)] = - \int d\mathbf{r} n(\mathbf{r}, t) \nabla [v(\mathbf{r}, t) - v_s(\mathbf{r}, t)] = \int d\mathbf{r} n(\mathbf{r}, t) \nabla v_{\text{Hxc}}(\mathbf{r}, t) \quad (3.25)$$

The last equation represents the force applied by the Hxc potential, which is originated by internal forces. Thus, the total force applied to the system must vanish identically, according to Newton's law. It happens that both vanish separately as the Hartree contribution vanishes by itself [7].

The generalized translational invariance

Another exact condition any Hxc potential must fulfill is what is known as generalized translational invariance, and in this section, we proceed to announce it without proof. For a detailed derivation, we refer to [7].

Let us consider a time-dependent density $n_a(\mathbf{r}, t)$ which is obtained by performing a translation in a time-dependent density $n(\mathbf{r}, t)$ with a vector $\mathbf{X}(t)$, ie $n_a(\mathbf{r}, t) = n(\mathbf{r} + \mathbf{X}(t), t)$. The theorem states that the Hxc potential associated with the translated density n_a is obtained by performing a translation of the Hxc potential associated with the original density n , i.e.,

$$v_{\text{Hxc}}[n_a](\mathbf{r}, t) = v_{\text{Hxc}}[n](\mathbf{r} + \mathbf{X}(t), t) \quad (3.26)$$

3.3.2 Temporal non-locality and initial state dependence of the time-dependent Hxc potential

In this section, we briefly comment on what is known as memory dependence of the Hxc potential as a function of the time-density. The complete knowledge of the interacting time-dependent N -electron wave function and its initial state are the needed objects for the calculation of any time-dependent quantum average. The time-dependent wave function is an object that depends on only one time t and no earlier times are needed for its determination of the time-dependent expectation values. Having substituted the fundamental variable from time-dependent wave function to the time-dependent

density in a KS scheme with a Hxc potential that reproduces the time-dependent density introduces a non-linear dependence of the Hxc potential as a function of the density which depends on it at all previous times. To understand what we mean by non-locality in time or memory dependence it is enough to analyze the procedure how the Hxc potential is constructed as a function of the time-dependent density. By virtue of the extended Runge-Gross theorem and assuming analyticity in time of the Hxc potential, the set of equations Eq.(3.22), Eq.(3.13), Eq.(3.14) give, as we explained previously, a systematic way to obtain the Taylor coefficients of the Hxc potential in a climbing way such that the $k + 1$ Taylor coefficient depends on the k Taylor coefficient, which in turn it depends on the derivatives of the density. It means that for the knowledge of the Hxc potential at a given time t it is required the knowledge of the density at the time t and all previous times, and also the initial states of both the interacting and non-interacting initial states Ψ_0 and Φ_0 . An explicit example showing how the Hxc potential depends on the density at previous times and the initial states of the interacting and non-interacting system can be found in [7].

3.3.3 The adiabatic approximation for the Hxc potential

Let us consider the most used approximation for the Hxc potential of TDDFT, which is the adiabatic approximation. The adiabatic approximation consists on to consider a Hxc potential that depends on the instantaneous density, discarding in this way all the density dependence at all previous times. To make the scheme practical, what is typically done is to take a Hxc potential of the ground-state DFT, which depends on the ground-state density, and replace it by the time-dependent density in the following way

$$v_{\text{Hxc}}^{\text{A}}[n](\mathbf{r}, t) = v_{\text{Hxc}}^0[n_0](\mathbf{r}) \Big|_{n_0(\mathbf{r}) \rightarrow n(\mathbf{r}, t)} \quad (3.27)$$

where $n_0(\mathbf{r})$ is the ground-state density. The functional $v_{\text{xc}}^0[n_0]$ is still a complicated functional of the ground-state density and therefore, to make it useful one takes one of the many approximate Hxc functionals constructed for ground-state DFT. This is indeed the case of the adiabatic local-density approximation (ALDA), in which the functional dependence of space and time of the Hxc potential are given by means the time-dependent density, and where all the space and time dependence comes from the local density. The adiabatic approximation then is supposed to work in the limit when the instantaneous density is at its ground state. In that situation, the functional dependence of the Hxc potential at the time t is only by means the instantaneous density and approximately it does not depend on the density at previous times. Again, and for making the ALDA a practical scheme, one relies on physical arguments and it is taken the energy per volume from HEG

$$v_{\text{Hxc}}^{\text{ALDA}}[n_0](\mathbf{r}, t) = \left. \frac{d\epsilon_{\text{Hxc}}^h(\bar{n}_0)}{d\bar{n}_0} \right|_{n(\mathbf{r}, t)} \quad (3.28)$$

where \bar{n}_0 is the density of the HEG which is replaced by the time-dependent density of the system of interest.

3.4 Linear-response theory

In this section we introduce the linear response function, an object of particular, interest since the knowledge of the response function provides information about the excitation energies and the absorption spectrum of a given time-independent system.

For the introduction of the density response function, we consider time-independent many-body system \hat{H}_0 to which we apply an small external time-dependent potential $\delta v(\mathbf{r}, t)$ for which $t \geq t_0$,

being $\delta v(\mathbf{r}, t) = 0$ for $t < 0$. We are interested in the study of the change in the ground-density caused by the time-dependent potential. The response in the ground-state density at first order perturbation theory that produces the time-dependent external potential is given by [6, 7]

$$\delta n(\mathbf{r}, t) = \int d\mathbf{r}' dt' \chi(\mathbf{r}, t; \mathbf{r}', t') \delta v(\mathbf{r}', t') \quad (3.29)$$

where the density response function is defined to be the functional derivative of the time-dependent density as a function of the external potential, evaluated at any external reference potential

$$\chi(\mathbf{r}, t; \mathbf{r}', t') = \left. \frac{\delta n(\mathbf{r}, t)}{\delta v(\mathbf{r}', t')} \right|_{\bar{v}(\mathbf{r}, t)} \quad (3.30)$$

which for our particular interest we will take to be the time-independent reference potential of the unperturbed system, i.e., the external potential at $t = 0$. The explicit form of the density response function is

$$\chi(\mathbf{r}, t; \mathbf{r}', t') = -i\theta(t - t') \langle \Psi_0 | [\hat{n}_H(\mathbf{r}, t), \hat{n}_H(\mathbf{r}', t')] | \Psi_0 \rangle \quad (3.31)$$

where $\theta(t - t')$ ensures the density response function to be a causal function, and where Ψ_0 is the ground-state of the time-independent Hamiltonian \hat{H}_0 . Because we choose the reference Hamiltonian to be time-independent, the density response function must depend only on the difference $t - t'$. We can then Fourier transform the Eq.(3.31) to frequency space and obtain the expression [6, 7]

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_n \left[\frac{\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_n \rangle \langle \Psi_n | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{\omega - \Delta E_n + i\eta} - \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}') | \Psi_n \rangle \langle \Psi_n | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{\omega - \Delta E_n + i\eta} \right] \quad (3.32)$$

which is known as the Lehmann representation of the response function, where η is a positive infinitesimal parameter that keeps the causal structure of the retarded response function and whose limit has to be taken to zero from the right. From the expression Eq.(3.32) it is shown explicitly how the poles of the linear response function are the excitation energies of the unperturbed system. We therefore see that the knowledge of the linear response function is enough for the knowledge of the excitation energies of the time-independent system.

3.5 The large frequency limit of the density response function

With the purpose of the study of the analytic structure in the time domain of the density response function and also the Hxc kernel of TDDFT, which we will introduce in the next section, we proceed to describe the large frequency limit of the density response function.

It can be shown that the inverse of the density response function in the large frequency limit admits the expansion [6]

$$\chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \omega^2 a(\mathbf{r}, \mathbf{r}') + b(\mathbf{r}, \mathbf{r}') + \tilde{h}_{\text{reg}}(\mathbf{r}, \mathbf{r}', \omega), \quad (3.33)$$

where the coefficients a can be constructed from the ground-state density and the second coefficient b is derived by the so-called third frequency moment sum rule. Transforming back the response function in the high-frequency limit to the time domain, it attains the form

$$\chi^{-1}(\mathbf{r}, \mathbf{r}', t - t') = a(\mathbf{r}, \mathbf{r}') \delta''(t - t') + b(\mathbf{r}, \mathbf{r}') \delta(t - t') + h_{\text{reg}}(\mathbf{r}, \mathbf{r}', t - t'), \quad (3.34)$$

where δ'' is the second derivative of the delta function and where h_{reg} is the regular part of the density response function in the sense that it does not contain any delta functions in the time variable, and moreover it can be shown to be a causal function.

After having discussed the properties and the time/frequency structure of the density response function, we will show in the next section how to calculate it in the TDDFT framework.

3.6 Linear response function in TDDFT

The linear response function of the interacting system is calculated in the TDDFT formalism using the linear response function of a non-interacting system. Consider the KS potential Eq.(3.19), which depends on the external one-body potential of the interacting system, and let us apply a small time-dependent perturbation. The external potential of the interacting system and the KS potential both produce the same time-dependent ground-state density. By the extended Runge-Gross theorem, the variation of the KS potential due to the variation of the external potential of the interacting system will produce the same density variations. Taking variations of the KS potential as a function of the time-dependent density yields the following equation

$$\chi^{-1}(\mathbf{r}t, \mathbf{r}'t') = \chi_s^{-1}(\mathbf{r}t, \mathbf{r}'t') + f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \quad (3.35)$$

where we have defined the density response function of the non-interacting system to be the functional derivative of the KS potential as a function of the time-dependent density, evaluated at a time-dependent reference density

$$\chi^{-1}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{\tilde{n}(\mathbf{r}, t)} \quad (3.36)$$

which for our purposes we choose to be the ground-state density of the unperturbed system since it is the system we are interested in. The object f_{Hxc} is the so-called Hxc kernel of TDDFT, defined as the functional derivative of the Hxc potential with respect to the time-dependent density, evaluated at a reference density

$$f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{\text{Hxc}}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{\tilde{n}(\mathbf{r}, t)} \quad (3.37)$$

and also for our purposes, we will evaluate at the unperturbed density. Taking the inverse of the Eq.(3.35) yields the following equation

$$\chi(1, 2) = \chi_s(1, 2) + \int d3d4 \chi(1, 3) f_{\text{Hxc}}(3, 4) \chi_s(4, 2) \quad (3.38)$$

where we have introduced the compact notation $i = (\mathbf{r}_i, t_i)$. We see that the Hxc kernel is, therefore, the operator that connects the density response function of the non-interacting system with the density response function of the interacting one, and as it was the case in the KS scheme for the Hxc potential, for practical purposes, it needs to be approximated.

For the discussion in the next section Sec. 4, it is important to note a formal property regarding the Hxc kernel, that is, the functional derivative Eq.(3.37) is not a uniquely defined function [55], since for a system with a fixed number of particles the density variations must integrate to zero. If we define a new Hxc kernel in the following way

$$\tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') + g(\mathbf{r}, t, t') + h(\mathbf{r}', t, t') \quad (3.39)$$

with g and h arbitrary functions, then the change in the Hxc potential produced by the kernel of Eq.(3.39) due to a density change δn is given by

$$\begin{aligned} \delta \tilde{v}_{\text{Hxc}}(\mathbf{r}t) &= \int d\mathbf{r}' dt' \tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t') = \int d\mathbf{r}' dt' f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t') \\ &+ \int d\mathbf{r}' dt' [g(\mathbf{r}, t, t') + h(\mathbf{r}', t, t')] \delta n(\mathbf{r}'t') = \delta v_{\text{Hxc}}(\mathbf{r}t) + C(t) \end{aligned} \quad (3.40)$$

which as consequence of the particle conservation, the integral over g integrates to zero, and the integral over h yields only a time-dependent constant. We therefore see that \tilde{f}_{Hxc} and f_{Hxc} are

physically equivalent Hxc kernels. The quantity that is defined unambiguously is the mixed spatial derivative [3]

$$\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t'), \quad (3.41)$$

a property that will be used in the next chapter.

It is instructive to write explicitly the density response function of the non-interacting system for further comprehension and subsequent analysis. The non-interacting KS ground-state and excited states are pure Slater determinant. Since the density operator is a one-body operator, it connects only two orbitals of both the ground-state and the excited state Slater determinants, and therefore, the excited states can only be single particle excited states for the matrix element of the KS density response function not to be zero. Otherwise the matrix element $\langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_n \rangle$ is zero. The KS density response function therefore reads

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{j,k=1}^{\infty} (f_k - f_j) \frac{\varphi_j^0(\mathbf{r}) \varphi_k^{0*}(\mathbf{r}) \varphi_j^{0*}(\mathbf{r}') \varphi_k^0(\mathbf{r}')}{\omega - \omega_{jk} + i\epsilon} \quad (3.42)$$

where f_j and f_k are the occupation numbers for the KS ground-state, i.e., 1 for occupied and 0 for unoccupied orbitals, and where $\omega_{jk} = \varepsilon_j - \varepsilon_k$ are the KS eigenvalues which are the excitation energies of the single excited state. We see that the KS density response function has information about single excitations, but in general, in an interacting system, we can have all kind of excitations and not only single excitations ones. As we will see in the next section, the Hxc kernel does the job to correct the KS excitation energies to the ones of the interacting system.

For ending this section and with the purpose to use it in the next one, we comment the analytical decomposition of the Hxc kernel for the high-frequency limit which reads [6]

$$f_{\text{Hxc}}(\mathbf{r}, t, \mathbf{r}', t') = f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega = \infty) \delta(t - t') + f_{\text{Hxc}}^{\text{reg}}(\mathbf{r}, \mathbf{r}', t - t') \quad (3.43)$$

where we defined

$$f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega = \infty) = b_s(\mathbf{r}, \mathbf{r}') - b(\mathbf{r}, \mathbf{r}') \quad (3.44)$$

which is the high-frequency limit of the Hxc kernel. The remaining part, which is

$$f_{\text{Hxc}}^{\text{reg}}(\mathbf{r}, \mathbf{r}', t - t') = h_{\text{reg},s}(\mathbf{r}, \mathbf{r}', t - t') - h_{\text{reg}}(\mathbf{r}, \mathbf{r}', t - t') \quad (3.45)$$

is the subtraction of the regular parts, which do not contain delta functions and is a causal function. From the expression Eq.(3.45) we can see that the Hxc kernel consists of a piece $f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega = \infty)$ which is instantaneous in time, i.e., it has no memory depth and the remaining part in which all the memory effects are incorporated. Therefore, the analytical decomposition of the Hxc kernel allows studying at the linear response level the memory dependence of the Hxc potential as a function of the time-dependent density, which is the discussion will be addressed in the next section.

3.6.1 The memory dependence

We have seen that the inverse of the density response function in the time domain is compound of one part that is instantaneous in time and the regular part that has a memory depth Eq.(3.45). As we already announced, this decomposition is useful to study in an explicit way the memory and initial state dependence of the Hxc potential that is generated by a small perturbation on the time-dependent density given by its linear response. The Hxc potential that is created by the Hxc kernel reads [56, 57]

$$\delta v_{\text{Hxc}}(\mathbf{r}t) = \int d\mathbf{r}' dt' f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t'). \quad (3.46)$$

Inserting in the above expression the Hxc kernel in its high frequency limit decomposition Eq.(3.45), we see how the first term gives a contribution that depends on the density at instantaneous times while the regular part, which does not contain delta functions is the responsible to provide the dependence of the Hxc potential as a function of the density at time t , and at all previous times and as well both the initial states of the interacting and the non-interacting systems.

3.7 Local approximations for the Hxc kernel

As in the xc potential, the most used approximation for the Hxc kernel are based on local approximations, which we proceed to enumerate. The simplest approximation is the random-phase approximation, which consist on setting the Hxc kernel to zero

$$f_{xc}^{\text{RPA}}(\mathbf{r}, \mathbf{r}', \omega) = 0 \quad (3.47)$$

and which means that all the correlation effects are ignored. This simplification automatically approximates the linear density response of an interacting system by the KS one. Another common approximation for the Hxc kernel is the adiabatic approximation. By adiabatic at the regime of the Hxc kernel, we mean that we approximate the kernel such that it has no memory depth, i.e., we consider a kernel where we discard the regular part in the expression Eq.(3.45), being of the form

$$f_{\text{Hxc}}^{\text{A}}(\mathbf{r}, \mathbf{r}', \omega) = f(\mathbf{r}, \mathbf{r}') \quad (3.48)$$

where $f(\mathbf{r}, \mathbf{r}')$ is a function which does not depend on the frequency and which depends only on space coordinates. In particular, it is of interest the ALDA for the Hxc kernel that is obtained from the homogeneous electron gas, i.e.,

$$f_{\text{Hxc}}^{\text{A}}(\mathbf{r}, \mathbf{r}', \omega) = \left. \frac{d^2 e_{\text{Hxc}}^h(n)}{dn^2} \right|_{n \rightarrow n(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}'). \quad (3.49)$$

3.7.1 The zero-force theorem and the long-range property

In this section, we review the zero-force theorem in the linear response regime. Consider the zero-force theorem of TDDFT Eq.(3.25) and consider small variations of the Hxc potential produced by a small change in the ground-state density. Using the equation of the Hxc potential generated by the Hxc kernel, and after some manipulations, one arrives to [7, 58]

$$\int d\mathbf{r} f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \nabla' n_0(\mathbf{r}') = \nabla v_{\text{Hxc}}(\mathbf{r}) \quad (3.50)$$

From this expression, we can study the spatial range property of the Hxc kernel. Let us suppose that we have a frequency dependent Hxc kernel that has been derived from a local or a semi-local approximation in space, i.e., such that it contains Dirac delta functions in space $\delta(\mathbf{r} - \mathbf{r}')$ and derivatives of Dirac deltas. If we insert such Hxc kernel in the integral Eq.(3.50), we immediately see the consequences. The right-hand side does not depend on the frequency while the left-hand side depends on it, leading to a contradiction. The integration over space had to cancel the frequency dependence of the exact Hxc kernel to have a consistent result. The assumption therefore, which has been to construct a Hxc kernel which is frequency dependent and local in space is in contradiction. The contradiction means that the initial assumption was wrong and therefore there are no frequency dependent kernels that are constructed from local or semi-local approximations. A frequency dependent Hxc kernel, therefore, must be spatially non-local. Note that the contrary does not follow. We can still have a non-local Hxc kernel in space and local in time or adiabatic.

3.7.2 Calculation of the excitation energies: The Casida equation

A practical application of the density response function in TDDFT is to calculate the excitation energies. In this section we present Casida equation, which is an eigenvalue-like equation derived from the linear response TDDFT equation Eq.(3.38) and which solves for the excitation energies of the interacting system, i.e., for the poles of the density response of the interacting system, knowing the KS single excitations. The Casida equation is derived from the density response function observing that since the excitation energies are the poles of the density response function, and since the density variations once a small perturbation to the system is applied are always finite, we need the external potential to approach to zero in the same way the linear response diverges. Casida equation then is obtained by writing the equation Eq.(3.38) in a basis of KS orbitals, which in its matrix form reads [7]

$$\sum_{j,b} [\delta_{ij}\delta_{ab}\omega_{bj}^2 + 4\sqrt{\omega_{ai}\omega_{bj}} K_{ia,jb}(\Omega)] Z_{jb} = \Omega^2 Z_{ia} \quad (3.51)$$

where we defined the matrices

$$\begin{aligned} \varepsilon_{ia,jb} &= \omega_{ai}\delta_{ij}\delta_{ab} \\ K_{ia,jb}(\omega) &= \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i(\mathbf{r}_1)\varphi_a(\mathbf{r}_1)f_{\text{Hxc}}(\mathbf{r}_1, \mathbf{r}_2; \omega)\varphi_j(\mathbf{r}_2)\varphi_b(\mathbf{r}_2) \end{aligned} \quad (3.52)$$

and where i, j refer to KS occupied levels, a, b to unoccupied levels and $\omega_{ai} = (\varepsilon_a - \varepsilon_i)$ are the excitation energies of the KS system. The eigenvalues Ω are the excitation energies of the full many-body system, and the eigenvectors Z_{ia} are related with the probability of the excitation from the level i to level a to occur, and they will not be discussed in this introduction. We now see that for the knowledge of the excitation energies we have to calculate the KS orbitals and eigenvalues. For solving the equation, it is needed the exact ground-state Hxc potential and the exact frequency dependent Hxc kernel. We now see the role of the Hxc kernel. It is the object that corrects the KS excitation energies to the excitation energies of the fully interacting system. How does the Hxc kernel work to obtain the right excitation energies? We have seen that the KS excitation energies that appear on the density response function are single excitation energies. The poles of the KS system, as we commented previously contain only single excitations but multiple excitations are present in the interacting density response. It means that to reproduce such excitations, the matrix elements provided by the Hxc kernel Eq.(3.52) are needed to be frequency dependent since in this way the equation becomes a non-linear equation in the frequency, and therefore it is possible to create or destroy more poles than the number of the KS poles. On the other hand, if the Hxc kernel is frequency independent, it does not generate a different number of poles than the number of the KS excitations, but they suffer just a translation in the frequency axis. We then see that in order to calculate the excitation energies of an interacting system, we need a good approximation for the Hxc potential which produces the correct KS orbitals and KS eigenspectrum, and we need a good approximation for its functional derivative, the Hxc kernel which does the work to produce the excitation energies via Casida equation.

3.8 Performance of the ALDA for the calculation of excitation energies of a dissociating H₂ molecule

The ALDA approximation of TDDFT has been tested in the Casida formalism for the calculation of the lowest excitation energies of a dissociating H₂ molecule in [15–17], and it has been shown that it fails in reproducing the energy curve for such excitation. The reason why it fails is due to its

too simple spatial dependence of the Hxc kernel as a function of the density. For the case of the H₂ molecule using a minimal two orbital model, the correction term to the KS first excitation in Casida equation Eq.(3.52) reads [15]

$$(\varepsilon_u - \varepsilon_g)K_{gu,gu}, \quad (3.53)$$

where "g" and "u" stands for "gerade" and "ungerade", which have been defined in Eq.(2.63) and Eq.(2.64) respectively, and where gerade is the KS occupied orbital and ungerade the unoccupied orbital. An analysis of correction term indicates that since the first KS excitation approaches to zero in the limit of large bond distances, for obtaining a finite correction term and therefore finite excitation energy, the matrix elements $K_{gu,gu}$ must diverge in the same way the KS excitations approach to zero. The possible cases for making diverge the matrix elements are either a strong frequency-dependent Hxc kernel or an adiabatic Hxc kernel [15]. A study of the exact Hxc kernel for the limit of large bond distance using minimal models suggest that the spatial dependence of the kernel is rather more complicated than a kernel constructed by local approximations as a function of the density. Therefore, it is needed to construct a Hxc kernel such that it can capture the spacial non-local dependence that such a kernel must have to describe the strong correlation that a dissociation process shows.

3.9 Strictly correlated electrons in TDDFT

3.9.1 The adiabatic SCE functional

In this section we introduce the extension of the SCE formalism to the time domain, in the adiabatic approximation. Following the adiabatic approximation of the linear response theory in TDDFT, we use the ground-state theory that describes the strong interaction limit of DFT, in which the SCE formalism can be used in the adiabatic approximation for the construction of a Hxc kernel which, as it was explained in the previous section, it contains a non-local spacial dependence as a function of the density. For the ground-state SCE formalism, the Hxc energy functional is assumed to admit an expansion as a function of the square root of the interaction strength. Assuming then that we can take functional derivatives termwise of the expansion, the adiabatic Hxc kernel is defined as the second order variation of of the Hxc energy functional with respect to the density, which gives an expansion as a function of the square root of the interaction strength as follows

$$f_{\text{Hxc}}^{\text{A}}(\mathbf{r}, \mathbf{r}') = \lambda f^{\text{ASCE}}(\mathbf{r}, \mathbf{r}') + \sqrt{\lambda} f^{\text{AZPE}}(\mathbf{r}, \mathbf{r}') + f^{(3)}(\mathbf{r}, \mathbf{r}') + \mathcal{O}(\lambda^{-1/2}), \quad (3.54)$$

where the leading term of the expansion and the next to the leading term, the ASCE and the AZPE, are defined as

$$f^{\text{ASCE}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 V_{\text{SCE}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \quad (3.55)$$

$$f^{\text{AZPE}}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta^2 V_{\text{ZPE}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \quad (3.56)$$

It has been shown in [3] that the ASCE Eq.(3.55) satisfies the general constraints of many-body theories, like the generalized translational invariance or the zero-force theorem.

The ASCE functional has been calculated for one dimensional systems to be [3]

$$f^{\text{ASCE}}(x, x') = \int_{-\infty}^x ds \frac{w''(s - f(s))}{n(f(s))} [\theta(s - x') - \theta(f(s) - x')]. \quad (3.57)$$

The expression above derived for the Hxc kernel Eq.(3.57) has been studied for finite one-dimensional systems with different density profiles, some of which resemble the dissociation of two-electron molecules. It has been found that since the kernel is spatially non-local, it exhibits the correct analytical structure needed to describe a system under dissociation correctly, i.e., the kernel has an exponential growth as a function of the bond distance that makes diverge the matrix elements. This feature makes the ASCE kernel a good candidate for canceling the approach to zero of the KS eigenvalue difference and hence, producing the correct dissociation energies of a dissociating molecule.

It is our aim first to test whether the ASCE kernel can reproduce the kernel of a strongly interacting system. In the following chapter, therefore, we test the SCE formalism in the adiabatic approximation against an exact expression obtained from a model system such that the Schrödinger equation can be solved exactly, and therefore we can get the exact wave function, and in particular, we can compute with it the exact response properties we are interested in. In this work, we consider a model of two interacting electrons on a ring, for which we can compute the exact Hxc kernel and study it in the limit when the interaction between the electrons is strong. We can then compare the results with those given by the SCE formalism in the adiabatic approximation and establish if the SCE formalism in the adiabatic approximation can capture the correct physics of a strongly interacting system.

4 An exactly solvable system

4.1 Two interacting electrons on a ring

We consider an analytically solvable model, which consist on two interacting electrons of coordinates x_1, x_2 defined on a ring of length L , which we refer to as the quantum ring (QR) model. The Hamiltonian that describes the system reads

$$\hat{H} = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + \lambda V_0 \cos^2 \left[\frac{\pi}{L}(x_1 - x_2) \right] \quad (4.1)$$

where the first two terms are the kinetic energy of each electron and the last term is the two-body interaction. The strength of the interaction $\lambda \geq 0$ is a dimensionless, semi-continuous and positive parameter allowing in this way the Hamiltonian Eq.(4.1) to describe different physical situations, which range from $\lambda = 0$, describing a non-interacting system, until strongly interacting system. Since the external one-body potential is zero $v_{\text{ext}}(x) = 0$ the ground-state density of the system is homogeneous and $n(x) = \frac{2}{L}$.

The properties of the system are obtained by means the many-body wave function, which is the solution of the time-independent Schrödinger equation. For a system of two particles, the full solution of the Schrödinger is written as a product of the spatial wave function and the spin wave function as follows

$$\Psi(x_1\sigma_1, x_2\sigma_2) = \psi^\pm(x_1, x_2) \Xi^\pm(\sigma_1, \sigma_2).$$

where "+" refers to the singlet wave function, which is antisymmetric under the interchange of the spin variables and is given by

$$\Xi^+(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} (\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}) \quad (4.2)$$

and "-" refers to the triplet wave functions. There are three linearly independent symmetric spin functions under the interchange of spin variables, which we all denote by Ξ^- . The full two-electron wave function must be antisymmetric under the simultaneous interchange of both spin and space variables, and therefore the spatial wave function ψ^\pm needs to fulfill the following symmetry relations

$$\psi^\pm(x_1, x_2) = \pm \psi^\pm(x_2, x_1).$$

Also, we must impose to the full solution of the Schrödinger periodic boundary conditions both for the solution and for its first spatial derivatives which have to be invariant under the translation $x_1 = x_i + L$ for $i = 1, 2$. Under these conditions, the Schrödinger equation can be solved by means the coordinate transformation from the original coordinates to the center-of-mass coordinate defined as $R = \frac{1}{2}(x_1 + x_2)$ and the dimensionless relative coordinate, defined as $z = \frac{\pi}{L}(x_1 - x_2)$. Transforming the Hamiltonian Eq.(4.1) to the new set of coordinates, the Schrödinger equation reads

$$\left[-\frac{1}{4}\partial_R^2 - \frac{\pi^2}{L^2}\partial_z^2 + \lambda v_0 \cos^2(z) \right] \psi(R, z) = E\psi(R, z) \quad (4.3)$$

We can solve the Schrödinger equation by inserting a product Ansatz of the form $\psi(R, z) = f(R)M(z)$ where we find that the center-of-mass coordinate wave function becomes a free particle

$$-\frac{1}{4}f_k''(R) = \varepsilon_k f_k(R) \quad (4.4)$$

and then the solution can be written as

$$\psi^\pm(R, z) = N_L \exp\left(\frac{2\pi i k R}{L}\right) M^\pm(z) \quad (4.5)$$

where N_L is a normalization constant which depends on the length of the ring, where k is an integer label and the function $M^\pm(z)$ satisfies the Mathieu equation which reads

$$\left[-\frac{d^2}{dz^2} + 2q \cos(2z)\right] M_l^\pm(z) = a_l^\pm M_l^\pm(z) \quad (4.6)$$

where the constants q and a_l are defined as

$$q = \lambda V_0 \left(\frac{L}{2\pi}\right)^2 \quad (4.7)$$

$$a_l^\pm = -k^2 - 2q + \frac{EL^2}{\pi^2}. \quad (4.8)$$

where a_l is the Mathieu characteristic value and $l \geq 0$. The eigenfunctions M_l^+ are the Mathieu-cosine functions, which we denote by C_l and whose characteristic value is a_l^+ . Its label is a positive integer index which starts at $l = 0$. In turn M_l^- are the Mathieu-Sine functions which we denote by S_l , its characteristic value is a_l^- and its label is a positive index which starts from $l = 1$. The spatial part solution of the Schrödinger equation Eq.(4.5) then reads

$$\psi_{kl}^+(R, z; q) = \frac{\sqrt{2}}{L} \exp\left(\frac{2\pi i k R}{L}\right) C_l(z; q) \quad (4.9)$$

$$\psi_{kl}^-(R, z; q) = \frac{\sqrt{2}}{L} \exp\left(\frac{2\pi i k R}{L}\right) S_l(z; q) \quad (4.10)$$

where we have normalized the wave function according to the normalization criteria of the Mathieu functions, which is chosen to be

$$\int_0^\pi dz |C_l(z; q)| = \int_0^\pi dz |S_l(z; q)| = \frac{\pi}{2} \quad (4.11)$$

Since the center-of-mass wave function is a symmetric function under the interchange of the spatial coordinates and also the Mathieu-cosine are symmetric functions under the interchange of the spatial variable, the singlet wave function must be described by the solution Eq.(4.9). In turn, the triplet wave function must be described by the Mathieu-sine because they are antisymmetric under the interchange of the spatial coordinates Eq.(4.10). Note also that the Mathieu functions have the periodicity property $M_l^\pm(z) = (-1)^l M_l^\pm(z + \pi)$, ie, they are periodic in π for even values of l and anti-periodic for odd values of l . Since the center-of-mass wave function also has the periodicity property $f_k(R) = (-1)^k f_k(R)$ for the translation $x_i \rightarrow x_i + L$ for $x_i = 1, 2$, then in order for the wave function to satisfy the periodic boundary condition, the labels k and l have to be both even or both odd. Finally, from Eq.(4.8) we can isolate the energy spectrum, which reads

$$E_{kl}^\pm(q) = \left(\frac{\pi}{L}\right)^2 [k^2 + a_l^\pm(q) + 2q]. \quad (4.12)$$

and then, the excitation energies of the system are obtained subtracting the ground-state energy

$$\Delta E_{kl}^{\pm}(q) = E_{kl}^{\pm}(q) - E_{00}^{+}(q) \quad (4.13)$$

It is also useful to give the general expressions for both the two-body interaction and the kinetic energy expectation values for its subsequent analysis. Multiplying Mathieu equation Eq.(4.6) by $M_l^{p'}$ and applying orthogonality of Mathieu functions in the left-hand side of the equation we get an expression for the Mathieu characteristic value in terms of Mathieu functions. Taking its derivative as a function of q and making use of the Hellman-Feynman theorem we obtain the following expression for its derivative

$$\frac{da_l^p(q)}{dq} \delta_{ll'} \delta_{pp'} = \frac{2}{\pi} \int_{-\pi}^{\pi} dz \cos(2z) M_l^{p'}(z; q) M_l^p(z; q) \quad (4.14)$$

The above expression appears in the expectation values of both the two-body interaction and kinetic energy expectation values, and therefore we can write them as a single function of the Mathieu characteristic value as

$$\langle \widehat{W} \rangle_{kl}^{\pm}(q) = 2q \left(\frac{\pi}{L} \right)^2 \left[1 + \frac{1}{2} \frac{da_l^{\pm}(q)}{dq} \right] \quad (4.15)$$

$$\langle \widehat{T} \rangle_{kl}^{\pm}(q) = \left(\frac{\pi}{L} \right)^2 \left[k^2 + a_l^{\pm}(q) - q \frac{da_l^{\pm}(q)}{dq} \right] \quad (4.16)$$

Note that because the electron-electron two-body interaction depends on the distance between electrons, the two-body interaction energy expression Eq.(4.15) depends only on the relative coordinate quantum number l . On the other hand, the kinetic energy Eq.(4.16) receives a contribution from both k and l quantum numbers, being the k term a pure kinetic contribution since the center-of-mass wave function performs a free motion on the ring. This is special of the quantum ring system because we chose the system to be homogeneous.

Once the general solution of the Schrödinger equation is presented, we proceed to discuss the strong interaction limit of the quantum ring system.

4.2 The strong interaction expansion of the exact solution

In this section, we analyze both the eigenstates and the energy spectrum of the quantum ring model when the interaction strength is very large. As the interaction strength q grows, the two-body repulsive interaction becomes more important and the electrons repel each other to lye in opposite sides of the ring to minimize the two-body interaction energy. This behavior is shown in Fig. 4.1 where the two-body interaction is a well of height q . When the interaction strength becomes large, the well becomes deep and therefore the relative coordinate wave function M_l^{\pm} becomes localized around the relative position $z = \pi$, which also corresponds to a relative position of $x_1 - x_2 = L/2$. Based on this description we can qualitatively analyze the strong interaction limit by expanding the potential energy around its minimum and obtaining

$$2q \cos 2z = -2q + 4q \left(z - \frac{\pi}{2} \right)^2 + \dots \quad (q \rightarrow \infty) \quad (4.17)$$

We see that for large interaction strength the potential becomes harmonic with a frequency $\Omega = 2\sqrt{q}$ and therefore the Mathieu equation Eq.(4.6) becomes the harmonic oscillator equation whose eigenfunctions consist on Hermite functions which are centered around the relative coordinate $z = \pi/2$ with a width $1/\Omega = 1/\sqrt{2}q^{1/4}$

$$M_l^{\pm}(z; q) = \left[\frac{\Omega^{1/2}}{\pi^{1/2} l! 2^l} \right]^{1/2} H_l \left[\Omega^{1/2} \left(z - \frac{\pi}{2} \right) \right] \exp \left[-\frac{\Omega}{2} \left(z - \frac{\pi}{2} \right)^2 \right] \quad (4.18)$$

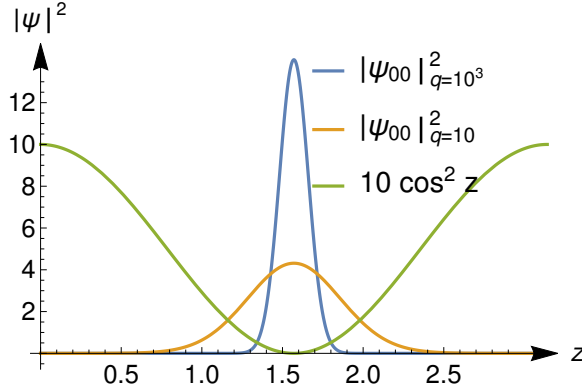


Figure 4.1: The squared ground-state wave function $|\psi_{00}|^2$ for two values of the interaction strength q , and the interaction $\cos^2 z$ using a suitable scaling for showing it in the same plot. For large q , the wave function localizes around $z = \pi/2$ where $\cos^2 z$ is almost parabolic and $|\psi_{00}|^2$ then tends to a sharp Gaussian.

where $H_l(x)$ are Hermite polynomials. We see that in the large interaction strength limit the frequency increases and the width of the Hermite functions decreases hence becoming the relative wave function more localized around $z = \pi/2$. From the general expression of the harmonic oscillator energy spectrum and by means the Mathieu equation Eq.(4.6) we deduce the following relation for the Mathieu characteristic value in the limit of large interaction strength $(a_l^\pm + 2q)/2 = \Omega(l + 1/2)$, which reads

$$a_l^\pm(q) = -2q + 2\sqrt{q}(2l + 1) + \dots \quad (4.19)$$

Inserting it in Eq.(4.12) we find an asymptotic expansion for the energy spectrum in the large interaction strength limit. We also note that in the large interaction limit the singlet and the triplet wave functions Eq.(4.9) and Eq.(4.10) have the same asymptotic expression for the large q limit, and as a consequence, the energy spectrum becomes degenerate for these states. These qualitative results and the connection with the harmonic oscillator are made rigorous by making the change of variable $u(z) = \sqrt{2}q^{1/4} \cos z$ and transforming the Mathieu equation Eq.(4.6) to the form

$$\left[-\frac{1}{2} \left(1 - \frac{u^2}{2\sqrt{q}} \right) \frac{d^2}{du^2} + \frac{u}{4\sqrt{q}} \frac{d}{du} + \frac{u^2}{2} \right] M_l^\pm[z(u)] = \epsilon_l^\pm M_l^\pm[z(u)] \quad (4.20)$$

where we defined $\epsilon_l^\pm = (a_l^\pm + 2q)/4\sqrt{q}$. From the transformed equation it becomes manifest how if we assume the wave function to be localized around $z = \pi/2$, which corresponds the new coordinate to be around $\frac{u^2}{\sqrt{q}} \sim 0$, then Mathieu equation reduces to the Schrödinger equation of the harmonic oscillator. Based on this qualitative analysis, we are interested in an asymptotic expansion of Mathieu functions for the large q limit. Such expansion is provided by the Sips expansion of Mathieu functions, which is accurate in the region around $z = \pi/2$. For our purposes, we just show the Sips expansion of the Mathieu-cosine, since it is the one that is relevant for the discussion of the singlet, which are the states our future derivations are based on. The interested reader can find the Sips expansion of Mathieu functions in [59, 60]. The Sips expansion of the Mathieu-Cosine reads

$$C_l(z; q) = C_l(q) \sum_{n=-\infty}^{\infty} g_{2n,l}(q) \mathcal{D}_{l+2n}[u(z)] \quad (4.21)$$

where $\mathcal{D}_m(u)$ are the parabolic cylinder functions, which are defined as

$$\mathcal{D}_m(u) = \frac{(-1)^m}{2^{m/2}} e^{u^2/2} \frac{d^m}{du^m} e^{-u^2} = \frac{1}{2^{m/2}} e^{-u^2/2} H_m(u) \quad (4.22)$$

where H_m are the "physicist" Hermite polynomials and where $\mathcal{D}_{m<0} = 0$. The prefactor $\mathcal{C}_l(q)$ is chosen such that the Sips expansion of the Mathieu-cosine satisfies the normalization condition Eq.(4.11), and the coefficients $g_{2n,l}(q)$ are decaying functions of the square root of the interaction strength q , whose explicit form is obtained from a recursion relation. We refer to [59, 60] for a more detailed discussion. The Mathieu-sine has a similar expansion, and the interested reader can consult the references [59, 60].

From the Sips' expansion we note that in the large q limit, for a $z \sim \pi/2$ we are allowed to keep only the leading order of the expansion for the Mathieu-cosine Eq.(4.21) where $c_{0,l}(q) = \mathcal{C}_l(q)$, (see Appendix B of [34]) recovering in this way the solution Eq.(4.18) we obtained from the qualitative discussion. For closing this section and making use of the large q limit of the Mathieu characteristic

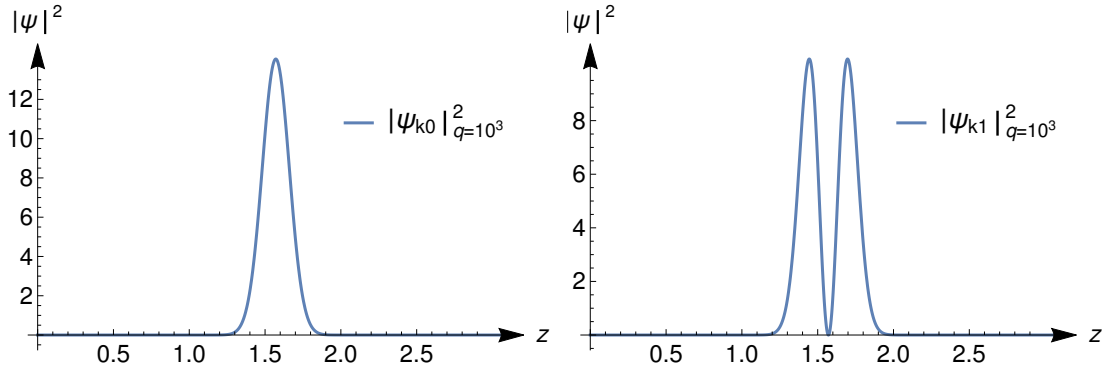


Figure 4.2: It is shown the square root of the excited-state of the center-of-mass excitations $|\Psi_{k0}|$ (left panel) and the relative coordinate excitations $|\Psi_{k1}|$ (right panel) for $q = 1000$. The center-of-mass excited states show the same probability distribution for all the ranges of the interaction strength, while the relative-coordinate excited-states show a probability distribution which has two maxima around the equilibrium position $z = \pi/2$.

value, we obtain an asymptotic expansion for k, l two-body interaction energy, kinetic energy and total energy as a function of the square root of the interaction strength. From the expression Eq.(4.12), Eq.(4.16) and Eq.(4.15), and using the first few leading terms of the expansion of the Mathieu characteristic value, their expressions for the QR (Appendix B of [Ref] for its derivation) in the limit of large interaction strengths read

$$\langle \widehat{W} \rangle_{kl}^{\pm}(q) = \left(\frac{\pi}{L}\right)^2 \left[\sqrt{q}(2l+1) + \frac{(2l+1)}{256\sqrt{q}} ((2l+1)^2 + 3) \right] + \mathcal{O}(q^{-1}) \quad (4.23)$$

$$\langle \widehat{T} \rangle_{kl}^{\pm}(q) = \left(\frac{\pi}{L}\right)^2 \left[k^2 + \sqrt{q}(2l+1) - \frac{1}{4}(2l^2 + 2l + 1) - \frac{3(2l+1)}{256\sqrt{q}} ((2l+1)^2 + 3) \right] + \mathcal{O}(q^{-1}) \quad (4.24)$$

$$E_{kl}^{\pm}(q) = \left(\frac{\pi}{L}\right)^2 \left[k^2 + 2\sqrt{q}(2l+1) - \frac{1}{4}(2l^2 + 2l + 1) - \frac{(2l+1)}{128\sqrt{q}} ((2l+1)^2 + 3) \right] + \mathcal{O}(q^{-1}) \quad (4.25)$$

If we consider the limit of large interaction strengths in the energy expressions, the k contribution becomes negligible, and they obey the relations $\langle \widehat{W} \rangle_{kl}^{\pm} = \langle \widehat{T} \rangle_{kl}^{\pm} = E_{kl}^{\pm}/2$, in agreement with the virial theorem for harmonic oscillators. From energy expressions, we also see that they are degenerate for the singlet and triplet, as we noticed before since their difference becomes exponentially small in the large q limit. To illustrate the q -dependence of the two-body interaction energy, kinetic energy and total energy we show in Fig. 4.3 some of the lowest eigenvalues and their respective asymptotic

expansion from Eq.(4.23), Eq.(4.24) and Eq.(4.25) as a function of q . We see that the asymptotic expansion converges more slowly for higher values of l , and for these l we need high values of q to have a reliable estimate. Let us have a study on the type of excitations that the system shows. From

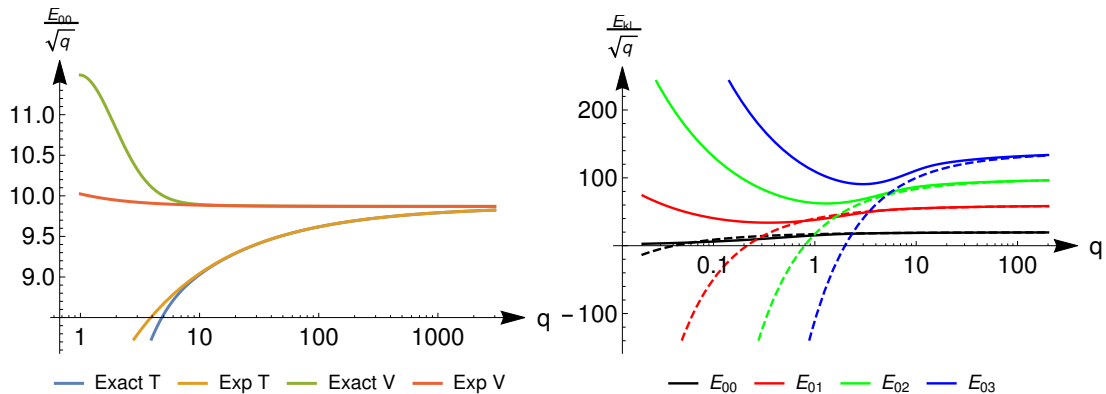


Figure 4.3: The ground-state ($l = 0$) and excited-state ($l = 1, 2, 3$) two-body interaction energy, kinetic energy and total energy divided by \sqrt{q} for $k = 0$ as function of the interaction strength q in units of L^{-2} . We plot the exact energies (solid lines) versus the approximate energies (dashed lines) from the expansion in Eq.(4.23), Eq.(4.24) and Eq.(4.25).

the expression Eq.(4.13) we see that ΔE_{k0} are excitations which are independent of the interaction strength, which is the center-of-mass excitations, and for $q = 0$ they are related as double excitations (see [7] for a detailed discussion). On the other hand, the excitations ΔE_{0l} are interaction strength dependent and they grow with the square root of the interaction strength. These excited-states are plotted in Fig. 4.2, where it is shown the square of the wave function as a function of the relative coordinate. The excitations ψ_{k0} give the same probability distribution as the ground state, to find the electrons in opposite sides of the ring (since the center-of-mass wave function is a phase). Conversely, the excitations ψ_{0l} are the excitations which are referred to the relative coordinate excited-states, which in the large q limit they give the probability to find the electrons a bit away of $z = \pi/2$ as it can be seen from Fig. 4.2. These excitations are caused by the small oscillations that the electrons perform around their equilibrium position. When the interaction strength becomes truly infinite the electrons relative position freezes in $z = \pi/2$ and the only allowed excitations are the center-of-mass ones since when the interaction strength grows, the two maxima become closer and higher until they merge in one maximum of infinite high at $z = \pi/2$. The approach of the maxima in the probability distribution costs energy which depends on the interaction strength and therefore, when the interaction strength grows, the excitations grow with it. These different types of excitations have a very important role in the density response function, which we proceed to analyze in the following.

4.3 Density response of the quantum ring system

4.3.1 Exact density response of the quantum ring system

This section is devoted to the study of the exact frequency dependent density response function of the QR system. The exact expression will allow for its calculation and analysis in the strong interaction limit regime, as well as its calculation and analysis in the non-interacting case $q = 0$, the

case which is needed for the density-functional theory discussion since for homogeneous systems the non-interacting case also corresponds to the KS case.

For the analysis of the density response function for the QR model, we start by expressing the density response function in frequency space in its the Lehmann representation Eq.(3.32), which reads

$$\chi(x, x', \omega) = \lim_{\eta \rightarrow 0^+} \sum_{k, l, p = \pm} \left[\frac{\langle \Psi_0^+ | \hat{n}(x) | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x') | \Psi_0^+ \rangle}{\omega - \Delta E_{kl}^p + i\eta} - \frac{\langle \Psi_0^+ | \hat{n}(x') | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x) | \Psi_0^+ \rangle}{\omega - \Delta E_{kl}^p + i\eta} \right] \quad (4.26)$$

where the sum runs over all the excited states of the quantum ring. The label k runs over all integers while for the label l the sum runs over the positive integers, constrained by the condition that k and l must be both even or both odd. In turn, the sum for p runs over the singlet and triplet states. Since the spin wave function is transparent to the density operator \hat{n} , the matrix elements $\langle \Psi_0^+ | \hat{n}(x) | \Psi_{kl}^- \rangle = 0$ and therefore the density response function receives contribution only from excited states with $p = +$, i.e., from the singlet. The remaining non-zero matrix elements read

$$\langle \Psi_{00}^+ | \hat{n}(x) | \Psi_{kl}^+ \rangle = 2 \int_0^L dx_2 \psi_{00}^{+*}(x, x_2) \psi_{kl}^+(x, x_2) = \frac{2}{L} e^{2\pi i k x / L} D_{kl}(q) \quad (4.27)$$

where ψ_{00}^+ is the spatial part of the singlet wave function, and the object D_{kl} is the so-called excitation amplitude, which reads

$$D_{kl}(q) = \frac{2}{\pi} \int_0^\pi dz C_0(z; q) C_l(z; q) e^{-ikz} \quad (4.28)$$

The excitation amplitude $D_{kl}(q)$ has a number of properties which are direct consequence of the properties of the Mathieu functions. Since $C_l(z; q)$ is real we have $D_{kl}^*(q) = D_{(-k)l}(q)$, and because of the orthogonality of the Mathieu functions, $D_{0l}(q) = \delta_{0l}$. Moreover if we use the features that $C_l(z + \pi; q) = (-1)^l C_l(z; q)$ and that Mathieu-cosine is a function with even parity in z , this property leads to $D_{kl}(q) = (-1)^{k+l} D_{kl}^*(q)$. Using the mentioned properties and using also that the excitation energies satisfy $\Delta E_{kl} = \Delta E_{(-k)l}$, we can write the response function in a more compact and convenient way as follows

$$\chi(x, x', \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} \chi(k, \omega) e^{2\pi i k (x-x') / L} \quad (4.29)$$

where

$$\chi(k, \omega) = \frac{4}{L} \sum_l \left(\frac{|D_{kl}(q)|^2}{\omega - \Delta E_{kl}^+(q) + i\eta} - \frac{|D_{kl}(q)|^2}{\omega + \Delta E_{kl}^+(q) + i\eta} \right) = \frac{8}{L} \sum_l \frac{\Delta E_{kl}^+(q) |D_{kl}(q)|^2}{(\omega + i\eta)^2 - (\Delta E_{kl}^+(q))^2} \quad (4.30)$$

and where the label l runs over even numbers for k even and over odd numbers for k odd. Because of the homogeneity of the quantum ring system we see that the linear response function satisfies that $\chi(x, x', \omega) = \chi(x - x', \omega)$. It is therefore convenient to define the expansion of a periodic function $f(x, \omega) = f(x + L, \omega)$ on the ring in terms of its Fourier series as

$$f(x, \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} e^{\frac{2\pi i k}{L} x} f(k, \omega) \quad (4.31)$$

where the coefficients of the expansion are given by

$$f(k, \omega) = \int_0^L dx e^{-\frac{2\pi i k}{L} x} f(x, \omega) \quad (4.32)$$

We see that the density response function can be written as a Fourier series with respect of the relative coordinate $z = x - x'$, whose coefficients are Eq.(4.30). For later analysis, we also write as a

Fourier series the linear response in the density produced by a small perturbing potential Eq.(3.29). The coefficients of the expansion are given by

$$\delta n(k, \omega) = \chi(k, \omega) \delta v(k, \omega) \quad (4.33)$$

We obtained an expression of the exact linear response function in terms of the excitation energies ΔE_{kl}^+ and the oscillator strengths Eq.(4.28) for arbitrary value of the interaction strength which is suitable for its analysis in the large interaction strength limit.

Before focusing on the strong interaction limit of the density response function and because in the TDDFT section the non-interacting linear response function is needed, we give the form of the response function for the non-interacting system $q = 0$, which is the the KS response function since the system is homogeneous and it has the same density for all values of q . For the non-interacting system, the excitation energies Eq.(4.12) read

$$E_{kl}(0) = \left(\frac{\pi}{L}\right)^2 [k^2 + l^2] \quad (4.34)$$

and the corresponding excitation amplitude can be calculated from Eq.(4.28) by making use of the non-interacting eigenstates, which is a Slater determinant of the form

$$\psi_{kl}^+(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\phi_{\frac{k+l}{2}}(x_1) \phi_{\frac{k-l}{2}}(x_2) + \phi_{\frac{k+l}{2}}(x_2) \phi_{\frac{k-l}{2}}(x_1) \right] \quad (4.35)$$

Apart from the amplitude $D_{00}(0) = 1$, which does not contribute to the sum since $\Delta E_{00}^+ = 0$, the excitation amplitudes read

$$D_{kl}(0) = \begin{cases} 1/\sqrt{2} & \text{if } l = |k| \\ \frac{\sqrt{2}}{\pi} \frac{ik}{k^2 - l^2} [(-1)^{k+l} - 1] & \text{if } l \neq |k|. \end{cases} \quad (4.36)$$

where only the terms where $k+l$ is even contribute to the sum and then the only non-zero excitation amplitudes that contribute to the linear response function are those ones with $l = |k|$, which we already discussed in Sec. 3.6 it corresponds to single excitations. Inserting Eq.(4.36) into Eq.(4.30) we find that the non-interacting response function $\chi_s(k, \omega)$ is given by

$$\chi_s(k, \omega) = \frac{4}{L} \frac{\Delta E_{kk}^+(0)}{(\omega + i\eta)^2 - (\Delta E_{kk}^+(0))^2} \quad (4.37)$$

with $\Delta E_{kk}^+(0) = 2(\pi k/L)^2$. We note that χ_s has only a single pole at $\omega = 2(\pi k/L)^2$, and no zeroes.

Having determined the non-interacting response function, the next section will be devoted to the study of the density response function in the limit of strong interaction strength.

4.3.2 Strong interaction expansion of the dynamic density response function

For the analysis of the linear response function in the strong interaction limit regime, we need to study the excitation energies $\Delta E_{kl}^+(q)$ and excitation amplitudes $D_{kl}(q)$ in the limit of large interaction strengths q . Since for $\Delta E_{kl}^+(q)$ explicit asymptotic expansions are known by using the asymptotic expansion of the Mathieu characteristic value [34, 59, 61], what is left is the determination of the

excitation amplitudes $D_{kl}(q)$ (4.28) for the limit of large interaction strengths q . For this purpose, we start by inserting the Sips expansion of the Mathieu-cosine Eq.(4.21) into Eq.(4.28), which gives

$$D_{kl}(q) = \frac{2}{\pi} \sum_{n_1, n_2 = -\infty}^{\infty} c_{2n_1,0}(q) c_{2n_2,l}(q) \mathcal{J}_{kl}^{n_1 n_2}(q) \quad (4.38)$$

where we defined

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \int_0^\pi dz e^{-ikz} \mathcal{D}_{2n_1}[u(z)] \mathcal{D}_{2n_2+l}[u(z)] \quad (4.39)$$

and where $u(z) = \sqrt{2}q^{1/4} \cos z$. The coefficients $c_{2n,l}(q)$ are given in [34]. It remains to evaluate $\mathcal{J}_{kl}^{n_1 n_2}(q)$ for the large q . For doing it, we change to the integration variable $u(z) = \sqrt{2}q^{1/4} \cos z$, obtaining the expression

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \frac{1}{\sqrt{2}q^{1/4}} \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du f_k \left(\frac{u}{\sqrt{2}q^{1/4}} \right) \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \quad (4.40)$$

where we defined the function

$$f_k(x) = \frac{e^{-ik \arccos(x)}}{\sqrt{1-x^2}} = \sum_{r=0}^{\infty} a_r(k) x^r \quad (4.41)$$

and $a_r(k)$ to be its Taylor coefficients. Inserting this Taylor series into Eq.(4.40), gives the expansion

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \sum_{r=0}^{\infty} \frac{a_r(k)}{(\sqrt{2}q^{1/4})^{r+1}} \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \quad (4.42)$$

where we interchanged the integral and sum provided that the Taylor series of the function $f(x)$ is an absolutely convergent series. Due to the Gaussian decay of the functions $\mathcal{D}_n(u)$ in the limit $q \rightarrow \infty$, the error we make if we replace $\sqrt{2}q^{1/4}$ in the limits of the integral by infinity is exponentially small (see Appendix G) and then, we obtain the asymptotic expansion.

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \sum_{r=0}^{\infty} \frac{a_r(k) I_{n_1 n_2, r}^l}{(\sqrt{2}q^{1/4})^{r+1}} \quad (4.43)$$

where we introduced coefficients

$$I_{n_1 n_2, r}^l = \int_{-\infty}^{\infty} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u). \quad (4.44)$$

The integral $I_{n_1 n_2, r}$ can be computed analytically, and also its explicit expression is given in Appendix G). We note that since the integral $I_{n_1 n_2, r}$ is performed in a symmetric interval and because the \mathcal{D}_n is an even function if n is even or an odd function if n is odd, then the integral vanishes unless r and l are both even or both odd, which implies that the sum $r+l$ is always even and the whole integrand is an even function. Therefore, the summation index r in Eq.(4.43) can be taken to run only over even or only over odd values depending on whether l is even or odd. With expression Eq.(4.38) together with Eq.(4.43) we developed an explicit and systematic procedure to calculate the asymptotic expansions of the excitation amplitudes analytically in the limit of large interaction strengths, whose expression D_{kl} and its modulus square $|D_{kl}|^2$ are given in the [34].

Inserting the asymptotic expansion of $|D_{kl}|^2$ and the asymptotic expansion of the excitation energies ΔE_{kl} into the general expression Eq.(4.30) we finally find the asymptotic expansion of the density

response function for large interaction strengths

$$\chi(k, \omega) = \begin{cases} \frac{8}{L} \frac{(\pi k/L)^2}{(\omega + i\eta)^2 - (\frac{\pi k}{L})^4} \left[1 - \frac{k^2}{4\sqrt{q}} + \frac{k^2(k^2-2)}{32q} \right] + \mathcal{O}(q^{-3/2}) & \text{if } k \text{ is even} \\ \frac{L}{2\pi^2} \left[-\frac{k^2}{q} + \frac{k^2(k^2-1)}{2q^{3/2}} - \frac{k^2}{q^2} \left(\frac{368k^4 - 928k^2 + 947}{2304} + \frac{1}{16} \left(\frac{L}{\pi} \right)^4 \omega^2 \right) \right] + \mathcal{O}(q^{-5/2}) & \text{if } k \text{ is odd.} \end{cases} \quad (4.45)$$

Let us analyze the pole structure of the density response function in the strong interaction limit Eq.(4.45). If we take the limit of infinite interaction strength, from the expression Eq.(4.45) we see the density response function attains for even values of k the form

$$\lim_{q \rightarrow \infty} \chi(k, \omega) = \frac{8}{L} \frac{(\pi k/L)^2}{(\omega + i\eta)^2 - (\frac{\pi k}{L})^4} \quad (4.46)$$

and it vanishes for odd values of k . We recognize the single pole as the center-of-mass excitations E_{k0} , which are the only excitations that do not shift towards infinity as q grows, since they are independent of the interaction strength. Therefore, in the limit $q \rightarrow \infty$ the center-of-mass excitations are the remaining poles that are kept in the density response function. This property is genuine of the quantum ring model because the system is separable and therefore the energy spectrum Eq.(4.12) splits in an interaction strength dependent and interaction strength independent parts. Despite for other inhomogeneous systems the separability does not hold anymore, as we will see in the next section, it can be shown that in the strong interaction limit the energy spectrum still splits in a weakly interaction strength dependent part and strong interaction strength dependent part which causes that there are excitation energies that move to infinity in the λ infinity limit while there are also remaining excitations that become independent on the interaction strength.

Let us now analyze the external one body potential which is needed to produce a change in the ground-state density for driving the system a bit far away from homogeneity. The external one body potential, in frequency and momentum space, reads

$$\delta v(k, \omega) = \chi^{-1}(k, \omega) \delta n(k, \omega) \quad (4.47)$$

If we perform a change the density $\delta n(k, \omega)$ such that in Fourier space it has general Fourier coefficients, the external one body potential given by the linear response Eq.(4.47) shows an expansion in terms of the square root of the interaction strength, as the density response function does, and it is dominated by the leading term which is linear in q and the next to the leading term, which grows as \sqrt{q} . The next term is independent of the interaction strength, and the rest terms are functions which decay as powers of \sqrt{q} . The dependence of the external potential as a function of the interaction strength can be understood in the following way. The generation of an external potential with an odd k implies a change in the density which fulfills antisymmetry at antipodal points of the ring, ie, $n(x, t) = -n(x + L/2, t)$ which requires in the linear response function to consider the excitations form the ground-state to states with l odd, and as we explained it requires a large energy when the interaction strength is large. Therefore the applied external potential for producing such a density change produces must grow with the interaction strength in order to counteract the two-body repulsion. On the other hand, the generation of a potential with only even Fourier components implies a change in the density which is symmetric at antipodal points of the ring, ie, $n(x, t) = n(x + L/2, t)$ which requires in the linear response function to consider the excitations to states with an l even and which in the limit of large interaction strengths the only contribution is for the $l = 0$ states, which we already discussed they are the center-of-mass excitations. Since they are independent of the interaction strength, the external potential that such a density change produces is a finite potential, and in the large q limit it does not depend on the interaction strength.

From the asymptotic expansion of the density response function Eq.(4.45), we see that for odd k , the response function is frequency independent, and therefore will produce an instantaneous density

variation, i.e. if a perturbation $\delta v(k, \omega)$ is applied to the system and its range of frequency is below from any of the excitation energies $\omega \ll \Delta E_{kl}$. Then we can regard the density response function to be frequency independent. Because of the excitation energies ΔE_{kl}^+ for odd k (which must have odd l as well) increase proportionally to \sqrt{q} , the frequency range of the applied external potential are much lower than any excitation energy, i.e., $\omega \ll \Delta E_{kl}$ and hence the density response function is in this case well approximated by a frequency independent function for $\omega \ll \sqrt{q}$. This can be seen from

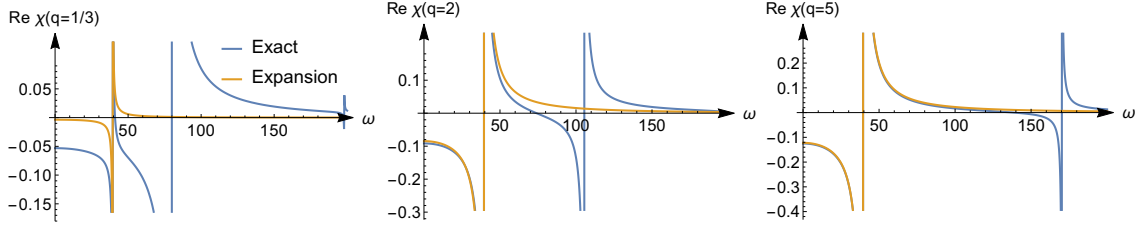


Figure 4.4: The real part of $\chi(k = 2, \omega)$ in units of L (top) in units of L^{-1} (bottom) for different values of the interaction strength q . The exact results are obtained by numerical integration, and the expansion of χ is taken up to the same order as shown in Eq. (4.45).

Fig. 4.4, where we show the plots of the expressions Eq.(4.45) we show the comparison of the exact response function and the expanded one as a function of the frequency, for $k = 2$ and for several values of the interaction strength. We see that for small interactions ($q = 1/3$) the exact response function has two poles; Since the value of q is small, one is located approximately at the same place as the KS pole ($\omega = 2(\pi k/L)^2$). A new pole with a weight given by the oscillation amplitude Eq.(4.28) also appears at the center-of-mass excitation energy, at $\omega = (\pi k/L)^2$, which is suppressed by the excitation amplitude as the interaction strength becomes smaller and it vanishes for $q = 0$ according to Eq.(4.36). For further details of see [34].

4.4 TDDFT in the strong interaction limit

4.4.1 The exchange-correlation kernel

This section is devoted to analyzing the strong interaction limit of the Hxc kernel of TDDFT defined by means Eq.(3.35) for the QR model system.

Since the density response function is diagonal in momentum space for all values of the interaction strength, it is immediate to obtain the inverse of the density response and hence also the Hxc kernel. The Fourier coefficients of the Hxc kernel for the QR system read

$$f_{\text{Hxc}}(k, \omega) = \chi_s^{-1}(k, \omega) - \chi^{-1}(k, \omega) \quad (4.48)$$

being well-defined for all values of k except for $k = 0$ for which the density response function is not invertible since in this case, it vanishes. Because of the system is homogeneous, the KS response function coincides with the response function of non-interacting one of Eq.(4.37). Combining it together with the expansion of Eq.(4.45), we obtain an explicit expression for the Hxc kernel in the

strong interaction limit, which reads

$$f_{\text{Hxc}}(k, \omega) = \begin{cases} -\frac{3\pi^2 k^2}{8L} - \frac{1}{\sqrt{\lambda}} \frac{L^2}{\sqrt{V_0}} \frac{1}{16\pi} \left[\omega^2 - \left(\frac{\pi k}{L} \right)^4 \right] + \frac{1}{\lambda} \frac{L}{V_0} \frac{k^2+2}{64} \left[\omega^2 - \left(\frac{\pi k}{L} \right)^4 \right] + \mathcal{O}(\lambda^{-3/2}) & \text{if } k \text{ is even} \\ \lambda \frac{V_0 L}{2k^2} + \sqrt{\lambda} \frac{\sqrt{V_0} \pi (k^2-1)}{2k^2} - \frac{\pi^2 (368k^4 + 224k^2 + 371)}{1152k^2 L} + \mathcal{O}(\lambda^{-1/2}) & \text{if } k \text{ is odd} \end{cases} \quad (4.49)$$

where the variable λ has been reintroduced back instead of q by means the expression Eq.(4.7) due to that the λ notation is commonly used in the DFT context, from the coupling constant integration construction, and which will be the focus of the discussion in the next section, we will therefore refer to the large interaction regime as when either q and/or λ approaches to infinity. We see that the Hxc kernel is adiabatic in the leading terms and the frequency dependence start to play a role in the $\lambda^{-1/2}$ term. The adiabatic character of the λ^0 term comes from the fact that the response function has the same prefactor for all interaction strengths, and the non-interacting response, as well as the large interaction strength response functions, have no zeroes. Therefore the Hxc kernel does not present any pole in this order of expansion. The frequency dependence starts to appear in the next term, a feature that in principle is genuine of the quantum ring system since the non-interacting response function of a general system would present zeroes and poles, which would imply to have a frequency dependence already at the λ^0 order. Since the Hxc kernel is the object that corrects the KS poles to the poles of the interacting system, for even Fourier components, in the large q limit the Hxc kernel shifts the KS pole to the strongly interacting one. Because for each k value there is the same number of poles both in the KS response function and the interacting response function, there is no need for the Hxc kernel to be frequency dependent. On the other hand, for general Fourier coefficients and also for odd Fourier coefficients the kernel has to correct the KS pole to the poles of the interacting system which in this case have shifted to infinity in the large q limit. Since the KS density response does not depend on the interaction strength, the leading term and the next to the leading term of the kernel are $f_{\text{Hxc}}(k, \omega) = -\chi^{-1}$ and therefore they will be adiabatic as the response function is. The kernel, therefore, is frequency independent when we consider frequencies $\omega \ll \Delta E_{kl}$ and the frequency dependent terms start to appear at order $\lambda^{-1/2}$. To illustrate the accuracy of the expansion in Eq.(4.49) we show the exact Hxc kernel and the expanded one in the bottom panels of Fig. 4.5 for $k = 2$ and several values of the interaction strength. where we can see that the expansion

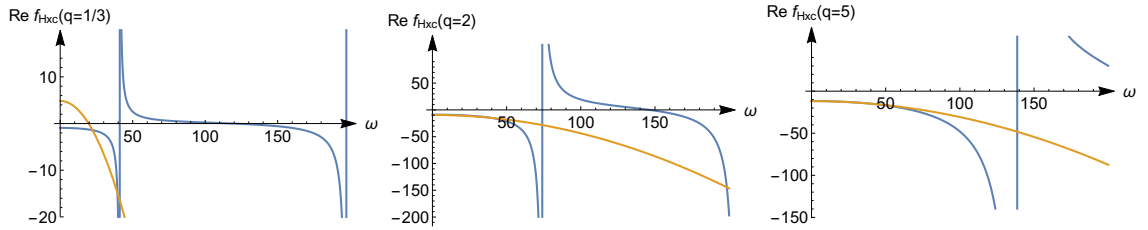


Figure 4.5: The real part of $\chi(k = 2, \omega)$ in units of L (top) and $f_{\text{Hxc}}(k = 2, \omega)$ in units of L^{-1} (bottom) for different values of the interaction strength q . The exact results are obtained by numerical integration, and the expansion of χ and f_{Hxc} is taken up to the same order as shown in Eq. (4.45).

is accurate up to the lowest excitation energy .

Once the non-locality in time of the Hxc kernel is studied, we proceed to study its spacial dependence. For this purpose, we write the Hxc kernel in real space transforming back Eq.(4.49) according to

$$f_{\text{Hxc}}(r, \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} f_{\text{Hxc}}(k, \omega) e^{\frac{2\pi i k r}{L}} \quad (4.50)$$

where $r = x - x'$ is the relative distance between the points x and x' . Because both x, x' belong to the interval 0 to L , the variable $r \in (-L, L]$ and then we find that the asymptotic expansion in real space of the Hxc kernel reads

$$f_{\text{Hxc}}(r, \omega) = \lambda f_1(r) + \sqrt{\lambda} f_2(r) + f_3(r) + \mathcal{O}(\lambda^{-1/2}) \quad (4.51)$$

where $r = x - x'$. Because in the next section we will study the leading term and the next to the leading term of the Hxc kernel in the limit of strong interaction, we just transform Fourier back $f_1(r)$ and $f_2(r)$, which read respectively

$$f_1(r) = \frac{V_0 \pi^2}{2L} \left[-|r| + \left| r + \frac{L}{2} \right| + \left| r - \frac{L}{2} \right| - \frac{3L}{4} \right] \quad (4.52)$$

in which we choose the freedom Eq.(3.39), which in Fourier space is translated to add an arbitrary constant function for homogeneous systems, to define the Hxc kernel such that the Fourier coefficient of f_1 becomes zero for $k = 0$. For f_2 we find that

$$f_2(r) = \frac{\sqrt{V_0} \pi}{4} \left[\delta(r) - \delta\left(r + \frac{L}{2}\right) - \delta\left(r - \frac{L}{2}\right) \right] - \frac{\sqrt{V_0} \pi^3}{2L^2} \left[-|r| + \left| r + \frac{L}{2} \right| + \left| r - \frac{L}{2} \right| - \frac{3L}{4} \right]. \quad (4.53)$$

In the figure Fig. 4.6 we show the leading term of the Hxc kernel f_1 . As it can be seen from its

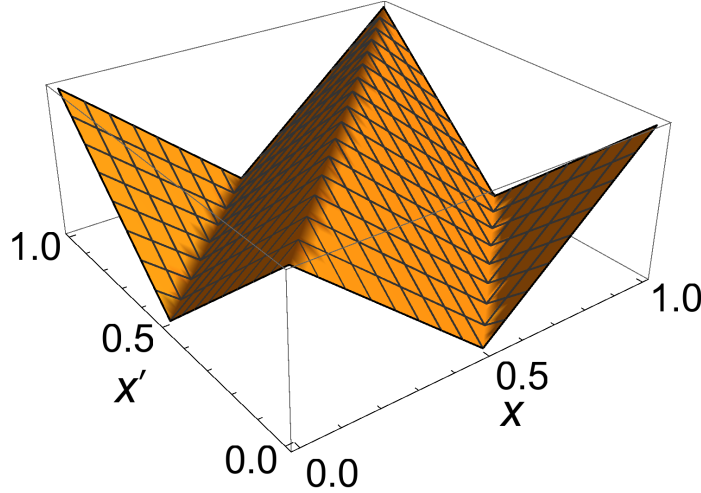


Figure 4.6: The Hxc kernel $f_1(x - x')$ of Eq.(4.52). The x and x' -axes are in units of L and f_{Hxc} is given in arbitrary units.

expression Eq.(4.52) and Eq.(4.53), the kernel encodes information of the whole space where it is defined, being hence a non-local function of the space. We can study the spacial non-locality of the Hxc kernel by studying the Hxc potential that a small change in the density produces. The change in the Hxc potential is given in linear response theory by the Hxc kernel according to with Eq.(3.37). In the strong interaction limit, to the leading order in the interaction strength, it reads

$$\delta v_{\text{Hxc}}(x, t) = \lambda \int_0^L dx' f_1(x - x') \delta n(x', t) \quad (4.54)$$

and inserting the expression for f_1 Eq.(4.52) and taking the second derivative with respect to the coordinate x of the Hxc potential we find

$$\partial_x^2 \delta v_{\text{Hxc}}(x, t) = \lambda \frac{V_0 \pi^2}{L} [-\delta n(x, t) + \delta n(x + L/2, t) + \delta n(x - L/2, t)], \quad (4.55)$$

where since the second derivative of the Eq.(4.52) yields delta functions, we use them to integrate the density variations. From Eq.(4.55) we see how a change in the density in a point x not only induces a change in the Hxc potential in x , but also induces a change in the Hxc potential in $x \pm L/2$, ie, in precisely the other side of the ring. The above expression shows clearly how the Hxc potential depends on the density locally in time but non-locally in space.

Let us briefly compare the results given by the Hxc kernel in the strong interaction limit with those results given by the usual local in space and time approximations. The simplest approximation is the random phase approximation, which sets to zero the Hxc kernel $f_{\text{Hxc}}^{\text{RPA}}(x - x'', \omega) = 0$. The adiabatic local density approximation reads

$$f_{\text{Hxc}}^{\text{ALDA}}(x - x', \omega) = C(x)\delta(x - x'), \quad (4.56)$$

where for the case of homogeneous systems, the function $C(x)$ can only be a constant function $C(x) = C$. We can use the freedom we have in the Hxc potential in Fourier space for choosing the arbitrary constant such that it cancels the contribution of the constant C , and therefore, the $f_{\text{Hxc}}^{\text{ALDA}}(k, \omega) = 0$. As a consequence, both local Hxc kernels do not yield any correction of the KS poles, which means that they predict the poles of the interacting system to be the poles of the non-interacting one, showing the drastic result of the approximation. We can already see how bad is the ALDA if we compare it with the one given by the asymptotic expansion Eq.(4.51). By looking at the plot of Eq.(4.6) we realize that while f_1 has information of the whole space where it is defined, the ALDA is zero everywhere except in the diagonal $x = x'$, losing all the information of the rest of space, thus being this the reason of the bad approximation. This fact shows that in the strong interaction regime, local functionals of the density do not provide a good answer since the Hxc kernel does depend on the density in a non-local way and therefore non-local functional need to be developed.

4.4.2 SCE formalism for the quantum ring

Ground-state SCE for the quantum ring system

In this section, we briefly comment on how the ground-state SCE formalism performs to describe the properties of the strong interaction limit of DFT for the QR model system. In the SCE formalism, the spin-integrated square of the wave function is a distribution which is zero everywhere except in the subspace M where the energy functional reaches its degenerate minimum. The set Eq.(2.70) is given by the co-motion functions, which in turn they are determined by the density. For the case of the QR system, there is one co-motion function $f : [0, L] \rightarrow [0, L]$, given by

$$f(x) = \begin{cases} x + \frac{L}{2} & \text{if } x \in [0, \frac{L}{2}[\\ x - \frac{L}{2} & \text{if } x \in [\frac{L}{2}, L]. \end{cases} \quad (4.57)$$

The meaning of the co-motion function is that if one electron is at the reference position x , the co-motion function Eq.(4.57) puts the other electron in the opposite side of the ring, hence, minimizing in this way the interaction energy. Since $|x - f(x)| = L/2$ we have from our interaction $w(x) = V_0 \cos^2(\pi x/L)$ it is straightforward to obtain the SCE energy for the QR model which applying Eq.(2.68) we obtain $V_{\text{SCE}} = 0$. When the zero-point oscillations start to appear, they give an energy contribution which can be obtained using Eq.(2.78) with Eq.(2.79). If we calculate this frequency for our quantum ring we find $\omega_1(x) = 2\pi\sqrt{V_0}/L$ and $V_{\text{ZPE}} = \pi\sqrt{V_0}/(2L)$. Since the KS kinetic energy, as well as the external potential, is zero for the quantum ring system, E_{Hxc}^λ coincides with the total energy, which is known in the strong interaction limit from the large interaction limit expansion of the lowest Mathieu characteristic value given by Eq.(4.25). Regarding the SCE and ZPE potential,

we can use the expressions obtained in the App.(C) and App.(D) where we obtain Eq.(D.1) and Eq.(D.7), which are the expressions of the SCE and ZPE respectively for the case of 2 particles in one dimension.

4.4.3 The ASCE for the quantum ring system

In this section, we want to test if the expansion Eq.(3.54) of the Hxc kernel in the adiabatic approximation can capture the strong interaction limit of a strongly correlated system. For it, we obtain the leading term, the (3.55) and the next to the leading term, (3.56) of the expansion for the QR model system. The ASCE kernel is obtained from the expression Eq.(3.57), which for the QR model system reads

$$\begin{aligned} f^{\text{ASCE}}(x, x') &= - \int_0^x dy \frac{w''(|y - f(y)|)}{n[f(y)]} [\theta(y - x') - \theta(f(y) - x')] \\ &= f_1(x - x') - f_1(x) - f_1(x') + f_1(0) \end{aligned} \quad (4.58)$$

where, by virtue of Eq.(3.39) $f_1(x)$ and $f_1(x')$ are the two arbitrary functions we have the freedom to add, and then we know that f_1 is physically equivalent Hxc kernel to the kernel f^{ASCE} . The function f_1 is calculated in the appendix App(H) for the case of the QR and its expression agrees with the leading term of the asymptotic expansion for the large interaction strength limit of the exact Hxc kernel, that is, the function obtained in Eq.(4.52). The next to the leading term, the AZPE kernel has been obtained in [34] and whose derivation is given in the App(E). Applying the resulting expression Eq.(F.2) for the QR model is done also in the App(H), and we find that the obtained expression agrees with the next to the leading term of the asymptotic expansion for the large interaction strength limit of the exact Hxc kernel Eq.(4.53), up to two additional functions of x and x' separately. we therefore conclude that the first two leading terms of the expansion of the Hxc kernel from the adiabatic SCE formalism agree with the exact results for the quantum ring in the limit of large interaction strength. We have thus seen that, in the QR model system, the ASCE and

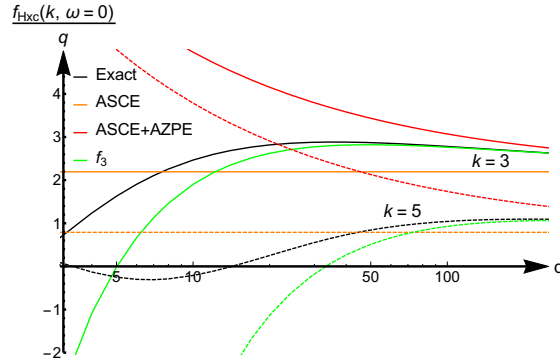


Figure 4.7: The static $f_{\text{Hxc}}(k, \omega = 0)/q$ as function of q , for $k = 3$ (solid lines) and $k = 5$ (dashed lines) in units of L^{-1} . We show the exact kernel obtained by numerical integration, and compare ASCE, ASCE+AZPE and ASCE+AZPE+ f_3 (denoted by f_3 in the figure) coming from Eq.(4.51). Note that we plot the kernel as function of q instead of λ in order to be consistent with the previous figures.

AZPE terms agree with the terms f_1 and f_2 respectively of the exact asymptotic expansion. Since in the SCE limit the position of one reference electron determines the position of the other electron, the response in the density under a small perturbation of the system is instantaneous, i.e., adiabatic and

hence, the Hxc kernel in this limit also is. Once the zero-point vibrations are introduced, we already introduce a characteristic frequency, i.e., the frequency of the vibrations which is proportional to the square root of the interaction strength. Even though a characteristic frequency is introduced, we still find that the response function is still adiabatic. A plausible explanation is that no external perturbation with a finite frequency can reach the harmonic frequency of the zero-point vibrations, which is proportional to $\sqrt{\lambda}$, but a more careful analysis is needed to state a strong conclusion. Thus, the second order expansion Hxc kernel is also adiabatic.

To end the analysis of the strong interaction limit of the Hxc kernel of TDDFT for the QR system, we show in Fig. 4.7 the first three terms of the asymptotic expansion of the exact QR Hxc kernel, all scaled by λ , and we compare them with the expression for the exact kernel in Fourier space, for $k = 3$ and $k = 5$. The ASCE term scaled with λ is a constant and it is a good approximation for very large interaction strength while the AZPE improves the approximation on it for large λ -values and worsens it for smaller ones. Finally, the third term, beyond the AZPE, improves the approximation for large values of the interaction strength, and it shows a non-negligible contribution when the interaction strength is small. We also observe that the accuracy of the expansion depends on the value of k , i.e., the higher k value is, the higher interaction strength is required for more accurate approximations for the Hxc kernel.

Based on the results of this work, we can conclude that the adiabatic SCE formalism and concretely, the SCE kernel constructed in the adiabatic approximation is a good candidate density functional to describe the features of the strong correlation limit correctly. The natural question that arises is whether the adiabatic SCE kernel can be used to predict the excitation energies of dissociating molecules correctly. Answering this question is the main focus of the next chapter. To attack this problem, we developed a simplified one-dimensional model of the hydrogen molecule having the main physical characteristics of the real three-dimensional hydrogen molecule and for which we can perform analytical mathematical results, and also obtain the many-body wave function for various bond distances numerically.

5 A simplified model for describing H_2

5.1 The model system

For the description of the simplified H_2 molecular model we consider two electrons of coordinates x_1, x_2 , defined on a ring of length L such that $x_1, x_2 \in [-\frac{L}{2}, \frac{L}{2}]$. The form of the Hamiltonian is given by

$$\hat{H}_\lambda(x_1, x_2) = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + v_\lambda(x_1) + v_\lambda(x_2) + \lambda \cos^2\left[\frac{\pi}{L}(x_1 - x_2)\right], \quad (5.1)$$

where the firsts two terms are the kinetic energy of each electron, v_λ is the one-body external potential, and the last term is the two-body electron-electron interaction, which is scaled with a strength λ . The strength of the interaction λ is a continuous semi-positive parameter $\lambda \geq 0$, and the external one-body potential is defined in a way that the ground-state density is the same for all λ according to the construction Sec. 2.3. This construction is possible by virtue to the HK theorem Sec. 2.1, which states that for fixed two-body interaction, i.e., for a fixed λ the ground-state density determines uniquely the one-body external potential provided that this potential exists. The external one-body potential is then a functional of the ground-state density $v_\lambda[n](x)$, and therefore the Hamiltonian Eq.(5.1) is uniquely determined by the ground-state density.

5.2 The H_2 molecular model

This section is devoted to constructing the model density able to mimic a real H_2 . Since the Hamiltonian Eq.(5.1) is built with the constraint that it produces the same density for each λ , one way of choosing a suitable density is to pick a particular external potential. The easiest and the most practical way to specify the given density is by means specifying the non-interacting system. Since the non-interacting or KS system is defined from the Hamiltonian Eq.(5.1) for $\lambda = 0$ interaction strength, which sets to zero the two-body electron-electron interaction, the resulting Hamiltonian reduces to a two-particle non-interacting Hamiltonian, which reads

$$\hat{H}_s(x_1, x_2) = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + v_s(x_1) + v_s(x_2), \quad (5.2)$$

where we write "s" as a subindex of the Hamiltonian instead of "0" because it stands for single particle Hamiltonian. The KS potential is chosen to be

$$v_s(x) = v_0 \left[\cos\left(\frac{4\pi x}{L}\right) + 1 \right], \quad (5.3)$$

where v_0 is a constant with units of energy. The choice of the KS potential is because it has two minima located at $x_0 = \pm \frac{L}{4}$, and therefore, the ground-state density produced by such potential will

have two maxima at $\pm\frac{L}{4}$, represented in this way two electrons, each of them located around the position $\pm\frac{L}{4}$ and separated by the bond distance $L/2$. We are interested in constructing a model such that the density mimics a H₂ molecule. In particular, we are interested in the model to reproduce molecular dissociation for all the range of the interaction strength λ . For that purpose, we need to impose the ground-state density to be independent of the interaction strength when we stretch the molecule. We do that by imposing the width of the density maxima to be independent of the bond distance $L/2$ while the distance between the maxima varies. This condition is guaranteed by demanding the constraint that the width of the potential has to be independent of the L , i.e., $u_0 \sim L^2$, or in other words, we have to demand that the curvature of the potential at $x_0 = \pm\frac{L}{4}$ has to be independent of the length. This condition reads

$$v_s''(x)|_{x_0} = \left(\frac{4\pi}{L}\right)^2 v_0 \equiv \alpha, \quad (5.4)$$

where α is independent of L . As a consequence, the amplitude of the KS potential is enforced to have the specific shape $v_0 = \alpha \left(\frac{L}{4\pi}\right)^2$ for an arbitrary but length independent curvature α . The KS equation for the 2-spin compensated system read

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + v_0 \cos\left(\frac{4\pi x}{L}\right)\right] \varphi_l(x) = (\varepsilon_l - v_0) \varphi_l(x) \quad (5.5)$$

The KS equations Eq.(5.5) must be solved together with the boundary conditions $\varphi_l(-L/2) = \varphi_l(L/2)$, and the same for its derivatives. For solving them, it is now convenient to define the non-dimensional coordinate $z = \frac{2\pi x}{L}$ and write the KS equations in terms of the new coordinate as follows

$$\left[-\frac{d^2}{dz^2} + 2\nu \cos(2z)\right] M_l^\pm(z) = a_l^\pm M_l^\pm(z), \quad (5.6)$$

where we have defined the following constants

$$a_l^\pm = 2 \left(\frac{L}{2\pi}\right)^2 (\varepsilon_l^\pm - v_0) \quad (5.7)$$

$$\nu = \left(\frac{L}{2\pi}\right)^2 v_0 = \frac{\alpha}{4} \left(\frac{L}{2\pi}\right)^4 \quad (5.8)$$

and where the equation Eq.(5.8) has been written in terms of the constraint Eq.(5.4). The equation (5.6) is the Mathieu equation, its eigenfunctions M_l^+ are the Mathieu-cosine, which we denote by C_l and M_l^- is the Mathieu-sine which is denoted by S_l . In turn, its eigenvalue a_l^\pm is the Mathieu characteristic value. Now the boundary conditions for the Mathieu functions in terms of z read $M_l^\pm(-\pi) = M_l^\pm(\pi)$. Choosing the normalization convention of Mathieu functions to be Eq.(4.11), we therefore see that the KS orbitals are Mathieu functions up to a multiplicative normalization constant, which are expressed as follows

$$\begin{aligned} \varphi_l^+(x) &= \sqrt{\frac{2}{L}} C_l\left(\frac{2\pi x}{L}; \nu\right) \\ \varphi_l^-(x) &= \sqrt{\frac{2}{L}} S_l\left(\frac{2\pi x}{L}; \nu\right) \end{aligned} \quad (5.9)$$

and the orbitals φ_l^+ are labeled starting at $l = 0$, while the orbitals φ_l^- are labeled starting at $l = 1$. Moreover, the single particle energies obey the relation $\epsilon_0^+ < \epsilon_1^- < \epsilon_2^+ < \epsilon_3^- \dots$. The KS eigenspectrum in terms of the Mathieu characteristic reads

$$\varepsilon_l^\pm(\nu) - v_0(\nu) = \frac{1}{2} \left(\frac{2\pi}{L}\right)^2 a_l^\pm(\nu), \quad (5.10)$$

Once the solution of the KS equation is analyzed, we proceed to describe the density of the molecular model. The ground-state density is chosen to be

$$n(x) = 2|\varphi_0^\pm(x)|^2. \quad (5.11)$$

As we anticipated before, such a ground-state exhibit two maxima at $\pm\frac{L}{4}$, representing in this way two electrons which each of them is located around the position $\pm\frac{L}{4}$ and separated by the bond distance $L/2$. It is interesting to study the model density Eq.(5.11) for large bond distances. We note that by the definition Eq.(5.8), the parameters L and ν differ just a multiplicative constant. Therefore, from now on, we will refer to the large/small bond distance limit as the limit in which either two variables tends to infinity/zero. Using the Sips expansion for large ν limit of the Mathieu functions [35], the density attains the form

$$n(x) = \sqrt{\frac{\alpha^{1/2}}{\pi}} \left[e^{-2\sqrt{\alpha}(x-\frac{L}{4})^2} + e^{-2\sqrt{\alpha}(x+\frac{L}{4})^2} \right]. \quad (5.12)$$

We can now see the condition Eq.(5.4) we enforced implemented. From the above expression we see that for large bond distances, the density becomes two Gaussian centered in $x = \pm L/4$ whose widths are independent of L . This picture is represented in Fig. 5.1 from where we can see the plots of the KS potential and the ground-state density for different bond distances. It is shown that as the bond distance L increases, the curvature of the potential and the width of the density are kept independent of the length L . As a consequence, the two density maxima show an overlap that decreases when the bond distance L increases, showing that in the symmetry point $x = 0$ the ground-state density decays to zero as a function of the length L , depicting in this way the right features of a dissociation process. We can then assert that the model density proposed, Eq.(5.11), reproduces properly the main features of the H₂ molecule. Because we are interested in spatially symmetric solutions, ie,

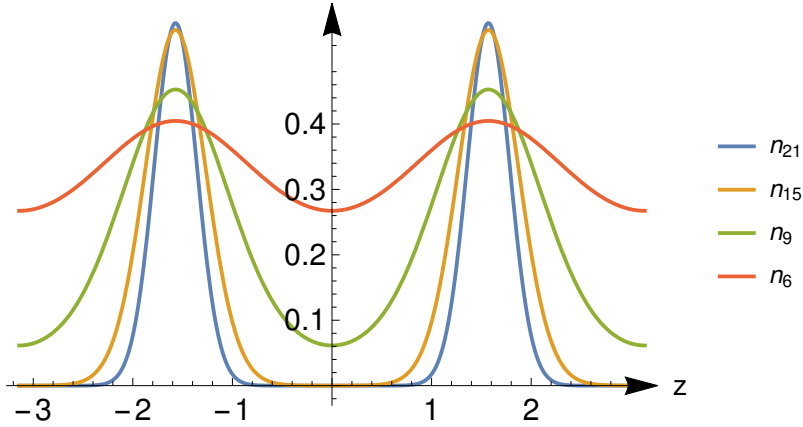


Figure 5.1: Plot of the ground-state density n/L^2 Eq.(5.11) as a function of the scaled coordinate $z = 2\pi x/L$. It is shown how the width of the density is kept independent of L . As a consequence, when the bond length is increased, the overlap between maxima becomes negligible in the large separation limit $L \rightarrow \infty$.

those solutions such that the spin component is always the singlet, we identify the ground-state wave function to be the Mathieu-Cosine C_0

$$\Psi_s^{\text{GS}}(x_1, x_2) = \varphi_0^+(x_1)\varphi_0^+(x_2), \quad (5.13)$$

and we construct the spatially symmetric first excited-state as

$$\Psi_s^{\text{1st}}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\varphi_0^+(x_1)\varphi_1^-(x_2) + \varphi_0^+(x_2)\varphi_1^-(x_1) \right], \quad (5.14)$$

where we have added two Slater determinant to fulfill the required symmetries for the full space-spin wave-function. It is shown in Fig. 5.2 the Kohn-sham ground-state and the first symmetric excited-state wave functions. From the solution of the KS equation, the ground-state and the first-excited

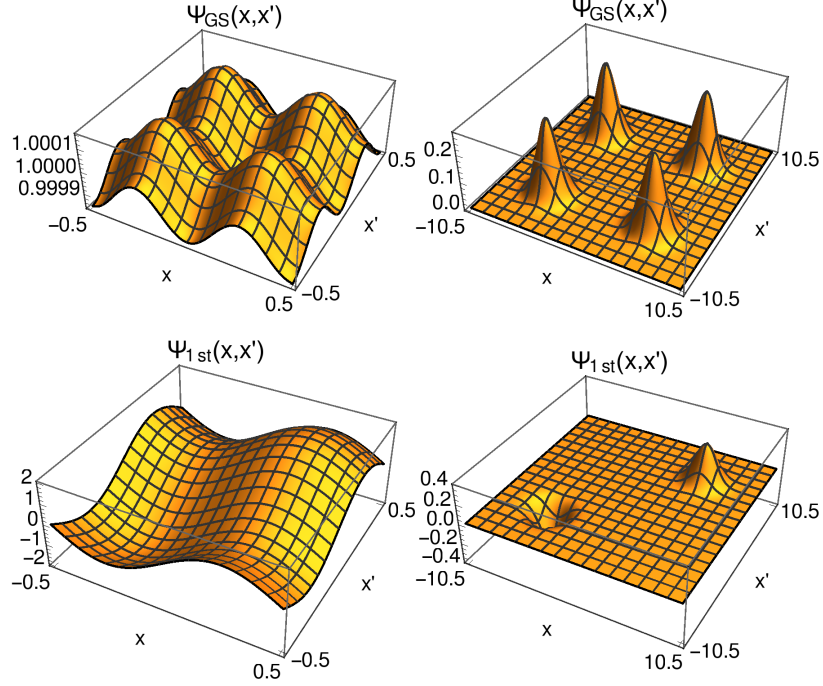


Figure 5.2: Plot of the Kohn-Sham ground state (above) and the first symmetric excited state (below) wave function for bond distances $L = 1$ (left) and $L = 21$ (right).

state energies read

$$E_s^{\text{GS}}(\nu) = 2\varepsilon_0^+(\nu) = \left(\frac{2\pi}{L}\right)^2 a_0^+(\nu) + 2\nu_0 \quad (5.15)$$

$$E_s^{\text{1st}}(\nu) = \varepsilon_1^-(\nu) + \varepsilon_0^+(\nu) = \frac{1}{2} \left(\frac{2\pi}{L}\right)^2 [a_1^-(\nu) + a_0^+(\nu)] + 2\nu_0. \quad (5.16)$$

By subtraction of the KS ground-state and the first-excited state, and using the asymptotic expansion for the Mathieu characteristic value for $L, \nu \rightarrow \infty$, we get

$$\varepsilon_1^-(\nu) - \varepsilon_0^+(\nu) \xrightarrow{L \rightarrow \infty} 0, \quad (5.17)$$

which decays exponentially to zero as a function of the bond distance L . We can then identify for the molecular model the localized orbitals "bonding" ϕ_a and "anti-bonding" ϕ_b as follows

$$\phi_a(x) = \frac{1}{\sqrt{2}} [\varphi_0^+(x) + \varphi_1^-(x)] \quad (5.18)$$

$$\phi_b(x) = \frac{1}{\sqrt{2}} [\varphi_0^+(x) - \varphi_1^-(x)]. \quad (5.19)$$

For ending this section, we comment that taking the limit $\nu \rightarrow 0$, the external potential becomes 0 for all interaction strength and the density becomes homogeneous, recovering in this way the homogeneous solution Sec. 4.

Our goal now is to construct the Hamiltonian Eq.(5.1) that produces the ground-state density Eq.(5.11). Once the Hamiltonian is built, the solution of the Schrödinger equation will provide the exact eigenstates and the exact excitation energies for all range of parameters of interest L and λ . In particular, we are interested in describing the exact eigenstates and energy spectrum of the simplified hydrogen model as a function of the bond distance L and the interaction strength λ . We will then analyze them in the limit of large bond distances, which describes the dissociation processes of the H₂ molecular model, for arbitrary but finite interaction strength and also in the limit of large interaction strength for arbitrary bond distance. We are also interested in studying the external one body potential v_λ that produces the ground-state density for all the range of parameters L and λ .

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation

The properties of the system are given by means the many-body wave function, which is the solution of the Schrödinger equation. For the 2-electron system, the full solution to the Schrödinger equation can be written as a product of a spatial wave function and a spin wave function as follows

$$\Psi(x_1\sigma_1, x_2\sigma_2) = \psi^\pm(x_1, x_2)\Xi^\pm(\sigma_1, \sigma_2). \quad (5.20)$$

For the singlet case, which is the case we focus on, the normalized spin wave function reads

$$\Xi^\pm(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}(\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}). \quad (5.21)$$

Regarding the triplet case, there are three independent symmetric wave functions which we denote by $\Xi^-(\sigma_1, \sigma_2)$. Since the full two-electron wave function $\Psi(x_1\sigma_1, x_2\sigma_2)$ must be antisymmetric under the simultaneous interchange of space and spin variables, the spatial wave functions ψ^\pm must satisfy the following symmetry relations

$$\psi^\pm(x_1, x_2) = \pm\psi^\pm(x_2, x_1). \quad (5.22)$$

The solution of the Schrödinger equation has to be solved imposing periodic boundary conditions on the variables x_1 and x_2 , i.e., the wave function has to be invariant under the substitution $x_i \rightarrow x_i + L$ for $i = 1, 2$, and the same for its derivatives.

For solving the Schrödinger equation, we constructed first the one-body external potential $v_\lambda[n]$ as a function of L and λ that produces the density 5.11. With the external potential determined, the Hamiltonian Eq.(5.1) is also uniquely determined, and then we can solve the Schrödinger equation obtaining in this way the eigenstates and the energy spectrum as a function of the bond distance and the interaction strength. Practically, this inversion problem involves an iterative procedure from where the external one-body potential that yields the prescribed density, and the ground-state wave function are calculated at a time within one iteration step, keeping the iteration procedure going until the desired convergence is reached. This problem has already been studied, and the algorithm we have used in our numerical calculations is explained in detail in [62, 63]. For calculating the one-body external potential that yields our model density Eq.(5.11) for a nonzero interaction strength and the subsequent resolution of the Schrödinger equation, we have kept the width of the density to be $\alpha = 1$ for all the numerical calculations. The numerical reason for having picked this particular two-body interaction in Eq.(5.1) becomes clearer, and it is because if we perform the limit $\nu \rightarrow 0$, we recover the homogeneous quantum ring system which we can solve analytically, and whose study has been explained in Sec. 4 and [34]. For the set of parameters L ranging from 1 to 21 and λ ranging from

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation 63

0 to 10000 we have obtained the external one-body potential that yields the prescribed density, the ground-state and the first spatially symmetric excited-state wave functions with their corresponding energy spectrum.

Because we are interested in the solution of the wave function and the energy spectrum for the limits of large bond distance and large interaction strength for its subsequent comparison, the following sections, therefore, are devoted to the detailed analysis of such limits, and as well to develop analytic models that are useful for the better understanding of both physical situations.

5.3.1 The limit of large bond distance: The HL system

The HL system is defined from the Hamiltonian (5.1) by doing the limit of large bond distances $L \rightarrow \infty$ no matter the strength of the interaction λ , provided that it is finite. We are interested in giving approximate expressions for the Hamiltonian Eq.(5.1), the ground-state and the spatially symmetric excited-states and its corresponding excitation energies for the limit of large bond distances L , for all but finite interaction strengths. For a H_2 molecule, for the limit of large bond distances, the external potential in the near neighborhood of each atom is approximately the external potential of this single atom, since the two-body interaction is negligible. Then the Hamiltonian that describes the system in the dissociation limit is Eq.(5.1) with the one-body potential given by

$$v_{\lambda,\text{HL}}(x) = v_0 \left[\cos \left(\frac{4\pi x}{L} \right) + 1 \right]. \quad (5.23)$$

The ground-state wave function that describes the limit of large bond distances and finite interaction strength is the HL ground-state wave function, whose spatial part reads

$$\Psi_{\lambda,\text{HL}}^{\text{GS}}(x_1, x_2) = \frac{1}{\sqrt{2}} [\varphi_0^+(x_1)\varphi_0^+(x_2) - \varphi_1^-(x_2)\varphi_1^-(x_1)]. \quad (5.24)$$

For the calculation of the ground-state energy, if we take into account the expressions Eq.(5.5), Eq.(5.10) for the limit of large bond distance, and the fact that the difference $a_k^+ - a_{k+1}^-$ for fixed k is exponentially small [35], we can write $a_0^+ = a_1^- \equiv a_0$, and then the ground-state HL energy reads

$$E_{\lambda,\text{HL}}^{\text{GS}} = 2\varepsilon_0^+ = \sqrt{\alpha} - \frac{\pi^2}{L^2} + \mathcal{O}(L^{-4}), \quad (L \rightarrow \infty). \quad (5.25)$$

Since we are interested in the description of excited states in molecular dissociation, we focus our attention in that HL spatially symmetric excited-state wave function that represents each electron located in each atom, and one of the electrons promoted to the first excited-state of any of the atoms. The first excited-state of this kind reads

$$\Psi_{\lambda,\text{HL}}^{(1)}(x_1, x_2) = \frac{1}{2} [\varphi_1^+(x_1)\varphi_1^-(x_2) + \varphi_1^-(x_1)\varphi_1^+(x_2) - \varphi_0^+(x_1)\varphi_2^-(x_2) - \varphi_2^-(x_1)\varphi_0^+(x_2)]. \quad (5.26)$$

For the calculation of the HL first excited energy we again make use of the Eq.(5.5) and Eq.(5.10), and the fact that the difference $a_0^+ - a_1^-$ is exponentially small such that we can write $a_0^+ = a_1^- \equiv a_0$ and $a_1^+ = a_2^- \equiv a_1$. Then, the energy of the first excitation reads

$$E_{\lambda,\text{HL}}^{(1)} = \varepsilon_0 + \varepsilon_1 = 2\sqrt{\alpha} - \frac{3\pi^2}{L^2} + \mathcal{O}(L^{-4}), \quad (L \rightarrow \infty). \quad (5.27)$$

Subtracting the ground-state HL energy, we get the excitation energy for large bond distance and arbitrary but finite interaction strength, which in the very limit of large bond distances reads

$$E_{\lambda,\text{HL}}^{(1)} - E_{\lambda,\text{HL}}^{\text{GS}} = \sqrt{\alpha}, \quad (L \rightarrow \infty). \quad (5.28)$$

We have derived expressions for the ground-state wave function, the 1st spatially symmetric excited states and their corresponding eigenenergies which can be compared with the numerical results given by the exact solution of the Schrödinger equation.

We show in the plot Fig. 5.3 the ground-state and first symmetric excited state energy curves as a function of the bond distance, for the various strength of the interaction, in comparison with the asymptotic expressions derived for large bond distance for all but finite interaction strength. For the ground-state, the plot shows how the exact energy curves converge to the asymptotic expression Eq.(5.25) as the bond distance grows. In turn, for the first excited state, the plot shows that the convergence of the exact energy curves to the asymptotic expression Eq.(5.27) occurs much slower than in the ground-state, which means that larger bond distance is needed for considering the system completely dissociated.

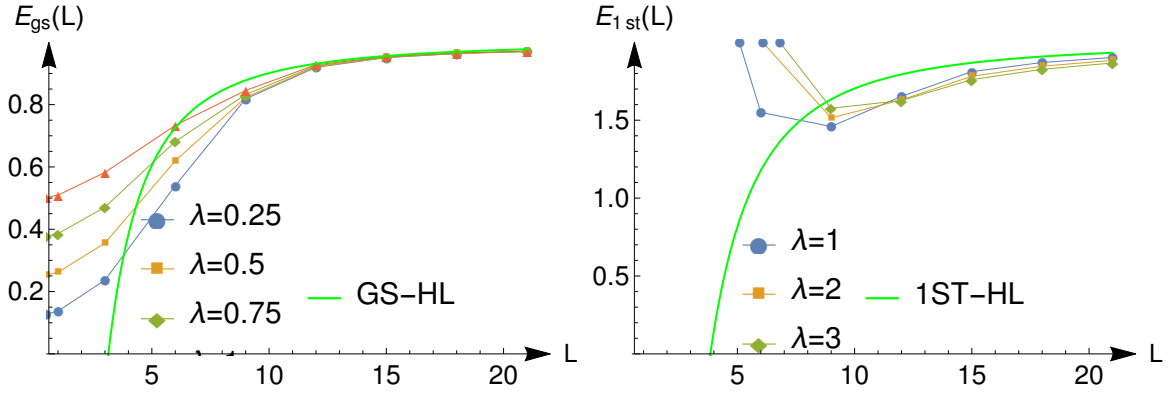


Figure 5.3: Plot of the exact ground-state energy curve for $\lambda = 0.25, 0.5, 0.75, 1$, in comparison with the asymptotic expression Eq.(5.25) (left panel). Plot of the first symmetric excited-state for $\lambda = 1, 2, 3$ in comparison with the asymptotic expression Eq.(5.27) (Right panel). Unlike the ground-state, the excited-state wave function is still described by the KS one for the values of $\lambda 0.25, 0.5$, and the excited state HL starts to appear at higher values of the interaction strength, which means that higher values of the bond distances are needed for bringing the excited-state to the dissociation regime.

We also show in Fig. 5.4 how the HL wave functions both for the ground-state Eq.(5.24) and the first symmetric excited state Eq.(5.26) fit to the exact wave function for large bond distances, where it is plotted the exact wave functions and the error made by approximating them by the HL wave functions. We then see that for large enough bond distances the HL wave functions approximate well the exact wave function around $x_1, x_2 = \pm L/4$, since the error made in this zone is about one order of magnitude less than the maximum value of the exact wave function.

For finishing the analysis of the large bond distances, we show in the plots Fig. 5.5 the comparison of the exact external one body potential that yields the density Eq.(5.11) versus the HL potential Eq.(5.23). It is shown that for large bond distances, the exact external potential is well described by

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation 65

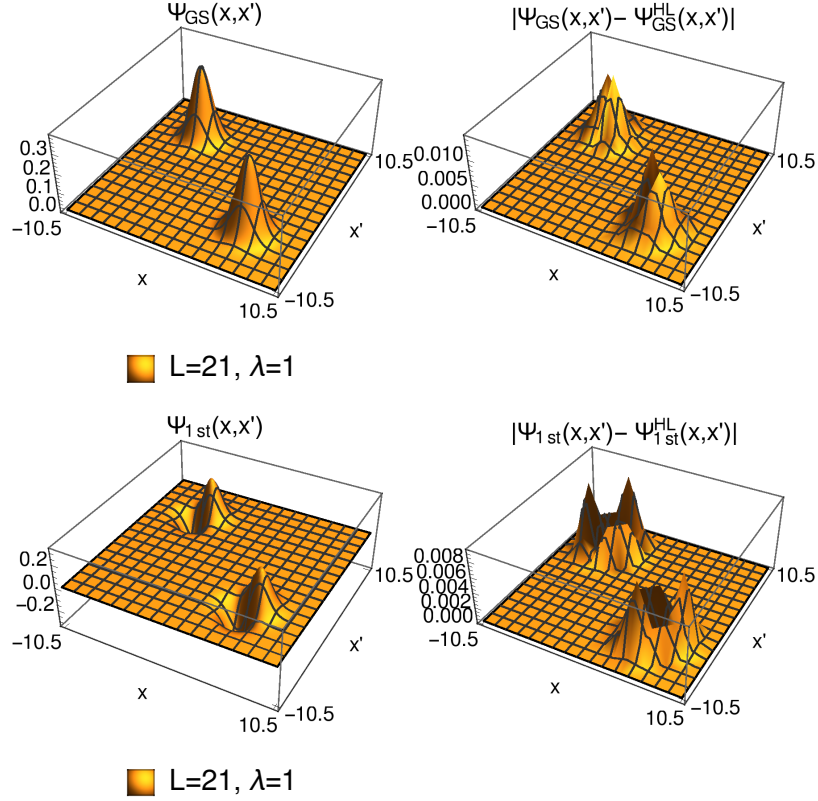


Figure 5.4: Exact ground-state and first symmetric excited state for $L = 21$ and $\lambda = 1$. It is also shown the absolute value of the difference between the exact wave function and its approximation by the HL wave functions Eq.(5.24) and Eq.(5.26).

the HL potential in almost all the domain of the potential. However, the exact potential displays a central pick in the midpoint which is not described by the HL potential. The pick decreases as the difference between the bond distances and the interaction strength increases, and it is related with the Hxc potential, as we will see in the DFT section. A thorough analysis of the effect of molecular dissociation on the Hxc potential is given in [64, 65].

5.3.2 The limit of large interaction strength: The strongly correlated system

In this section, we proceed to analyze the strong interaction limit of the model system. The strongly correlated system is defined from the Hamiltonian (5.1) by doing the limit $\lambda \rightarrow \infty$ for any bond distance. We are interested in doing a general description of the system for the limit of large interaction strength for any bond distance, and give approximate expressions for the Hamiltonian, its eigenstates and its energy spectrum. For a proper analysis of the large interaction strength limit, it is convenient to introduce the coordinates of the center of mass $R = \frac{x_1 + x_2}{2}$ and relative coordinate

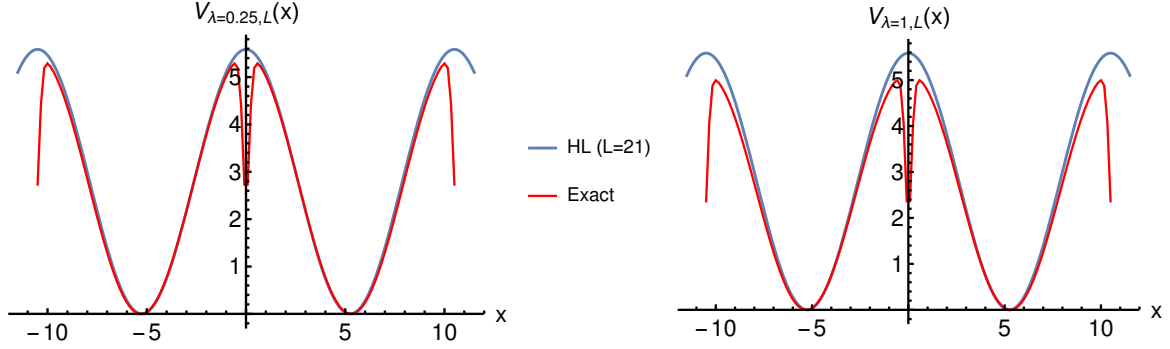


Figure 5.5: Exact external potential in comparison with the HL potential Eq.(5.23) for the bond distances $L = 21$ and interaction strength $\lambda = 0.25, 1$. The HL potential approximates well the exact potential around $x = \pm L/4$ and displays the characteristic pick related with the Hxc potential of a dissociating system.

$r = x_1 - x_2$. The Hamiltonian (5.1) in the new coordinates reads

$$\hat{H}_\lambda(s, z) = -\frac{1}{4}\partial_R^2 - \partial_r^2 + v_\lambda\left(R + \frac{r}{2}\right) + v_\lambda\left(R - \frac{r}{2}\right) + \lambda \cos^2\left(\frac{2\pi r}{L}\right). \quad (5.29)$$

To analyze the strong interaction limit and based on the numerical resolution of the Schrödinger equation, we make the following plausible assumption for the one-body external potential in the large λ limit: We assume that in the large λ limit, the external potential admits a Taylor expansion around the lines $r = \pm L/4$ as follows

$$v_\lambda\left(R + \frac{r}{2}\right) + v_\lambda\left(R - \frac{r}{2}\right) = 2v_\lambda(R) + \left.\frac{\partial^2 v_\lambda\left(R - \frac{r}{2}\right)}{\partial r^2}\right|_{r=\pm \frac{L}{2}} \left(-r \pm \frac{L}{2}\right)^2 + \mathcal{O}(r^4), \quad (5.30)$$

and we also assume that its derivatives along the r direction, i.e., the corrections of the expansion to the leading term in the r direction are decaying functions of the interaction strength. Under these assumptions, the Hamiltonian (5.1) in the large λ limit attains the form

$$\hat{H}_{\text{SC},\lambda}(R, r) \equiv \left(-\frac{1}{4}\partial_R^2 - \partial_r^2\right) + 2v_\lambda(R) + \lambda \cos\left(\frac{2\pi r}{L}\right), \quad (5.31)$$

where the subindex "SC" stands for strong coupling. We now write the Schrödinger equation in terms of the non-dimensional coordinates $s = \frac{\pi}{L}R$ and $z = \frac{\pi}{L}r$, which reads

$$\left[\left(-\frac{1}{4}\partial_s^2 - \partial_z^2\right) + 2\left(\frac{L}{\pi}\right)^2 v_\lambda\left(\frac{Ls}{\pi}\right) + 2q \cos(2z)\right] \Psi_{\text{SC},\lambda}(s, z) = \tilde{E}_{\text{SC},\lambda} \Psi_{\text{SC},\lambda}(s, z) \quad (5.32)$$

where we have defined

$$\tilde{E}_{\text{SC},\lambda} = \left(\frac{L}{\pi}\right)^2 E_{\text{SC},\lambda} - 2q \quad (5.33)$$

$$q = \lambda \omega_0 \left(\frac{L}{2\pi}\right)^2. \quad (5.34)$$

As before, since the parameter q and λ differ only a multiplicative constant, we will, therefore, refer to the large interaction strength limit when either both variables tend to infinity. Since the

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation 67

Hamiltonian (5.31) is separable, the Schrödinger equation (5.32) admits a product solution. Note that the Schrödinger equation is only separable in the very limit of large interaction strengths. If we consider adding the next to the leading order in the expansion of the external potential for large interaction strength in Eq.(5.30), it already mixes both coordinates and the equation becomes non-separable. We can write the solution of the Schrödinger Eq.(5.32) as a product ansatz as $\Psi_{\text{SC},\lambda}\left(\frac{Ls}{\pi}, \frac{Lz}{\pi}\right) = N_\lambda \varphi_\lambda(s) M_\lambda(z)$ where N_λ is a normalization factor. Inserting the ansatz into the Schrödinger equation (5.32) we get one equation for each coordinate

$$\left[-\frac{1}{4}\partial_s^2 + 2\left(\frac{L}{\pi}\right)^2 v_\lambda\left(\frac{Ls}{\pi}\right)\right] \varphi_\lambda(s) = a\varphi_\lambda(s) \quad (5.35)$$

$$[-\partial_z^2 + 2q \cos(2z)] M_l(z; q) = a_l(q) M_l(z; q), \quad (5.36)$$

where $\tilde{E}_{\text{SC},\lambda} = a + a_l(q)$. We can solve the equation for the z coordinate since it is the Mathieu equation, its solutions M_l^\pm are Mathieu functions, and the eigenvalue is the Mathieu characteristic value a_l^\pm . We do not know still the one-body potential v_λ in the limit of the strong interaction, but we know that by the density constraint, it is the unique external potential that produces the given ground-state density, and hence it must be determined entirely by means the ground-state density. This is indeed the case, and if we calculate the ground density, we get

$$\begin{aligned} n(x) &= \int_{-L/2}^{L/2} dx_2 |\Psi_{\text{SC},\lambda}(x, x_2)|^2 \\ &= \frac{4}{L^2} \int_{-L/2}^{L/2} dx_2 \varphi_\lambda^{(0)}\left[\frac{\pi}{L}\left(\frac{x+x_2}{2}\right)\right]^2 C_0\left[\frac{\pi}{L}(x-x_2); q\right]^2. \end{aligned} \quad (5.37)$$

But the above expression has only sense in the limit $\lambda \rightarrow \infty$. Therefore we use the explicit form of the Mathieu-cosine function for the large q limit given by the Sips expansion [35], which reads

$$\lim_{q \rightarrow \infty} C_0^2(z; q) = \frac{\pi}{2} \left[\delta\left(z - \frac{\pi}{2}\right) + \delta\left(z + \frac{\pi}{2}\right) \right] \quad (5.38)$$

and which inserted in Eq.(5.37), we finally get

$$n(x) = \frac{4}{L} \varphi_\lambda^{(0)}\left[\frac{\pi}{L}\left(x \pm \frac{L}{4}\right)\right]^2, \quad (5.39)$$

wherein the last step we have used the symmetry properties of $\varphi^{(0)}$ to gather both terms into one. For our particular density 5.11, and knowing that in the limit of large interaction strength $s = \frac{\pi}{L}\left(x + \frac{L}{4}\right)$, then we can finally calculate the external potential for the large interaction strength, which is given explicitly by the ground-state density by equation (5.35)

$$\begin{aligned} v_\lambda\left(\frac{Ls}{\pi}\right) &= \left(\frac{\pi}{2L}\right)^2 \frac{\partial_s^2 \sqrt{n(2s)}}{\sqrt{n(2s)}} \\ &= \left(\frac{\pi}{2L}\right)^2 \frac{\partial_s^2 \varphi_\lambda^{(0)}(s)}{\varphi_\lambda^{(0)}(s)} + \frac{v_0}{4} = \frac{v_0}{4} [\cos(4s) + 1], \quad (q \rightarrow \infty), \end{aligned} \quad (5.40)$$

which is independent of the interaction strength in the large λ limit, being consistent with the assumption made Eq.(5.30). With the external potential for large interaction strength determined, the part of the Schrödinger equation for the center-of-mass coordinate Eq.(5.35) can be solved by doing the change of variable $t = 2s$ in the equation (5.41), which becomes a Mathieu equation again.

$$[-\partial_t^2 + 2\nu \cos(2t)] M_k(t; \nu) = \left[\epsilon_k^\pm(\nu) - \frac{v_0}{4}\right] M_k(t; \nu), \quad (5.41)$$

where we wrote the potential in terms of the parameter ν given by Eq.(5.8). Finally, changing back to the original coordinates, the full solution for the Schrödinger equation for the large λ limit Eq.(5.32) reads

$$\Psi_{\text{SC},\lambda}^{(k,p;l,p')} (R, r) = \frac{2}{L} M_k^p \left(\frac{2\pi R}{L} \pm \frac{\pi}{2}; \nu \right) M_l^{p'} \left(\frac{\pi r}{L}; q \right), \quad (5.42)$$

where $p, p' = \pm$. Since the Mathieu functions have the periodicity property $M_n^\pm(x) = (-1)^l M_n^\pm(x + \pi)$, they are periodic in π for even values of n and anti-periodic for odd values of n . Therefore, for the wave function Eq.(5.42) to satisfy the periodic boundary conditions under the change $x_i \rightarrow x_i + L$ for $i = 1, 2$, the labels k and l must be both even or both odd. In turn, the energy spectrum reads

$$\begin{aligned} E_{\text{SC},\lambda}^{(k,\pm;l,\pm)} &= \left(\frac{\pi}{L} \right)^2 [a_k^\pm(\nu) + a_l^\pm(q) + 2\nu + 2q] \\ &= \frac{\pi^2}{L^2} \left[a_k^\pm(\nu) + 2\nu + 2(2l+1)\sqrt{q} - \frac{1}{4}(2l^2 + 2l + 1) + \mathcal{O}(q^{-1/2}) \right], \end{aligned} \quad (5.43)$$

where we have used in the last step again the large q asymptotic expansion for the Mathieu characteristic value.

To illustrate how the wave functions for large interaction strength look like, we showed in Fig. 5.6 the plots of the exact ground-state and the first symmetric excited-state, and how they deviate from the product solution Eq.(5.42). For large interaction strength, the exact wave function is well represented by the product solution around $r = \pm L/4$, which justifies our initial assumption. We see from the plots that for any bond distance, both the ground-state and the first symmetric excited-state wave function get squeezed along the r direction, which according to the product solutions for large interaction strength, Mathieu functions become Hermite functions with a width proportional to $1/\sqrt{2q}^{1/4}$. The Mathieu function along the r direction is modulated by the Mathieu function along the R direction, which for small ν are well approximated by plane waves and we obtain back the homogeneous QR, and for large ν they are also represented by Hermite functions.

After having obtained the wave functions for both systems, we can see that the wave function of large bond distance and large interaction strength look very different between them. To better understand their physical meaning, let us have a look at the conditional probability of having one reference electron at $x = -L/4$, constructed by both HL and SC wave functions. Both conditional probabilities are shown in Fig. 5.7. We see that both probability distributions correlate the other electron around $L = L/2$, but the SC probability distribution becomes narrower in the limit of large interaction strength with a broadening which is due to the zero-point oscillations around the equilibrium relative position. In the very limit, the SC probability distribution becomes a Dirac delta function while the HL probability distribution maintains the width invariant.

Let us discuss the type of excitations that the system shows in the limit of large interaction strength. Consider the excitations Eq.(5.43) from the ground-state to another state with $k = 0$. These excitations are given by

$$E_{\text{SC},\lambda}^{(0+;l+)} - E_{\text{SC},\lambda}^{(0+;0+)} = \left(\frac{2\pi}{L} \right)^2 l\sqrt{q}. \quad (5.44)$$

These are excitations of the relative coordinate while keeping the center-of-mass excitations in its ground-state, and therefore they cost an amount of energy that grows with the interaction strength. It is plotted in Fig. 5.8 the exact ground-state and first symmetric excited-state energy as a function of the interaction strength, for various bond distances, and they are compared with the asymptotic expressions Eq.(5.42) for the ground-state and first symmetric excited-state that were obtained for the strong interaction limit. We see that when the interaction strength is large enough, the energy spectrum follow the square root behavior Eq.(5.43) as a function of the interaction strength, for any bond distance.

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation 69

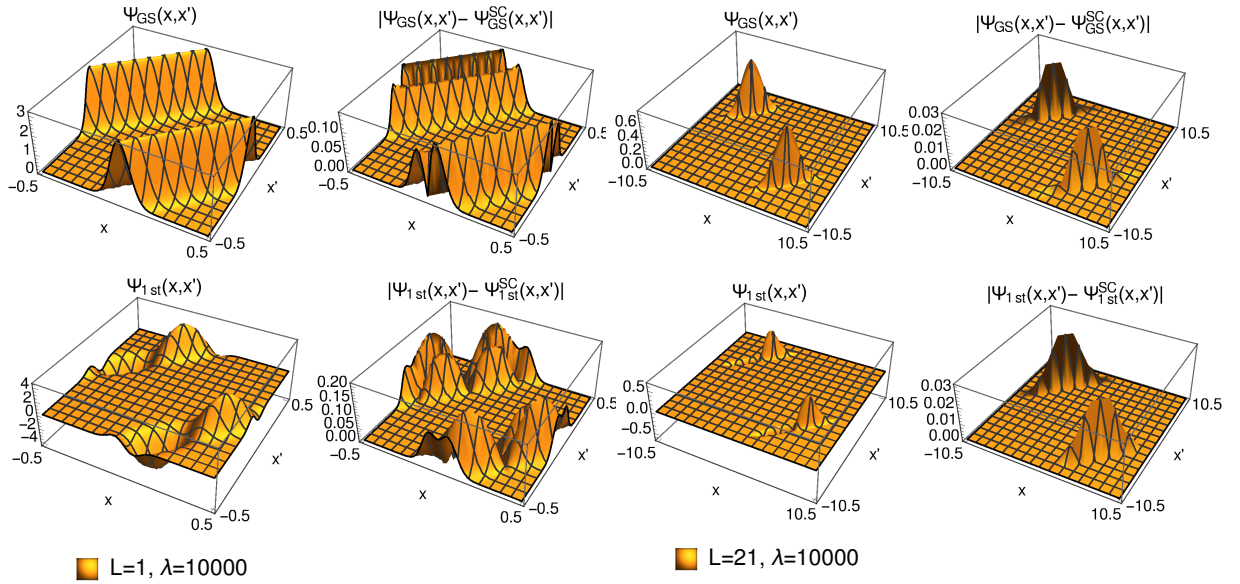


Figure 5.6: Plot of the ground-state, the first symmetric-excited state for $L = 1$ and $\lambda = 10000$ (left) and for $L = 21$ and $\lambda = 10000$ (right). It is also shown the absolute value of the difference between the exact wave function and its approximation by the SC wave functions, showing that for the large interaction strength limit, the product solution Eq.(5.42) is a good approximation to the exact wave function around $r = \pm L/4$.

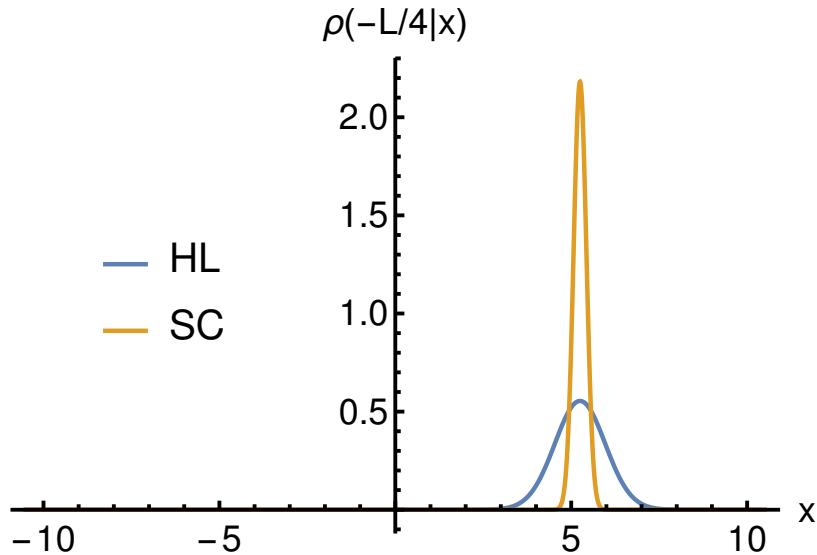


Figure 5.7: Ground state conditional probability of finding an electron at position $x = L/4$ having put a reference electron at the position $x_1 = -L/4$ for both HL and SC systems, for $L = 21$ and $\lambda = 10000$

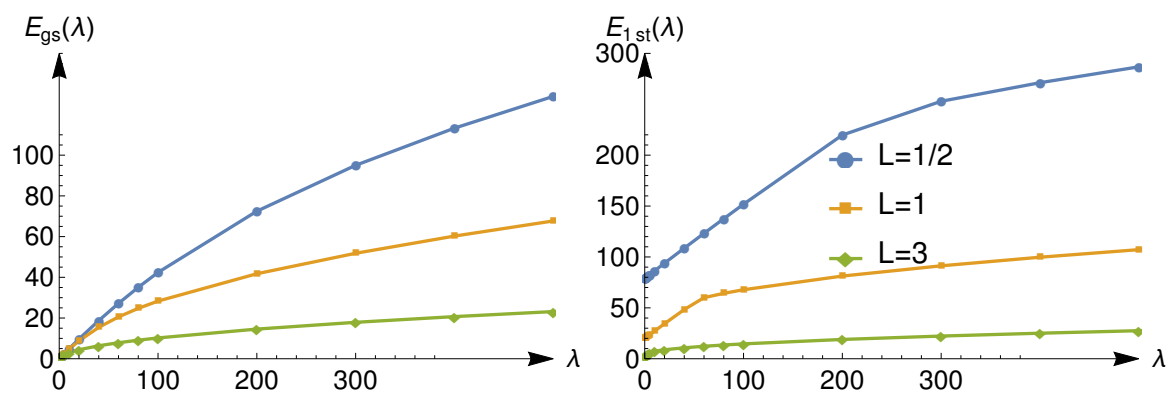


Figure 5.8: Plots of the ground-state and the first excited-state curves as a function of λ for values of the bond distance $L = 0.5, 1, 3$. It can be seen that for large values of the interaction, both the ground-state and the excited-state grow proportional to $\sqrt{\lambda}$.

5.3 Construction of the Hamiltonian and exact solution of the Schrödinger equation 71

Consider now the excitations Eq.(5.43) from the ground-state to another excited state with $l = 0$. These excitations are given by

$$E_{\text{SC},\lambda}^{(k+;0+)} - E_{\text{SC},\lambda}^{(0+;0+)} = \frac{\pi^2}{L^2} [a_k^\pm(\nu) - a_0^+(\nu)], \quad (5.45)$$

which are excitations independent of the interaction strength. These excitations correspond to the center-of-mass excitations, keeping the relative coordinate in its ground-state and therefore the energy does not grow with the interaction strength. In the plot Fig. 5.9 we show the excitation energy Eq.(5.45) for $k = 2, l = 0$. As the interaction strength grows, the exact curve approaches to the asymptotic excitation, having a total agreement for very large interaction strengths. Moreover, we note that performing the limit of small bond distances, we recover the center-of-mass excitations of the homogeneous QR, since when $\nu \rightarrow 0$, $a_k^\pm(\nu) = k^2$. If we now consider the excitations that are independent of the interaction strength in the large q limit expansion, and we perform the large L expansion of Eq.(5.45), using the asymptotic expansion of the Mathieu eigenvalue [35], we get

$$\lim_{\nu \rightarrow \infty} E_{\text{SC},\lambda}^{(k+;0+)} - E_{\text{SC},\lambda}^{(0+;0+)} = \frac{\sqrt{\alpha}}{2} k. \quad (5.46)$$

where k must be an even number, because $l = 0$ and both k, l must be both even or both odd. Taking in the above expression the value $k = 1$, we see that the center-of-mass excitations in the large L limit coincide with the HL first excitation Eq.(5.28).

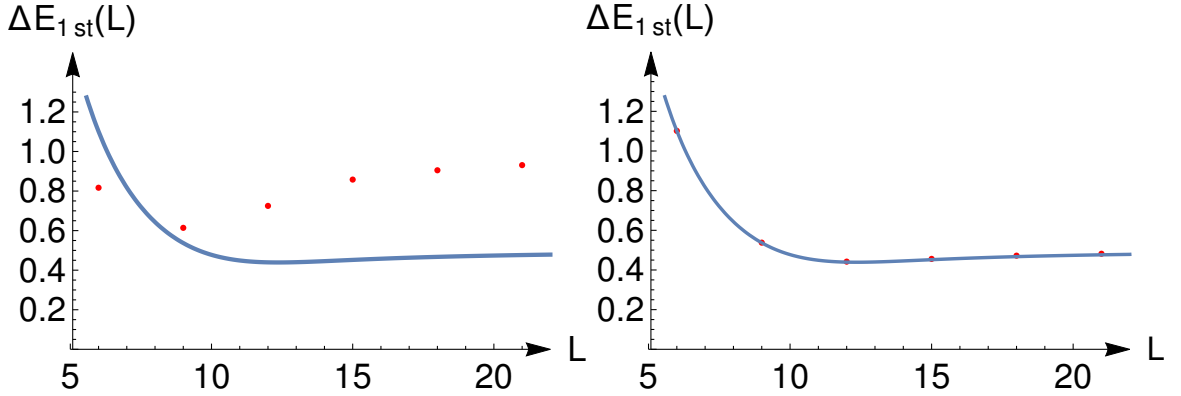


Figure 5.9: Exact first symmetric excitation energy ($k = 2, l = 0$) (red dots) in comparison with the asymptotic expression for the large interaction limit as a function of the bond distance (blue line) for $\lambda = 1$ (left panel) and for $\lambda = 10000$ (right panel). We see that the exact excitation energy approaches to the asymptotic expansion $\frac{\pi^2}{L^2} [a_2^-(\nu) - a_0^+(\nu)]$ as the interaction strength grows.

Finally and for completing the strong interaction limit discussion, in the plot Fig. 5.10 we show how the exact external one-body potential fits the external one-body potential when the interaction strength is large enough, given by the expression Eq.(5.40), for different values of the bond distance. We see also in the SC regime that the exact potential displays a pick, which is reduced the bigger is the strength of the interaction. In the strong interaction limit, the external potential is assumed to follow a power law expansion as a function of the $\sqrt{\lambda}$ [2]. The power law dependence of the external potential in the strong interaction limit can be studied analytically at the linear response regime. For bond distances near homogeneity, the external potential is well determined by means the linear response function of the homogeneous system. The response function was calculated exactly for the homogeneous QR in the previous chapter, and then the external potential is obtained according

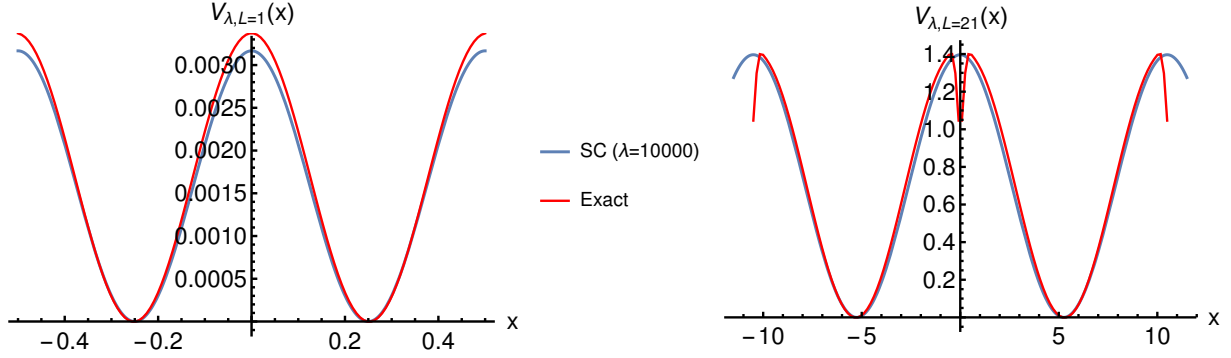


Figure 5.10: Exact external one body potential in comparison with the external potential obtained for the large interaction strength limit Eq.(5.40) for $L = 1$ (left panel) and for $L = 21$ (right panel), and for an interaction strength $\lambda = 10000$. The SC potential reproduces the exact potential except in the midpoint, where the remaining $\frac{\tilde{v}(x)}{\sqrt{\lambda}}$ becomes important and therefore, very big interaction strength are needed to make vanish the remaining term, since it is suppressed very weakly, i.e., by the square root of the interaction strength.

to the expression Eq.(4.47), where the response function in the strong interaction limit is given by Eq.(4.45) for k even, since the density Eq.(5.11) has only even Fourier coefficients. After transforming back to real space the Fourier coefficients according to

$$\delta v(x, \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} \chi^{-1}(k, \omega) \delta n(k, \omega) e^{\frac{2\pi i k x}{L}}, \quad (5.47)$$

then, the leading order and the next to the leading order of the one-body external potential in the linear response regime read

$$v_{\lambda}(x) = \frac{L}{32} \partial_x^2 n(x) - \frac{L^2}{256\pi\sqrt{\lambda}w_0} \partial_x^4 n(x), \quad (\lambda \rightarrow \infty). \quad (5.48)$$

from where we can see the power law expansion as a function of the $\sqrt{\lambda}$.

The next section is devoted to describe with the SCE formalism both the ground-state and for the excited-states.

5.4 Strictly correlated electrons

In this section, we apply the formalism of SCE for the molecular model system. In the formalism of SCE, the co-motion function determines the position of $N - 1$ electrons given the position one reference electron. For a 2-electron system and for a general density on the ring with even symmetry such that $n(x + L/2) = n(x)$, it can be shown that the co-motion function is always a linear function. Using the cumulant function Eq.(A.2) to be the function that counts the number of particles on the ring, i.e., defined from $-L/2$ to the point x with $x \in [-L/2, L/2]$ and with $N(L) = 2$ as

$$N(x) = \int_{-L/2}^x n(s) ds, \quad (5.49)$$

and using the even symmetry properties of the density and the fact that the density always integrates to one particle if we integrate at half of the circle, we get

$$1 = \int_x^{f(x)} n(s) ds = \int_x^{f(x)} n(s \mp L/2) ds = \int_{x \pm L/2}^{f(x) \pm L/2} n(s) ds = \int_{x \pm L/2}^{f(x \pm L/2)} n(s) ds, \quad (5.50)$$

from where we obtain

$$\int_{f(x \pm L/2)}^{f(x) \pm L/2} n(s) ds = 0. \quad (5.51)$$

Taking inverse of the cumulant function we have that $f(x \pm L/2) = f(x) \pm L/2$, and thus the co-motion function must be linear. Therefore, for a system of two particles producing a general even density like $n(x + L/2) = n(x)$ on the ring, the co-motion function reads $f : [-L/2, L/2] \rightarrow [-L/2, L/2]$, given by

$$f(x) = \begin{cases} x + \frac{L}{2} & \text{if } x \in [-\frac{L}{2}, 0[\\ x - \frac{L}{2} & \text{if } x \in [0, \frac{L}{2}]. \end{cases} \quad (5.52)$$

This is a particularity of the two-electron system, since the density always integrates to one particle in half of the ring, no matter the origin of integration we choose.

Following the SCE formalism, the square of the wave function becomes a probability distribution that is zero everywhere except where the energy functional attains its degenerate minimum, i.e., in the set $M = \{s, f(s)\}$ Eq.(2.70). As we explained before, for large but still finite interaction strength, the electrons are expected to perform small oscillations around the energy minimum, and the Hamiltonian can be expanded around the set M , i.e., around $(x_1, x_2) = (s, f(s))$. Performing such an expansion, it leads to the set of equations Eq.(5.35) and Eq.(5.36), and the energy spectrum that SCE formalism predict agrees with the ground-state energy given by Eq.(5.43). We conclude that the SCE formalism describes well the model system in the limit of large interaction strength limit, as it was expected.

5.4.1 Kohn-Sham SCE approach

In this section, we study whether the Hxc kernel given by the SCE formalism can reproduce bond breaking dissociation for our one-dimensional model system. Because the SCE Hxc functional has a spacial non-local dependence on the density by means the co-motion functions, we showed in the last section Sec. 4 it can capture the strong correlation that a strongly interacting system shows. Moreover, in Sec. 5, we showed that despite the conditional probabilities formed by the HL and the SC systems to have a reference electron at $x_1 = -L/2$ are not the same probability distribution, they both correlate the other electron around $x_2 = L/2$. Thus, the question now is if the SCE Hxc functional can as well describe the correlation that bond breaking of molecules shows. As we explained in Sec. 2.7, the question whether the SCE Hxc functional can reproduce ground-state breaking dissociation curves for the H_2 molecule has already been addressed, and it was shown that the leading order in the SCE expansion of the Hxc potential evaluated in the realistic system $\lambda = 1$ dissociates correctly. For our molecular model system, KS equations for the spin compensated system read

$$\left[-\frac{1}{2} \partial_x^2 + v_e(x) + v_{\text{Hxc}}[n](x) \right] \varphi_i(x) = \varepsilon_i \varphi_i(x), \quad (5.53)$$

and according to the KS-SCE formalism, we choose the Hxc potential given by the SCE asymptotic expansion evaluated at $\lambda = 1$. Consider in the first place to take as a Hxc potential the leading term and the next to the leading term, the SCE and the ZPE potentials, which for our model system they

are identically zero. Since in the limit of large bond distances the one-body external potential becomes Eq.(5.23), we can conclude that not only the SCE potential dissociates correctly, in agreement with [33, 51], but also the ZPE potential does. This is a particularity of our periodic system, and the fact that the density fulfills even symmetry, which is the reason that makes vanish both SCE and ZPE potentials. Now introduce the third term in the expansion Eq.(2.77), the term $v_{(3)}$, which by means of the exact relation $v_s(x) = v_\lambda(x) + v_{\text{Hxc},\lambda}(x)$, and knowing that the external potential obtained previously for the strong interaction limit is $v_\lambda(x) = v_s(x)/4$, the Hxc potential reads

$$v_{(3)}(x) = v_s(x) - v_\lambda(x) = \frac{3}{4}v_s(x), \quad (\lambda \rightarrow \infty) \quad (5.54)$$

which added to the expansion for the Hxc potential and inserted in the KS equations gives the wrong prediction. What went wrong is that we have used an asymptotic expansion for the Hxc potential for the large interaction limit and we evaluated it at the realistic system $\lambda = 1$, and the fact that we add more terms of the expansion does not guarantee a better result.

The nature of correlations in both large bond distances limit and large interaction limit can be better understood if we directly analyze the Hxc potential for both cases. The Hxc potential is plotted in Fig. 5.11 for various bond distances and interaction strengths. We see that the one corresponding to the system under dissociation is entirely different than the Hxc potential that describes an SC system. The Hxc potential which corresponds to a system under dissociation tends asymptotically to zero since in the dissociation limit the one-body external potential tends asymptotically to the Eq.(5.23). We also see that the Hxc potential displays the pick in the central region that we were commenting before, which we refer to [64, 65] for a detailed discussion. On the other hand, the Hxc potential of the SC system attains the value Eq.(5.54), showing explicitly the very different nature of these correlated systems. Since the SCE formalism in the ground-state theory reproduces the

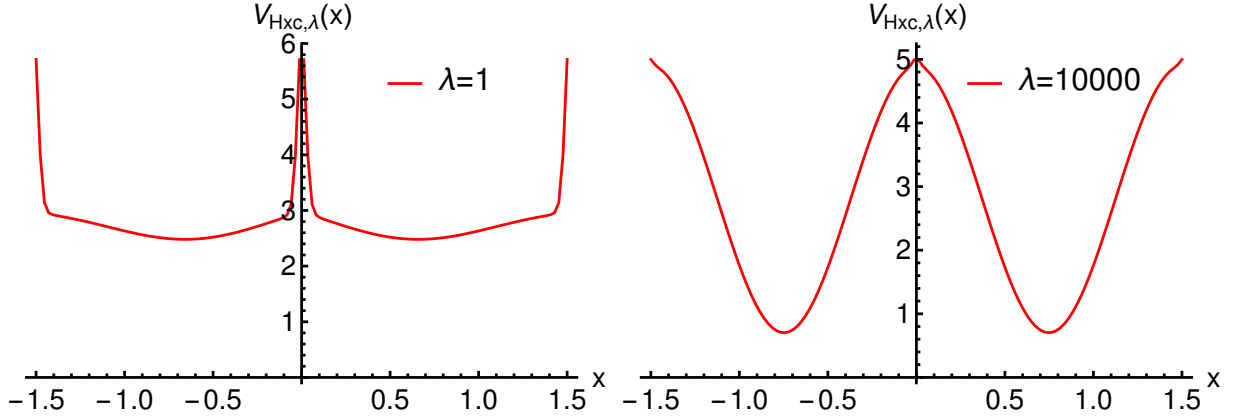


Figure 5.11: The Hxc potential for various bond distances $L = 21$ and interaction strength $\lambda = 1$ (left panel) and $\lambda = 10000$ (right panel). It can be seen that the Hxc potential of a system under dissociation tends asymptotically to zero, displaying the characteristic pick, while the Hxc potential of the SC system tends asymptotically to the Eq.(5.54).

dissociation limit of a dissociating molecule correctly, these trends are a good motivation to study

within the SCE formalism if it can predict the excitation energy curves accurately for large bond distances. The next section is therefore devoted to studying how the SCE Hxc functional performs to calculate excited states of the molecular model.

5.4.2 Calculation of the excitations in the SCE formalism

For the calculation of the excitation energies, we need to solve the eigenvalue equation we introduced in 3.51. Our goal is to check if the leading term of the large interaction strength expansion for the Hxc kernel in the adiabatic approximation can reproduce the excitation energies of the molecular model in the dissociation process. We will compare them with the excitation energies obtained by direct solution of the Schrödinger equation and with the model we elaborated for describing both the system under dissociation and the strongly correlated system.

The ASCE Hxc kernel

We start by writing the leading term of the large interaction strength expansion for the Hxc kernel in the adiabatic approximation, the ASCE kernel 3.57, which for the molecular model reads

$$f^{\text{ASCE}}(x, x') = \int_{-L/2}^x dy \frac{w''(y - f(y))}{n(f(y))} [\theta(y - x') - \theta(f(y) - x')], \quad (5.55)$$

being w the two body interaction and $n(x)$ the electronic ground-state density of the system. For its calculation, we first define the function $\mathcal{P}(x)$ to be

$$\mathcal{P}(x) \equiv \int_{-L/2}^x dy \frac{w''(y - f(y))}{n(f(y))} \quad (5.56)$$

and we construct the kernel for $x > 0, x' > 0$ and $x < 0, x' < 0$ [35].

$$f^{\text{ASCE}}(x, x') = \mathcal{P}(-x)\theta(x - x') + \mathcal{P}(-x')\theta(x' - x) \quad (5.57)$$

and for $x > 0, x' < 0$ and $x < 0, x' > 0$ we have

$$f^{\text{ASCE}}(x, x') = [\mathcal{P}(x) - \mathcal{P}(x') + \mathcal{P}(0)]\theta(f(x) - x'). \quad (5.58)$$

We see from Eq.(5.56) that the integral gets its main contribution when the density is small. In the limit of large bond distances this contribution is bigger in the bond midpoint when the density has the lowest value, and since the overlap of the maxima of the density decreases exponentially, the contribution to the integral will grow exponentially precisely at that point. This exponential growth of the kernel, as was explained in Sec. 3.8 is what is needed to compensate the exponential decreasing of the KS orbitals to produce a finite excitation energy [3, 15]. Since in the limit of the large bond distance the KS orbitals get localized around $\pm L/4$, the main contribution of the Hxc kernel to the eigenvalue equation is around $x, x' = \pm L/4$. For the limit of large bond distance, it can be shown [35] that the ASCE kernel around $x, x' = \pm L/4$ attains the form

$$f^{\text{ASCE}}(x, x') = \frac{1}{2}\mathcal{P}(0) [\theta(x)\theta(x') + \theta(-x)\theta(-x')], \quad (5.59)$$

for $x, x' \neq 0, \pm L/2$, and where $\mathcal{P}(0)$ is the value of $\mathcal{P}(x)$ evaluated in the midpoint, which is given by

$$\mathcal{P}(0) = \omega''(\pm L/2) \left[\frac{L^2}{16(2\pi^3)} \right] \frac{e^{4\sqrt{\nu}}}{\nu^{3/4}}. \quad (5.60)$$

In Fig. 5.12 it is plotted the Hxc kernel for different bond distances. We can see that as the bond distance grows, the kernel develops two "plateaux" in the first and the third quadrant that grows exponentially as a function of the bond distance, while the kernel tends to zero in the second and the fourth quadrant. For showing the exponential growth of the plateaux, we plot in Fig. 5.13 diagonal of the ASCE kernel $f^{\text{ASCE}}(x, x')$ divided by $\mathcal{P}(0)$, for various bond distances. When the bond distance is large enough and for $x, x' \neq 0, \pm L/2$, the function f^{ASCE} attains the value $\mathcal{P}(0)$, whose explicit expression is given by Eq.(5.60).

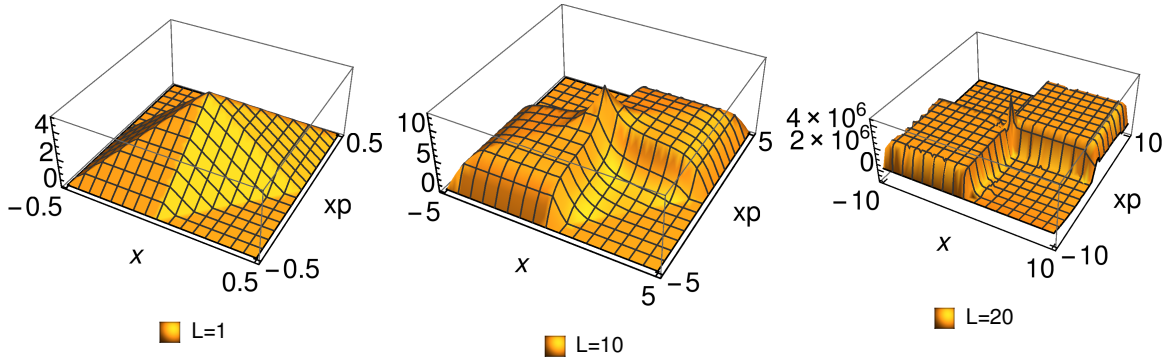


Figure 5.12: Plot of the $f^{\text{ASCE}}(x, x')$ for $L = 1$ (left panel), $L = 10$ (central panel) and $L = 20$ (right panel). For $L = 1$ we recover the homogeneous case while as soon as the bond distance grows, the kernel develops the exponential growing and a function of the bond distance.

As a final remark in the analysis of the Hxc kernel for large bond distances, let us now consider the variation in the Hxc potential when we perform a small change of the density. This variation is given by

$$\delta v_{\text{Hxc}}^\lambda(x) = \int_{-L/2}^x dx' f_{\text{Hxc}}^\lambda(x, x') \delta n(x'). \quad (5.61)$$

In the limit of large interaction strength, the Hxc kernel is given by the ASCE Eq.(5.55) and therefore, the change in the Hxc potential caused by a small change in the density reads

$$\delta v_{\text{Hxc}}^\lambda(x) = \lambda \delta v_{\text{SCE}}(x), \quad (5.62)$$

where

$$\delta v_{\text{SCE}}(x) = \int_{-L/2}^x dx' f^{\text{ASCE}}(x, x') \delta n(x'). \quad (5.63)$$

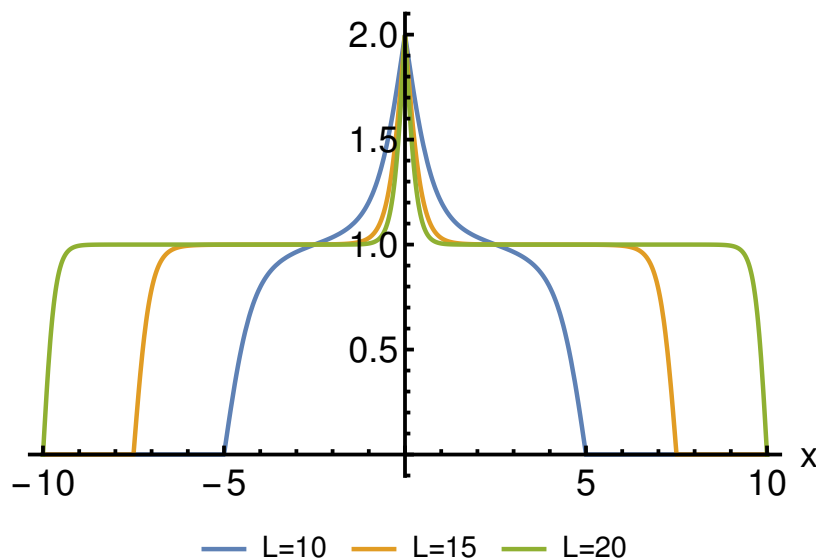


Figure 5.13: Plot of the diagonal $x = x'$ of ASCE kernel normalized with the height of the plateaux $\frac{f^{\text{ASCE}}(x,x)}{\mathcal{P}(0)}$ for $L = 10, 15, 20$. It is manifest how the curve becomes flat in the central region.

Since $v_{\text{SCE}}(x) = 0$ for all densities which fulfill the symmetry property $n(x) = n(x + L/2)$, from the equation Eq.(5.63) it must hold that if the small variations of the density have the same property, $\delta v_{\text{SCE}}(x) = 0$. For a density that does not fulfill the even symmetry, $\delta v_{\text{SCE}}(x)$ is in general different than zero, as it was explicitly shown in the case of the homogeneous QR in Eq.(4.55). Consider now a small change in the Hxc potential caused by a small change in the density, now in the limit of large bond distances. Since the ASCE Hxc kernel becomes a constant Eq.(5.59), we get $\delta v_{\text{Hxc}}^\lambda(x) = 0$ provided that the number of particles is conserved, a result that is independent of the symmetry of the density variations. When the interaction strength is very large, if we apply a general change in the density to the system with no particular symmetry, it is also needed an infinite one-body external potential which can counteract the two-body interaction and therefore generate a finite density change in the system. In the limit of large bond distance, when the interaction becomes negligible, such a potential is not needed anymore since every density change can be done without any cost. We are now ready to calculate the excitation energies provided by the ASCE Hxc kernel

5.4.3 The excitation energies

For studying if the leading order of the expansion for the large interaction strength of the Hxc kernel, the ASCE Hxc kernel, can reproduce the excitation energies of the molecular model in the dissociation regime, it is enough to look at the first excitation. Because there is only one occupied level, which is the lowest KS level, and in the region where the Hxc kernel gives the main contribution, the kernel becomes a constant for the limit of large bond distances. Therefore, in this limit, the only non-zero contribution for the excitation energies will be given when the non-occupied state is the first KS excited state. The other non-occupied excited states give zero contribution because they vanish because of orthogonality. We are then allowed to take the small-matrix approximation (SMA) where the off-diagonal terms of $K_{ia,jb}$ are small contributions. In the (SMA) the eigenvalue equation

is reduced to [7]

$$\Omega_{\pm}^2 = \omega_{ug}^2 + 4\omega_{ug}K_{gu,gu}(\Omega), \quad (5.64)$$

where we have written "g" for the occupied state, standing for "gerade" and "u" for the unoccupied state, standing for "ungerade". Once we have an expression for the ASCE kernel, we can calculate the matrix element $K_{gu,gu}$. Assuming we can take the leading term of the asymptotic expansion for the large bond distances of the matrix elements, we perform the asymptotic expansion inside the integral and therefore we use the leading term expression for the ASCE kernel in the limit of large bond distance, i.e., the expression Eq.(5.59). Performing the integral, we obtain

$$\begin{aligned} \frac{K_{gu,gu}^{\text{ASCE}}}{\lambda} &= \frac{\mathcal{P}(0)}{2} \int_{-L/2}^{L/2} dx \psi_g(x)\psi_u(x) \int_{-L/2}^{L/2} dx' [\theta(x)\theta(x') + \theta(-x)\theta(-x')] \psi_g(x')\psi_u(x') \\ &= \mathcal{P}(0) \int_0^{L/2} dx \psi_g(x)\psi_u(x) \int_0^{L/2} dx' \psi_g(x')\psi_u(x') = \frac{\mathcal{P}(0)}{4}, \end{aligned} \quad (5.65)$$

and using the value for the $\mathcal{P}(0)$, Eq.(5.60), we get

$$\frac{\omega_{ug}K_{gu,gu}}{\lambda} = \frac{\mathcal{P}(0)}{4} (\varepsilon_1^- - \varepsilon_0^+) = \frac{\mathcal{P}(0)}{4} \left[\frac{1}{2} \left(\frac{2\pi}{L} \right)^2 (a_1^- - a_0^+) \right] = \frac{w''(\pm L/2)}{2}. \quad (5.66)$$

Putting all together, the excitation energies given by the f^{ASCE} read

$$\Omega_{\pm}^2 = 2\lambda w''(\pm L/2) \quad (5.67)$$

Particularizing for our interaction strength $w(z) = \cos^2\left(\frac{2\pi z}{L}\right)$ being $z = x_1 - x_2$, the excitation energy reads $\Omega = \frac{2\pi}{L}\sqrt{\lambda\omega_0}$, which is exactly the first excitation $l = 1$ for the relative coordinate we obtained in the limit of large interaction strength (5.44) if we replace the value of the interaction strength Eq.(5.34). We can understand this result: Despite the ASCE kernel in the limit of large bond distances has the right asymptotic behavior for producing finite excitations in the eigenvalue equation Eq.(3.51), it cannot produce single atomic excitations of a dissociating molecule, i.e., the HL atomic excitations Eq.(5.28), since the ASCE kernel by construction involves a strong dependence on the interaction. Thus, it produces the interaction strength dependent excitation energies of a strongly interacting system, which are the zero-point vibrations excitations. Nevertheless, for producing the zero-point vibration excitations, we still have used a Hxc kernel in the adiabatic approximation, obtaining the right harmonic excitations. As was the case in the homogeneous QR, a plausible explanation of this fact is because the characteristic frequency of the vibrations is proportional to the square root of the interaction strength, and therefore no external potential with a finite frequency can produce such vibration, but as in the case of the homogeneous QR, a deeper analysis needs to be done about this issue.

6 Summary & Outlook

In the first work [34], we have considered an exactly solvable interacting system, which consists of two electrons on a ring. Because we can obtain the exact solution of the system for all the range of the interaction, we have got the exact energy spectrum, the density response function and the Hxc kernel of TDDFT. We have studied the behavior of the wave function and the energy spectrum in the limit of large interaction strength, obtaining an expansion in powers of the square root of the interaction strength. We also have developed an asymptotic expansion in the limit of large interaction strength for both the response function and the Hxc kernel in powers of the square root of the interaction strength. We found that the leading order and the next to the leading order of the expansion of the exact Hxc kernel are local in time, i.e., adiabatic, but non-local in space, showing that a local and a semi-local approximation would fail for modeling a Hxc kernel in the strongly interacting regime. We have tested the expansion of the Hxc kernel functional Eq. (3.54) based on the ground-state SCE formalism in the adiabatic approximation, which by construction is a non-local functional in space, and we found that the leading term functional that was derived in [3] predicts the first term of the asymptotic expansion we derived from the exact solution. We obtained the next to the leading order SCE Hxc kernel in the adiabatic approximation, and we also find agreement with the second order term of the asymptotic expansion, which indicates that the SCE kernel in the adiabatic approximation indeed captures the spatial non-local dependence correctly as a function of the density to reproduce the physics of strongly interacting systems. We found for the QR system that the third term in the expansion is still adiabatic, but we showed that the adiabatic character of such term for a general system would not be adiabatic, showing in this way the limitations of the adiabatic approximation.

In this work [35], we have constructed a one-dimensional model system consisting of two interacting electrons on a ring, whose ground-state density can model the main features of a dissociating molecule. We have solved the Schrödinger equation exactly, and we have calculated the ground-state, the first symmetric excited-state wave function, and their energy spectrum as a function of the bond distance and the interaction strength. We also obtained and analyzed the external potential that produces the prescribed model density. For the limit case of large bond distance and any finite interaction strength, the wave functions and their energy spectrum are described by their HL system, while for the limit of large interaction strength and any finite bond distance, the wave function and the energy spectrum are described by the SC model that has been derived in this work and whose description is well captured by the SCE formalism. We found that even though the wave functions of both systems are different, they exhibit similar probability distributions although the SC one over correlates the electron in the very limit of large interaction strength. For the SC limit, we found that the energy spectrum splits in a part that is interaction strength dependent and a part that does not depend on the strength of the interaction, and we found that these last excitations coincide with those HL excitations that represent each electron located in each atom. Nevertheless, one cannot conclude anything general since the model system is a very particular system. We also have tested the KS-SCE formalism with the model system for the calculation of the ground-state dissociation curve of the H_2 model, and we found that the SCE and the ZPE Hxc potentials correctly predict dissociation, but we found that the scheme fails if we add more terms of the large interaction strength expansion of the Hxc potential. For the calculation of the excitation energies of a dissociating H_2 model molecule in TDDFT theory, we used the expansion of the Hxc kernel as a function of the

square root of the interaction strength, based on the SCE formalism in the adiabatic approximation. We took the leading order of the Hxc kernel expansion, the ASCE kernel and we obtained it for large bond distances with the purpose of the determination of the first excitation energy of the dissociating system. What is found is that although the ASCE Hxc kernel is adiabatic, it still produces the harmonic excitations, i.e., the interaction strength dependent excitations of the SC system, but it does not reproduce the single atomic excitations. Therefore, we conclude that the ASCE kernel is not able to describe excitation energies of a dissociating molecule.

Appendix A:

Co-motion functions in one dimension

Given a one dimensional system of N electrons in a density $n(x)$, we can formally construct the $N - 1$ co-motion functions $x, \dots, f_N(x)$, by using that the probability to find an electron between the space points f_i and f_{i+1} is always one. Using the convention that $f_1(x) = x$, we express this condition as follows [49].

$$\int_{f_i(x)}^{f_{i+1}(x)} ds n(s) = 1 \quad (\text{A.1})$$

Let us define the cumulant function as the function that counts the number of electrons N in the region of the space $N \in (-\infty, x)$ as

$$N(x) = \int_{-\infty}^x ds n(s) \quad (\text{A.2})$$

we can then express the equation Eq.(A.1) in terms of the cumulant function as

$$N[f_{i+1}(x)] - N[f_i(x)] = 1 \quad (\text{A.3})$$

Let us now count the number of electrons in the region of space such that $x < f_i(x)$. This number can be expressed in terms of the cumulant function as

$$N[f_i(x)] - N(x) = i - 1 \quad (\text{A.4})$$

and then we can express the co-motion function by taking the inverse of the cumulant function as

$$f_i^+(x) = N^{-1}[N(x) + i - 1], \quad x \leq N^{-1}[N - i + 1] \quad (\text{A.5})$$

where the condition in Eq.(A.5) means that the highest x_0 allowed in the domain $x < f_i(x)$ is that one such that $N(x_0) = N - i + 1$. On the other hand, the number of electrons in the region of space such that $x > f_i(x)$ amounts to

$$N(x) - N[f_i(x)] = N - (i - 1) \quad (\text{A.6})$$

and then, inverting the relation, the co-motion function reads

$$f_i^-(x) = N^{-1}[N(x) + i - 1 - N], \quad x > N^{-1}[N - i + 1] \quad (\text{A.7})$$

We can put all together as

$$f_i(x) = f_i^+(x)\theta(a_{N-i+1} - x) + f_i^-(x)\theta(x - a_{N-i+1}) \quad (\text{A.8})$$

where we defined a_k by means the relation $N(a_k) = k$.

Appendix B:

Functional derivative of the co-motion function in one dimension

In this appendix we take the functional derivative of the co-motion function Eq.(A.8) with respect to the density. First of all, we notice that the functional derivative of the cumulant function Eq.(A.2) with respect to the density gives

$$\frac{\delta N(x)}{\delta n(x')} = \int_{-\infty}^x ds \delta(s - x') = \theta(x - x') \quad (\text{B.1})$$

Taking now the functional derivative with respect to the density to Eq.(A.4), using the above relation Eq.(B.1) and applying chain rule, we get

$$\frac{\delta N [f_i^+(x)]}{\delta n(x')} - \frac{\delta N(x)}{\delta n(x')} = n(f_i^+(x)) \frac{\delta f_i(x)}{\delta n(x')} + \theta(f_i^+(x) - x') - \theta(x - x') = 0 \quad (\text{B.2})$$

from where we can isolate the functional derivative of the co-motion

$$\frac{\delta f_i(x)}{\delta n(x')} = \frac{\theta(x - x') - \theta(f_i^+(x) - x')}{n(f_i^+(x))} \quad (\text{B.3})$$

For the next sections we will need the second functional derivative of the co-motion function with respect to the density. Applying the chain rule to Eq.(B.3) we obtain

$$\frac{\delta^2 f_i(x)}{\delta n(x'') \delta n(x)} = - \left\{ \left[\frac{\theta(x - x') - \theta(f_i^+(x) - x')}{n^2(f_i^+(x))} \frac{dn(s)}{ds} \Big|_{s=f_i^+(x)} \right] + \frac{\delta(f_i^+(x) - x')}{n(f_i^+(x))} \right\} \frac{\delta f_i(x)}{\delta n(x')} \quad (\text{B.4})$$

Appendix C:

The SCE potential in one dimension

In this appendix we perform the functional derivative of the SCE energy functional with respect to the density for the 1D case. For simplicity, we consider the SCE functional for two electrons, such that there is only one co-motion function $f(x)$. In this case, the SCE energy functional reads

$$V_{\text{SCE}}[n] = \frac{1}{2} \int ds n(s) w(|s - f(s)|) \quad (\text{C.1})$$

and the SCE potential is defined as

$$v_{\text{SCE}}(x) = -\frac{\delta V_{\text{SCE}}[n]}{\delta n(x)} \quad (\text{C.2})$$

Taking the first variation of the SCE functional with respect to the density we get

$$-2v_{\text{SCE}}(x) = w(|x - f(x)|) - \int ds n(s) w(|s - f(s)|) \text{Sgn}(s - f(s)) \frac{\delta f[n](s)}{\delta n(x)} \quad (\text{C.3})$$

where $\text{Sgn}(x)$ is the sign function which is 1 for $x > 0$ and -1 for $x < 0$. Now, using the expression for the co-motion function derived in the previous appendix and taking the derivative with respect to x of the SCE potential, we get

$$\begin{aligned} -2v'_{\text{SCE}}(x) &= w'(|x - f(x)|) \text{Sgn}(x - f(x)) [1 - f'(x)] \\ &\quad - \int ds n(s) w'(|s - f(s)|) \text{Sgn}(s - f(s)) \left[\frac{-\delta(s - x) + \delta(f(s) - x)}{n(f(s))} \right] \end{aligned} \quad (\text{C.4})$$

Using the equation for the co-motion functions in its differential form, which reads $f'(s) = \frac{n(s)}{n(f(s))}$, and using the properties of the Dirac delta, we get for the first term of the integral in Eq.(C.4)

$$\int ds \frac{n(s)}{n(f(s))} w'(|s - f(s)|) \text{Sgn}(s - f(s)) \delta(s - x) = f'(x) w'(|x - f(x)|) \text{Sgn}(x - f(x)) \quad (\text{C.5})$$

We can manipulate the second term of the integral in Eq.(2.77) by using the Dirac delta property of composite functions, which states

$$\delta(g(x)) = \sum_i \frac{\delta(x - x_i)}{|g'(x_i)|} \quad (\text{C.6})$$

where x_i are the zeroes of the function $g(x)$. Applying this property to the second term of the integral gives

$$\begin{aligned} \int ds \frac{n(s)}{n(f(s))} w'(|s - f(s)|) \text{Sgn}(s - f(s)) \delta(f(s) - x) &= \\ = \frac{1}{f'(f^{-1}(x))} \frac{n(f^{-1}(x))}{f(x)} w'(|x - f(x)|) \text{Sgn}(f^{-1}(x) - x) &- w'(|x - f(x)|) \text{Sgn}(x - f(x)) \end{aligned} \quad (\text{C.7})$$

where in the second step we used again the co-motion function equation and the cyclic properties of the co-motion functions, which for the case of two particles is $f(x) = f^{-1}(x)$. Using also the fact that $\text{Sgn}(f^{-1}(x) - x) = -\text{Sgn}(x - f^{-1}(x))$, all together combined with the equation Eq.(C.3) amounts for the expression

$$v_{\text{SCE}}(x) = - \int_c^x ds w'(|s - f(s)|) \text{Sgn}(s - f(s)) \quad (\text{C.8})$$

where c is an arbitrary integration constant. The above expression is the one we already announced in the main text Eq.(2.77), but for the dimensional systems.

Appendix D:

The ZPE potential

In this appendix we perform the derivative of the ZPE energy functional. The ZPE energy functional for a system of N electrons in one dimension is given by the expression Eq.(2.78) with Eq.(2.79). In the special case of two particles, there is only one harmonic frequency, and the ZPE energy functional explicitly reads

$$E_{\text{ZPE}}[n] = \frac{1}{4} \int dx n(x) \sqrt{w''(|x - f(x)|) \left[\frac{n(x)}{n(f(x))} + \frac{n(f(x))}{n(x)} \right]} \quad (\text{D.1})$$

Defining

$$\mathcal{B}(x) = w''(|x - f(x)|) \quad (\text{D.2})$$

$$\mathcal{C}(x) = \frac{n(x)}{n(f(x))} + \frac{n(f(x))}{n(x)} \quad (\text{D.3})$$

the ZPE term reads

$$E_{\text{Hxc}}^{\text{ZPE}}[n] = \frac{1}{4} \int dx n(x) \mathcal{B}^{1/2}(x) \mathcal{C}^{1/2}(x) \quad (\text{D.4})$$

The ZPE potential is obtained by taking the functional derivative of the ZPE energy functional with respect to the density

$$v_{\text{ZPE}}[n](x') = \frac{\delta E_{\text{Hxc}}^{\text{ZPE}}[n]}{\delta n(x')} \quad (\text{D.5})$$

Applying the chain rule we have

$$v_{\text{ZPE}}(x') = \frac{1}{4} \int dx \left[\frac{\delta n(x)}{\delta n(x')} \mathcal{B}^{1/2}(x) \mathcal{C}^{1/2}(x) \right. \quad (\text{D.6})$$

$$\left. + \frac{n(x)}{2} \mathcal{B}^{-1/2}(x) \frac{\delta \mathcal{B}(x)}{\delta n(x')} \mathcal{C}^{1/2}(x) + \frac{n(x)}{2} \mathcal{B}^{1/2}(x) \mathcal{C}^{-1/2}(x) \frac{\delta \mathcal{C}(x)}{\delta n(x')} \right] \quad (\text{D.7})$$

and the ZPE potential reads

$$v_{\text{ZPE}}(x') = \frac{1}{4} \int dx \left[\delta(x - x') \mathcal{B}^{1/2}(x) \mathcal{C}^{1/2}(x) \right. \quad (\text{D.8})$$

$$\left. + \frac{n(x)}{2} \mathcal{B}^{-1/2}(x) \dot{\mathcal{B}}(x, x') \delta n(x') \mathcal{C}^{1/2}(x) + \frac{n(x)}{2} \mathcal{B}^{1/2}(x) \mathcal{C}^{-1/2}(x) \dot{\mathcal{C}}(x, x') \right] \quad (\text{D.9})$$

Working out each of the terms we get

$$\dot{\mathcal{B}}(x, x') \equiv \frac{\delta \mathcal{B}(x)}{\delta n(x')} = -\text{Sgn}(x - f(x)) w'''(|x - f(x)|) \frac{\delta f(x)}{\delta n(x')} \quad (\text{D.10})$$

$$\dot{\mathcal{C}}(x, x') \equiv \frac{\delta \mathcal{C}(x)}{\delta n(x')} = \left[1 - \frac{1}{\left(\frac{df(x)}{dx} \right)^2} \right] \frac{d}{dx} \left(\frac{\delta f(x)}{\delta n(x')} \right) \quad (\text{D.11})$$

Appendix E:

Functional derivative of the SCE potential

In this appendix we give the expression for the ASCE Hxc kernel, which is defined to as the functional derivative of the SCE potential with respect to the density as

$$f^{\text{ASCE}}[n](x', x'') = \frac{\delta v_{\text{SCE}}[n](x')}{\delta n(x'')} \quad (\text{E.1})$$

Consider a composite function of the co-motion functions $g(f_i(s))$, where g is a general function of the co-motion function. Because of the general shape of the co-motion function for one dimensional systems Eq.(A.8), this composite function can be written as

$$g(f(x)) = g(f_i^+(x))\theta(a-x) + g(f_i^-(x))\theta(x-a) \quad (\text{E.2})$$

where for simplicity we call $a_{N-i+1} \equiv a$ since it is always the same. We want now to take variations of this general function with respect to the density. Applying the chain rule, we get

$$\begin{aligned} \frac{\delta g(f_i(x))}{\delta n(x')} &= \frac{\partial g(f_i^+)}{\partial f_i^+} \frac{\delta f_i^+(x)}{\delta n(x')} + \frac{\partial g(f_i^-)}{\partial f_i^-} \frac{\delta f_i^-(x)}{\delta n(x')} - [g(f_i^+ x) - g(f_i^- x)]\delta(x-a) \frac{\theta(a-x')}{n(a)} \\ &= \frac{\partial g(f_i)}{\partial f_i} \frac{\theta(x-x') - \theta(f_i^+(x) - x')}{n(f_i^+(x))} - [g(f^+(a) - g(f^-(a))]\delta(x-a) \frac{\theta(a-x')}{n(a)} \end{aligned} \quad (\text{E.3})$$

We are now interested in taking as a special case of g the SCE potential Eq.(C.8). Then, using the general rule Eq.(E.3) we obtain

$$\begin{aligned} f^{\text{ASCE}}(x, x') &= - \int_c^x ds w''(|s-f(s)|) \left[\frac{\theta(s-x') + \theta(f(s)-x')}{n(f(s))} \right] \\ &\quad - \int_c^x ds [w'(|s-f^+(s)|)\text{Sgn}(s-f^+(s)) - w'(|s-f^-(s)|)\text{Sgn}(s-f^-(s))] \\ &\quad \times \frac{\theta(a-x')\delta(s-a)}{n(a)} \\ &= - \int_c^x ds w''(|s-f(s)|) \left[\frac{\theta(s-x') + \theta(f(s)-x')}{n(f(s))} \right] \\ &\quad + \int_c^x ds [w'(|s-f(s)|) + w'(|s-f(s)|)] \frac{\theta(a-x')\delta(s-a)}{n(a)} \end{aligned} \quad (\text{E.4})$$

where in the second step we have reorganized the + and - branches of the co-motion function, and where c is an arbitrary integration constant

Appendix F:

Functional derivative of the ZPE potential

In this appendix we give the expression for the AZPE Hxc kernel, which is defined to as the functional derivative of the ZPE potential with respect to the density as

$$f^{\text{AZPE}}[n](x', x'') = \frac{\delta v_{\text{ZPE}}[n](x')}{\delta n(x'')} \quad (\text{F.1})$$

$$\begin{aligned} f^{\text{ZPE}}(x', x'') &= \frac{1}{4} \int dx \left\{ \frac{\delta(x-x')}{2} \left[\mathcal{B}^{-1/2}(x) \dot{\mathcal{B}}(x, x') \mathcal{C}^{-1/2}(x) + \mathcal{B}^{1/2}(x) \dot{\mathcal{C}}(x, x') \mathcal{C}^{-1/2}(x) \right] \right. \\ &+ \frac{1}{2} \left[\delta(x-x'') \mathcal{B}^{-1/2}(x) \mathcal{C}^{1/2}(x) \dot{\mathcal{B}}(x, x') - \frac{1}{2} n(x) \mathcal{B}^{-3/2}(x) \dot{\mathcal{B}}(x, x'') \mathcal{C}^{1/2}(x) \dot{\mathcal{B}}(x, x') \right. \\ &\quad \left. + \frac{1}{2} n(x) \mathcal{B}^{-1/2}(x) \dot{\mathcal{C}}(x, x'') \mathcal{C}^{-1/2}(x) \dot{\mathcal{B}}(x, x') + n(x) \mathcal{B}^{-1/2}(x) \ddot{\mathcal{B}}(x, x', x'') \mathcal{C}^{1/2}(x) \right] \\ &+ \frac{1}{2} \left[\delta(x-x'') \mathcal{B}^{1/2}(x) \mathcal{C}^{-1/2}(x) \dot{\mathcal{C}}(x, x') + \frac{1}{2} n(x) \mathcal{B}^{-1/2}(x) \dot{\mathcal{B}}(x, x'') \mathcal{C}^{-1/2}(x) \dot{\mathcal{C}}(x, x'') \right. \\ &\quad \left. - \frac{1}{2} n(x) \mathcal{B}^{-1/2}(x) \dot{\mathcal{C}}(x, x'') \mathcal{C}^{-3/2}(x) \dot{\mathcal{C}}(x, x') + n(x) \mathcal{B}^{1/2}(x) \ddot{\mathcal{C}}(x, x', x'') \mathcal{C}^{-1/2}(x) \right] \left. \right\} \quad (\text{F.2}) \end{aligned}$$

having defined the quantities

$$\begin{aligned} \ddot{\mathcal{B}}(x, x', x'') &\equiv \frac{\delta \dot{\mathcal{B}}(x, x')}{\delta n(x'')} \\ &= w''''(|x-f(x)|) \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} - w''''(|x-f(x)|) \text{Sgn}(x-f(x)) \frac{\delta^2 f(x)}{\delta n(x'') \delta n(x')} \quad (\text{F.3}) \end{aligned}$$

$$\begin{aligned} \ddot{\mathcal{C}}(x, x', x'') &\equiv \frac{\delta \dot{\mathcal{C}}(x, x')}{\delta n(x'')} \\ &= \frac{2}{f'(x)^3} \frac{d}{dx} \left[\frac{\delta f(x)}{\delta n(x')} \right] + \left[1 - \frac{1}{\left(\frac{df(x)}{dx} \right)^2} \right] \frac{d}{dx} \left[\frac{\delta^2 f(x)}{\delta n(x'') \delta n(x')} \right] \quad (\text{F.4}) \end{aligned}$$

Appendix G: Expansion of the excitation amplitudes

In this appendix we show how the integral Eq.(4.40) can be approximated by the expression Eq.(4.42). Consider the expression Eq.(4.42)

$$\mathcal{J}_{kl}^{n_1, n_2}(q) = \frac{1}{\sqrt{2}q^{1/4}} \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du f_k \left(\frac{u}{\sqrt{2}q^{1/4}} \right) \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \quad (\text{G.1})$$

The integral $\mathcal{J}_{kl}^{n_1 n_2}$ is convergent

$$\begin{aligned} |\mathcal{J}_{kl}^{n_1 n_2}(q)| &\leq \frac{1}{\sqrt{2}q^{1/4}} \int_{-\sqrt{2}q^{-1/4}}^{\sqrt{2}q^{1/4}} du \frac{|\mathcal{D}_{2n_1}(u)| |\mathcal{D}_{2n_2+l}(u)|}{\left(1 - \frac{u^2}{2q^{1/2}}\right)^{1/2}} \\ &\leq \frac{c_{2n_1} c_{2n_2}}{\sqrt{2\pi}q^{1/4}} \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} \frac{du}{\left(1 - \frac{u^2}{2q^{1/2}}\right)^{1/2}} = c_{2n_1} c_{2n_2+l} \sqrt{\pi} < \infty \end{aligned} \quad (\text{G.2})$$

with $c_n =$ and where we have used Cramér's inequality for Hermite functions, ie $|\psi(x)| \leq c \pi^{-1/4}$

We can expand the function the function f_k in its Taylor expansion, which reads

$$f_k(x) = \frac{e^{-ik \arccos(x)}}{\sqrt{1-x^2}} = \sum_{r=0}^{\infty} a_r(k) x^r \quad (\text{G.3})$$

and inserted the above expansion in $\mathcal{J}_{kl}^{n_1 n_2}$ we have

$$\begin{aligned} |\mathcal{J}_{kl}^{n_1 n_2}(q)| &\leq \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du \frac{e^{ik \arccos\left(\frac{u}{\sqrt{2}q^{1/4}}\right)}}{\left(1 - \frac{u^2}{2q^{1/2}}\right)^{1/2}} \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \\ &= \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du \left(\sum_{r=0}^{\infty} a_r(k) \frac{u^r}{q^{r/4}} \right) \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \end{aligned} \quad (\text{G.4})$$

and because of the radius of convergence of the series is $R = \left| \frac{u}{\sqrt{2}q^{1/2}} \right| < 1$, the series represent the function in all the interval.

We now show that we can interchange the sum and the integral. Because of the inequality Eq.(G.2), we can write

$$|\mathcal{J}_{kl}^{n_1 n_2}(q)| \leq \frac{1}{\sqrt{2}q^{1/4}} \int_{-\sqrt{2}\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du \left(\sum_{r=0}^{\infty} a_r \frac{u^{2r}}{(\sqrt{2}q^{1/4})^r} \right) |\mathcal{D}_{2n_1}(u)| |\mathcal{D}_{2n_2+l}(u)| < \infty \quad (\text{G.5})$$

and then, according to Fubini's Theorem ¹ we are allowed to write,

$$|\mathcal{J}_{kl}^{n_1 n_2}(q)| = \frac{1}{\sqrt{2}q^{1/4}} \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du \left(\sum_{r=0}^{\infty} a_r(k) \frac{u^r}{q^{r/4}} \right) \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) = \sum_{r=0}^{\infty} \frac{a_r(k)}{(\sqrt{2}q^{1/4})^{r+1}} I_{n_1, n_2, r}^l \quad (\text{G.6})$$

where we defined the coefficients

$$I_{n_1, n_2, r}^l = \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \quad (\text{G.7})$$

For showing the extension of the integral limits, it is enough to analyze $I_{n, m, r}^0$ for a particular value of n and m . Using the definition of the \mathcal{D}_n functions and the Hermite polynomials $H_n(x) = \sum_{l=0}^{\lfloor \frac{n}{2} \rfloor} b_l x^l$ with $b_l \equiv n! \frac{(-1)^l (2^{n-2l})}{l!(n-2l)!}$, the integral writes

$$I_{nm, r}^0 = 2^{(n+m)/2} \sum_{i=0}^{\lfloor \frac{n}{2} \rfloor} \sum_{j=0}^{\lfloor \frac{m}{2} \rfloor} b_i b_j \int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du e^{-u^2} u^{r+i+j}. \quad (\text{G.8})$$

Let us consider the integral in Eq.(G.8), which is the incomplete gamma function that we write as

$$\int_{-\sqrt{2}q^{1/4}}^{\sqrt{2}q^{1/4}} du e^{-u^2} u^{r+i+j} = \int_{-\infty}^{\infty} du e^{-u^2} u^{r+i+j} - \frac{[1 + (-1)^{i+j+r}]}{2} \Gamma\left(\frac{i+j+r+1}{2}, 2\sqrt{q}\right) \quad (\text{G.9})$$

In the large q limit, the incomplete gamma function has the following expansion

$$\Gamma\left(\frac{\alpha+1}{2}, 2\sqrt{q}\right) \underset{(q \rightarrow \infty)}{=} q^{\alpha/4} e^{-2\sqrt{q}} \sum_{l=0}^{\infty} c_l(\alpha) q^{-(2l+1)/4} \quad (\text{G.10})$$

where $c_l(\alpha)$ are some coefficients of the expansion and we defined $\alpha = i + j + r$. We are therefore allowed to extend the integral limits to infinite making an exponentially small error

$$I_{n_1, n_2, r}^l \underset{(q \rightarrow \infty)}{=} \int_{-\infty}^{\infty} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) \quad (\text{G.11})$$

¹If $\int \sum_n |f_n| < \infty$ or $\sum_n \int |f_n| < \infty$, then $\int \sum_n f_n = \sum_n \int f_n$

The explicit expression for $I_{n_1 n_2, r}^l$ is given by

$$I_{n_1 n_2, r}^l = \int_{-\infty}^{\infty} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u)$$

$$= \begin{cases} 0 & \text{If } r+l \text{ odd} \\ \frac{r!}{2^r} \sqrt{\pi} 2^{n_1+n_2+\frac{l}{2}} \sum_{p=\max(0, -s)}^{\min(2n_1, 2n_2+l)} \binom{2n_1}{p} \binom{2n_2+l}{p} \frac{p!}{2^{p(s+p)!}} & \text{otherwise} \end{cases}$$

where we defined $s = r/2 - n_1 - n_2 - l/2$ [66].

Appendix H:

ASCE and AZPE Hxc kernel for the homogeneous QR

In this appendix we apply the general expressions we derived for both the ASCE Eq.(E.4) and the AZPE Eq.(F.2) Hxc kernels for the case of the homogeneous QR, whose density is $n = \frac{2}{L}$, the co-motion function is given by Eq.(4.57) and the two body interaction is $V_0 \cos^2 \left[\frac{\pi}{L} z \right]$ with $z = x_1 - x_2$. We start with the general expression for the ASCE Eq.(E.4), which for the case of the homogeneous QR, it reduces to

$$f^{\text{ASCE}}(x, x') = \frac{\pi^2 V_0}{L} \int_0^x ds [\theta(s - x') - \theta(s - x' + L/2)\theta(s + L/2) - \theta(s - x' - L/2)\theta(s - L/2)] \quad (\text{H.1})$$

For its integration, we first compute the cross derivatives and then we integrate the result back. The cross derivatives read

$$\frac{\partial^2}{\partial x \partial x'} f^{\text{ASCE}}(x, x') = \frac{\pi^2 V_0}{L} [-\delta(x - x') + \delta(x - x' + L/2) + \delta(x - x' - L/2)] \quad (\text{H.2})$$

and making use of the relation $\frac{d^2|x|}{dx^2} = 2\delta(x)$, we integrate back Eq.(H.2) obtaining

$$f^{\text{ASCE}}(x, x') = \frac{\pi^2 V_0}{2L} (|x - x'| - |x - x' + L/2| - |x - x' - L/2|) + C \quad (\text{H.3})$$

where C is an arbitrary constant.

For the calculation of the AZPE kernel, we obtain for the quantities previously defined Eq.(D.2), Eq.(D.3), Eq.(D.10), Eq.(D.10), Eq.(F.3) and Eq.(F.4) for the case of the homogeneous QR the following values

$$\mathcal{B}(x) = \frac{2\pi^2}{L^2} V_0 \quad (\text{H.4})$$

$$\mathcal{C}(x) = 2 \quad (\text{H.5})$$

$$\ddot{\mathcal{B}}(x) = -\frac{8\pi^4}{L^4} \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} \quad (\text{H.6})$$

$$\ddot{\mathcal{C}}(x) = 2 \frac{d}{dx} \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} \quad (\text{H.7})$$

and $\dot{\mathcal{B}}(x) = \dot{\mathcal{C}}(x) = 0$. The expression from the general expression Eq.(F.2) therefore reduces to

$$f^{\text{AZPE}}(x', x'') = \frac{\pi\sqrt{V_0}}{2L^2} \int dx \frac{d}{dx} \left[\frac{\delta f(x)}{\delta n(x'')} \right] \frac{d}{dx} \left[\frac{\delta f(x)}{\delta n(x')} \right] - \frac{2\pi^3\sqrt{V_0}}{L^4} \int dx \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} \quad (\text{H.8})$$

and now we proceed to calculate the remaining integrals. Computing the first one, we obtain

$$\begin{aligned} \int dx \frac{d}{dx} \left[\frac{\delta f(x)}{\delta n(x'')} \right] \frac{d}{dx} \left[\frac{\delta f(x)}{\delta n(x')} \right] &= \frac{L^2}{4} \int dx [\delta(x-x'') - \delta(f(x)-x'')] [\delta(x-x') - \delta(f(x)-x')] \\ &= \frac{L^2}{4} [2\delta(x''-x') - \delta(f(x'')-x') - \delta(f(x')-x'')] \\ &= \frac{L^2}{4} [\delta(x''-x') - \delta(x''-x'-L/2) - \delta(x''-x'+L/2)] \end{aligned} \quad (\text{H.9})$$

where in the last step we made use of the explicit expression of the co-motion function. The second integral reads

$$\int dx \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} = \frac{L^2}{4} \int [\theta(x-x'') - \theta(f(x)-x'')] [\theta(x-x') - \theta(f(x)-x')] \quad (\text{H.10})$$

We now use the same way we used to obtain the ASCE kernel, ie, to obtain the cross derivatives and integrate back

$$\begin{aligned} \frac{\partial^2}{\partial x \partial x'} \left[\int dx \frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} \right] &= \frac{L^2}{4} \int dx [\delta(x-x'') - \delta(f(x)-x'')] [\delta(x-x') - \delta(f(x)-x')] \\ &= \frac{L^2}{4} [\delta(x''-x') - \delta(x''-x'-L/2) - \delta(x''-x'+L/2)] \end{aligned} \quad (\text{H.11})$$

where in the last step we have used the same argument that in the first integral. Making use again of the relation $\frac{d^2|x|}{dx^2} = 2\delta(x)$, we integrate back the cross derivatives to obtain

$$\frac{\delta f(x)}{\delta n(x'')} \frac{\delta f(x)}{\delta n(x')} = \frac{L^2}{4} [-|x'-x''| + |x''-x'+L/2| + |x''-x'-L/2|] \quad (\text{H.12})$$

Putting all together, we obtain for the AZPE Hxc kernel

$$\begin{aligned} f^{\text{AZPE}}(x', x'') &= -\frac{\pi^3 \sqrt{V_0}}{2L^2} [-|x'-x''| + |x''-x'+L/2| + |x''-x'-L/2|] \\ &\quad + \frac{\pi \sqrt{V_0}}{4} [\delta(x''-x') - \delta(x''-x'-L/2) - \delta(x''-x'+L/2)] + C \end{aligned} \quad (\text{H.13})$$

where C is an arbitrary constant.

References

- [1] M Seidl. Strong-interaction limit of density-functional theory. *Physical Review A*, 60:4387, 1999.
- [2] Paola Gori-Giorgi, Giovanni Vignale, and Michael Seidl. Electronic zero-point oscillations in the strong-interaction limit of density functional theory. *Journal of Chemical Theory and Computation*, 5(4):743–753, 2009.
- [3] G Lani, S Di Marino, A Gerolin, R van Leeuwen, and P Gori-Giorgi. The adiabatic strictly-correlated-electrons functional: kernel and exact properties. *Phys. Chem. Chem. Phys.*, 18:21092–21101, 2016.
- [4] E K U Gross, J F Dobson, and M Petersilka. *Density functional theory of time-dependent phenomena*, pages 81–172. Springer Berlin Heidelberg, Berlin, Heidelberg, 1996.
- [5] K Burke, J Werschnik, and E K U Gross. Time-dependent density functional theory: Past, present, and future. *The Journal of Chemical Physics*, 123(6):62206, 2005.
- [6] R van Leeuwen, Theoretical Chemistry, Materials Science Centre, and Rijksuniversiteit Groningen. Key concepts in time-dependent density-functional theory. *International Journal of Modern Physics B*, 15(14):1969–2023, 2001.
- [7] C A Ullrich. *Time-Dependent Density-Functional Theory*. Oxford University Press, Oxford, 2012.
- [8] M A L Marques, N T Maitra, F M S Nogueira, E K U Gross, and A Rubio, editors. *Fundamentals of Time-Dependent Density Functional Theory*, volume 837 of *Lecture Notes in Physics*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012.
- [9] M Ruggenthaler, M Penz, and R van Leeuwen. Existence, uniqueness, and construction of the density-potential mapping in time-dependent density-functional theory. *Journal of Physics: Condensed Matter*, 27(20):203202, 2015.
- [10] N T Maitra. Perspective: Fundamental aspects of time-dependent density functional theory. *Journal of Chemical Physics*, 144:220901, 2016.
- [11] T Stein, L Kronik, and R Baer. Reliable Prediction of Charge Transfer Excitations in Molecular Complexes Using Time-Dependent Density Functional Theory. *Journal of the American Chemical Society*, 131(8):2818–2820, nov 2009.
- [12] O Gritsenko and E J Baerends. Asymptotic correction of the exchange-correlation kernel of time-dependent density functional theory for long-range charge-transfer excitations. *Journal of Chemical Physics*, 121(2):655–660, 2004.
- [13] Neepa T. Maitra. Undoing static correlation: Long-range charge transfer in time-dependent density-functional theory. *Journal of Chemical Physics*, 122(23):234104, 2005.
- [14] J Autschbach. Charge-Transfer Excitations and Time-Dependent Density Functional Theory: Problems and Some Proposed Solutions. *Chem. Phys. Chem.*, 10(11):1757–1760, 2009.

- [15] O. V. Gritsenko, S. J A van Gisbergen, A. Görling, and E. J. Baerends. Excitation energies of dissociating H₂: A problematic case for the adiabatic approximation of time-dependent density functional theory. *The Journal of Chemical Physics*, 113(19):8478–8489, 2000.
- [16] W Hieringer and A Görling. Failure of time-dependent density functional methods for excitations in spatially separated systems. *Chemical Physics Letters*, 419(4-6):557–562, 2006.
- [17] K J H Giesbertz and E J Baerends. Failure of time-dependent density functional theory for excited state surfaces in case of homolytic bond dissociation. *Chemical Physics Letters*, 461(4-6):338–342, 2008.
- [18] A Dreuw, J L Weisman, and M Head-Gordon. Long-range charge-transfer excited states in time-dependent density functional theory require non-local exchange. *The Journal of Chemical Physics*, 119(6):2943–2946, 2003.
- [19] D Hofmann, T Körzdörfer, and S Kümmel. Kohn-Sham Self-Interaction Correction in Real Time. *Physical Review Letters*, 108(14):146401, 2012.
- [20] M Dierksen and S Grimme. The Vibronic Structure of Electronic Absorption Spectra of Large Molecules: A Time-Dependent Density Functional Study on the Influence of “Exact” Hartree-Fock Exchange. *The Journal of Physical Chemistry A*, 108(46):10225–10237, 2004.
- [21] M J G Peach, P Benfield, T Helgaker, and D J Tozer. Excitation energies in density functional theory: An evaluation and a diagnostic test. *The Journal of Chemical Physics*, 128(4):44118, 2008.
- [22] Andreas Görling. Exact exchange-correlation kernel for dynamic response properties and excitation energies in density-functional theory. *Physical Review A*, 57(5):3433–3436, 1998.
- [23] I V Tokatly and O Pankratov. Many-Body Diagrammatic Expansion in a Kohn-Sham Basis: Implications for Time-Dependent Density Functional Theory of Excited States. *Physical Review Letters*, 86(10):2078–2081, nov 2001.
- [24] U von Barth, N E Dahlen, R van Leeuwen, and G Stefanucci. Conserving approximations in time-dependent density functional theory. *Physical Review B*, 72(23):235109, 2005.
- [25] M Fuchs, Y.-M. Niquet, X Gonze, and K Burke. Describing static correlation in bond dissociation by Kohn–Sham density functional theory. *The Journal of Chemical Physics*, 122(9):94116, nov 2005.
- [26] M Hellgren and U von Barth. Exact-exchange kernel of time-dependent density functional theory: Frequency dependence and photoabsorption spectra of atoms. *The Journal of Chemical Physics*, 131(4):44110, 2009.
- [27] Maria Hellgren and Ulf Von Barth. Correlation energy functional and potential from time-dependent exact-exchange theory. *The Journal of Chemical Physics*, 132(4):44101, 2010.
- [28] A Heßelmann and A Görling. Correct Description of the Bond Dissociation Limit without Breaking Spin Symmetry by a Random-Phase-Approximation Correlation Functional. *Physical Review Letters*, 106(9):93001, 2011.
- [29] Andreas Heßelmann, Andreas Grling, and A Görling. Efficient exact-exchange time-dependent density-functional theory methods and their relation to time-dependent Hartree–Fock. *The Journal of Chemical Physics*, 134(3):34120, 2011.
- [30] Jefferson E. Bates and Filipp Furche. Random phase approximation renormalized many-body perturbation theory. *The Journal of Chemical Physics*, 139(17):171103, 2013.

- [31] J Erhard, P Bleiziffer, and A Görling. Power Series Approximation for the Correlation Kernel Leading to Kohn-Sham Methods Combining Accuracy, Computational Efficiency, and General Applicability. *Physical Review Letters*, 117(14):143002, 2016.
- [32] F Malet, A Mirtschink, K J H Giesbertz, L O Wagner, and P Gori-Giorgi. Exchange–correlation functionals from the strong interaction limit of DFT: applications to model chemical systems. *Physical Chemistry Chemical Physics*, 16(28):14551, 2014.
- [33] Stefan Vuckovic, Lucas O. Wagner, André Mirtschink, and Paola Gori-Giorgi. Hydrogen Molecule Dissociation Curve with Functionals Based on the Strictly Correlated Regime. *Journal of Chemical Theory and Computation*, 11(7):3153–3162, 2015.
- [34] Luis Cort, Daniel Karlsson, Giovanna Lani, and Robert van Leeuwen. Time-dependent density-functional theory for strongly interacting electrons. *Physical Review A*, 95(4):042505, apr 2017.
- [35] Luis Cort, Soeren Ersbak Bang Nielsen, and Robert van Leeuwen. Strictly-correlated-electron approach to excitation energies of dissociating molecules. *Physical Review A*, 99(2):022501, feb 2019.
- [36] David A Mazziotti. Structure of Fermionic Density Matrices: Complete N-Representability Conditions. *Physical Review Letters*, 108(26):263002, jun 2012.
- [37] E R Davidson. *Reduced Density Matrices in Quantum Chemistry*. Academic Press, 1976.
- [38] G Stefanucci and R van Leeuwen. *Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction*. Cambridge University Press, Cambridge, 2013.
- [39] P Hohenberg and W Kohn. Inhomogeneous electron gas. *Physical Review*, 155(1962), 1964.
- [40] R.M. Dreizler and E. K.U. Gross. *Density Functional Theory*. Springer-Verlag, Berlin, 1990.
- [41] Eberhard Engel and Reiner M. Dreizler. *DFT An Advanced Course*. Springer-Verlag, Berlin, Heidelberg, 2010.
- [42] C.-O. Almbladh and U. von Barth. Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues. *Physical Review B*, 31(6):3231–3244, mar 1985.
- [43] W. J. Carr and A. A. Maradudin. Ground-state energy of a high-density electron gas. *Physical Review*, 133(2 A), 1964.
- [44] W. J. Carr. Energy, specific heat, and magnetic properties of the low-density electron gas. *Physical Review*, 122(5):1437–1446, 1961.
- [45] W. J. Carr. Ground-state energy of metallic hydrogen. I. *Physical Review*, 128(1):120–125, 1962.
- [46] John P. Perdew and Stefan Kurth. Density Functionals for Non-relativistic Coulomb Systems in the New Century. In Carlos Fiolhais Marques, Fernando Nogueira, and Miguel A. L., editors, *A Primer in Density Functional Theory*, pages 1–55. 2003.
- [47] Andreas Görling and Mel Levy. Exact Kohn-Sham scheme based on perturbation theory. *Physical Review A*, 50(1):196–204, jul 1994.
- [48] Codina Cotar, Gero Friesecke, and Claudia Klüppelberg. Smoothing of Transport Plans with Fixed Marginals and Rigorous Semiclassical Limit of the Hohenberg–Kohn Functional. *Archive for Rational Mechanics and Analysis*, 228(3):891–922, 2018.

- [49] Michael Seidl, Paola Gori-Giorgi, and Andreas Savin. Strictly correlated electrons in density-functional theory: A general formulation with applications to spherical densities. *Physical Review A*, 75(4):042511, apr 2007.
- [50] Huajie Chen, Gero Friesecke, and Christian B Mendl. Numerical Methods for a Kohn-Sham Density Functional Model Based on Optimal Transport. *Journal of Chemical Theory and Computation*, 10(10):4360–4368, oct 2014.
- [51] F Malet and P Gori-Giorgi. Strong Correlation in Kohn-Sham Density Functional Theory. *Physical Review Letters*, 109(24):246402, 2012.
- [52] Robert van Leeuwen. Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory. *Physical Review Letters*, 82(19):3863–3866, may 1999.
- [53] M Ruggenthaler, K J H Giesbertz, M Penz, and R van Leeuwen. Density-potential mappings in quantum dynamics. *Physical Review A*, 85(5):52504, 2012.
- [54] Kai Luo, Johanna I. Fuks, Ernesto D. Sandoval, Peter Elliott, and Neepa T. Maitra. Kinetic and interaction components of the exact time-dependent correlation potential. *Journal of Chemical Physics*, 140(18), 2014.
- [55] M Hellgren and E K U Gross. Discontinuities of the exchange-correlation kernel and charge-transfer excitations in time-dependent density-functional theory. *Phys. Rev. A*, 85:22514, 2012.
- [56] Neepa T. Maitra and Kieron Burke. Demonstration of initial-state dependence in time-dependent density-functional theory. *Physical Review A - Atomic, Molecular, and Optical Physics*, 63(4):1–7, 2001.
- [57] Neepa T. Maitra, Kieron Burke, and Chris Woodward. Memory in Time-Dependent Density Functional Theory. *Physical Review Letters*, 89(2):1–4, 2002.
- [58] G Vignale. Sum rule for the linear density response of a driven electronic system. *Physics Letters A*, 209(3-4):206–210, 1995.
- [59] *NIST Digital Library of Mathematical Functions*. <http://dlmf.nist.gov/28.8>, Release 1.0.14 of 2016-12-21. F. W. J. Olver, A. B. Olde Daalhuis, D. W. Lozier, B. I. Schneider, R. F. Boisvert, C. W. Clark, B. R. Miller and B. V. Saunders, eds.
- [60] Robert Sips. Représentation asymptotique des fonctions de Mathieu et des fonctions sphéroïdales. II. *Transactions of the American Mathematical Society*, 90(2):340–340, feb 1959.
- [61] D Frenkel and R Portugal. Algebraic methods to compute Mathieu functions. *Journal of Physics A: Mathematical and General*, 34:3541–3551, 2001.
- [62] S. E.B. Nielsen, M. Ruggenthaler, and R. Van Leeuwen. Many-body quantum dynamics from the density. *Epl*, 101(3), 2013.
- [63] Soeren E B Nielsen, Michael Ruggenthaler, and Robert van Leeuwen. Numerical construction of the density-potential mapping. *The European Physical Journal B*, 91(10):235, oct 2018.
- [64] Oleg V Gritsenko and Evert Jan Baerends. Effect of molecular dissociation on the exchange-correlation Kohn-Sham potential. *Physical Review A*, 54(3):1957–1972, sep 1996.
- [65] N. Helbig, I. V. Tokatly, and A. Rubio. Exact Kohn-Sham potential of strongly correlated finite systems. *Journal of Chemical Physics*, 131(22), 2009.
- [66] E W Weisstein. "Hermite Polynomial." From MathWorld—A Wolfram Web Resource.

Article I

Time-dependent density-functional theory for strongly interacting electronsLuis Cort,¹ Daniel Karlsson,¹ Giovanna Lani,² and Robert van Leeuwen¹¹*Department of Physics, Nanoscience Center, P.O. Box 35 FI-40014, University of Jyväskylä, Jyväskylä, Finland*²*Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Université Pierre et Marie Curie, 4 place Jussieu, 75252, Paris cedex 05, France*

(Received 1 March 2017; published 11 April 2017)

We consider an analytically solvable model of two interacting electrons that allows for the calculation of the exact exchange-correlation kernel of time-dependent density functional theory. This kernel, as well as the corresponding density response function, is studied in the limit of large repulsive interactions between the electrons and we give analytical results for these quantities as an asymptotic expansion in powers of the square root of the interaction strength. We find that in the strong interaction limit the three leading terms in the expansion of the kernel act instantaneously while memory terms only appear in the next orders. We further derive an alternative expansion for the kernel in the strong interaction limit on the basis of the theory developed previously [Phys. Chem. Chem. Phys. **18**, 21092 (2016)] using the formalism of strictly correlated electrons in the adiabatic approximation. We find that the first two leading terms in this series, corresponding to the strictly correlated limit and its zero-point vibration correction, coincide with the two leading terms of the exact expansion. We finally analyze the spatial nonlocality of these terms and show when the adiabatic approximation breaks down. The ability to reproduce the exact kernel in the strong interaction limit indicates that the adiabatic strictly correlated electron formalism is useful for studying the density response and excitation properties of other systems with strong electronic interactions.

DOI: [10.1103/PhysRevA.95.042505](https://doi.org/10.1103/PhysRevA.95.042505)**I. INTRODUCTION**

Time-dependent density functional theory (TDDFT) [1–7] is a well-established approach to study the time-dependent and excitation properties of many-electron systems. One of the main reasons for its popularity is that within this formalism the time-dependent interacting many-body problem can be recast exactly into an equivalent one-particle framework, which is advantageous for numerical implementations. The corresponding one-particle equations, called the time-dependent Kohn-Sham equations, contain an effective potential, known as the Kohn-Sham potential, which is defined in such a way that the noninteracting system has the same time-dependent density as the original interacting many-body system. The Kohn-Sham potential is typically written as the sum of the external potential of the interacting system and of the Hartree and the exchange-correlation (xc) potential.

In practical applications of TDDFT, the xc potential v_{xc} is approximated. The type of approximation employed crucially determines the quality of the results, and therefore a considerable amount of research has gone into the difficult task of finding reliable and accurate approximations for this quantity. This task is simpler in the linear response regime where we consider small variations in the density caused by applied perturbations. This regime is of interest as the knowledge of the density response function is sufficient to calculate the excitation energies and the absorption spectrum of the system [8]. For this purpose, it is enough to know v_{xc} and its functional derivative $\delta v_{xc}/\delta n = f_{xc}$ with respect to the density n , evaluated at the ground-state density. The quantity f_{xc} is called the xc kernel and has been the subject of intense investigations.

The simplest possible approximation is the adiabatic local-density approximation (ALDA) in which the xc kernel is local in space and time. The ALDA has, however, a

number of deficiencies [4] such as, for example, the inability to produce correct charge transfer excitations [9–12], Born-Oppenheimer surfaces of excited states in dissociating molecules [13–15] and semiconductor band gaps [16]. Some improvements have been made using hybrid functionals which contain mixtures of exact exchange and traditional local functionals. These methods are nonlocal in space but still adiabatic. However, they are not systematic and the optimal mixture of exact exchange is often system dependent [17–20]. Other, more systematic, approximations for f_{xc} beyond the ALDA often rely on perturbative expansions [21–30] and many of them are restricted to the exchange-only approximation. Their perturbative nature makes these approaches questionable in the strong correlation regime which is relevant in various physical situations, notably the case of molecular dissociation, and hence it is highly desirable to develop new techniques to tackle this regime.

In a recent work [31], the so-called strictly correlated electrons (SCE) framework [32–34], a formalism well suited for the description of strong interactions, has been applied within the time-dependent domain. The authors derived an expression for the xc kernel in the so-called adiabatic approximation and established that the adiabatic SCE (ASCE) kernel satisfies the zero-force theorem [35], an exact property related to generalized translational invariance [36,37]. The kernel was furthermore studied for finite one-dimensional systems with different density profiles, some of which are prototypical of the dissociation of two-electron homonuclear molecules. It was found that the ASCE kernel is spatially nonlocal and exhibits a divergent behavior as the molecular bond is stretched. For adiabatic kernels, this diverging behavior is crucial [13] for describing bond-breaking excitations, which is a notoriously challenging problem in linear response TDDFT. Since the kernel was derived in the adiabatic approximation, not much

could be concluded about the limitations of its adiabatic nature in the context of the physics of strong static correlation. The case of infinitely strong electron-electron correlation is quite peculiar and to date it is not known how accurate the adiabatic approximation can be in such a regime.

One way to shed light on this issue is to benchmark the ASCE kernel against an exact expression for f_{xc} obtained from a model system where the density response function and thus the xc kernel can be calculated analytically. In this work, we consider such a model, namely two interacting electrons on a quantum ring [6,38–40], for which we not only compute the exact density response function and xc kernel but also obtain these quantities for various two-body interaction strengths, including the infinitely strong one, and we compare these results with those given by the SCE theory in the adiabatic approximation. The leading order of the asymptotic expansion for the exact f_{xc} and the expression for the ASCE kernel are found to be identical. We also derive the next-order correction term beyond the ASCE, called the adiabatic zero-point-energy approximation (AZPE), and show that also this adiabatic term is the same as the next order from the asymptotic expansion. The third order in the expansion for the kernel is still adiabatic, while a frequency dependence appears in the fourth order. In this order, an adiabatic approximation would break down. This is one of the central results of the paper and elucidates both the strengths and the weaknesses of the adiabatic approximation in the limit of strong electron-electron interaction.

The paper is organized as follows. In Sec. II we introduce the quantum ring model and, after computing the full spectrum of its Hamiltonian, we discuss asymptotic expansions for its eigenenergies and eigenstates in the case of strong interactions and analyze them. In Sec. III we study the density response function of strongly interacting systems, while in Sec. IV we focus on TDDFT in the same regime and give an asymptotic expansion for the xc kernel. Our conclusions are finally presented in Sec. V.

II. AN EXACTLY SOLVABLE SYSTEM

A. Two interacting electrons on a quantum ring

For our study of electron correlations, we consider an analytically solvable model, which we will refer to as the quantum ring model, of two electrons on a ring of length L which repel each other with a two-body interaction. The interaction strength can be adjusted using a parameter, which allows us to study the exact properties of the system ranging from weak to very strong interactions. The explicit form of the Hamiltonian of the quantum ring is given by

$$\hat{H} = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + \lambda V_0 \cos^2\left[\frac{\pi}{L}(x_1 - x_2)\right], \quad (1)$$

where $\lambda \geq 0$ is a dimensionless parameter and V_0 has units of energy. The coordinates x_1 and x_2 are the coordinates of the electrons on the ring which run from 0 to L . The ground-state density $n_0 = 2/L$ is spatially constant and independent of λ ; for this reason the model can be used to illustrate several features of the coupling strength dependence in density functional theory.

In order to calculate the properties of the system we have to determine the eigenfunctions Ψ which satisfy the stationary

Schrödinger equation $\hat{H}\Psi = E\Psi$, where E are the energy eigenvalues. For our two-particle system, these eigenfunctions can be written as a product of a spatial wave function and a spin function as follows:

$$\Psi(x_1\sigma_1, x_2\sigma_2) = \psi^\pm(x_1, x_2) \Xi^\pm(\sigma_1, \sigma_2).$$

For the singlet case (which we will focus on), the normalized spin function is given by

$$\Xi^+(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}(\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow})$$

and is antisymmetric in the spin variables. For the triplet, there are three linearly independent symmetric spin functions which we, for simplicity, all denote by $\Xi^-(\sigma_1, \sigma_2)$. Since the two-electron wave function Ψ is antisymmetric under the simultaneous interchange of space and spin variables, it follows that the spatial wave functions ψ^\pm satisfy the symmetry relation

$$\psi^\pm(x_1, x_2) = \pm \psi^\pm(x_2, x_1).$$

Apart from these symmetry conditions, the Schrödinger equation needs to be solved with periodic boundary conditions on the variables x_1 and x_2 ; i.e., the wave function and its first spatial derivatives are invariant under the substitution $x_i \rightarrow x_i + L$ for $i = 1, 2$. Using these conditions, we can solve the Schrödinger equation by a suitable coordinate transformation. Since these steps are carried out in detail in Ref. [41], here we just outline the main steps relevant for this work.

The Hamiltonian (1) becomes separable in the terms $R = (x_1 + x_2)/2$, the center-of-mass coordinate, and $z = \pi(x_1 - x_2)/L$, the dimensionless relative coordinate. This variable transformation gives

$$\hat{H} = -\frac{1}{4}\partial_R^2 - \frac{\pi^2}{L^2}\partial_z^2 + \lambda V_0 \cos^2(z).$$

By inserting a product ansatz of the form $\psi(R, z) = f(R)M(z)$ into the Schrödinger equation, we find that the spatial two-particle eigenfunctions are of the form

$$\psi(R, z) = \exp\left(\frac{2\pi i k R}{L}\right) M(z), \quad (2)$$

where k is an integer and the function $M(z)$ satisfies the Mathieu equation, which we write in its standard form as [42,43]

$$[-\partial_z^2 + 2q \cos(2z)]M(z) = a M(z), \quad (3)$$

where the constants q and a are given by

$$q = \lambda V_0 \left(\frac{L}{2\pi}\right)^2, \quad (4)$$

$$a = -k^2 - 2q + \frac{EL^2}{\pi^2}. \quad (5)$$

For a given value of q , the Mathieu equation (3) has only periodic solutions for particular values $a(q)$, which are called the Mathieu characteristic values. Moreover, this equation has either even or odd periodic solutions, which are called the Mathieu cosine and Mathieu sine functions respectively. Both sets of functions form a countable set; therefore its members can be labeled by a non-negative integer l . For

the Mathieu cosines, this label starts at $l = 0$ and for the Mathieu sines at $l = 1$. The even Mathieu cosine function is denoted by $C_l(z; q)$ and its characteristic value by $a_l^+(q)$, while the odd Mathieu sine function is denoted by $S_l(z; q)$ and its characteristic value by $a_l^-(q)$. Since the center-of-mass wave functions are symmetric under the interchange of the spatial coordinates of the electrons, we see from Eq. (2) that the singlet wave functions must be described by even Mathieu functions whereas the triplet ones must be described by odd Mathieu functions. The final form of the normalized singlet and triplet wave functions therefore is

$$\psi_{kl}^+(R, z; q) = \frac{\sqrt{2}}{L} \exp\left(\frac{2\pi i k R}{L}\right) C_l(z; q), \quad (6)$$

$$\psi_{kl}^-(R, z; q) = \frac{\sqrt{2}}{L} \exp\left(\frac{2\pi i k R}{L}\right) S_l(z; q), \quad (7)$$

in which the normalization of the Mathieu functions is chosen such that

$$\int_0^\pi dz |C_l(z; q)|^2 = \int_0^\pi dz |S_l(z; q)|^2 = \frac{\pi}{2}. \quad (8)$$

The Mathieu functions further have the periodicity property $M_l(z + \pi) = (-1)^l M_l(z)$; i.e., they are periodic in π for even values of l and antiperiodic for odd values of l . Furthermore, the center-of-mass wave function in Eq. (2) changes with a prefactor $(-1)^k$ when $x_i \rightarrow x_i + L$, for $i = 1, 2$. Therefore, for the wave functions in Eqs. (6) and (7) to satisfy periodic boundary conditions, the labels k and l must be both even or both odd. Note that k runs over all integers while l only runs over the non-negative integers. From Eq. (5) we see that the energy eigenvalues are given by

$$E_{kl}^\pm(q) = \left(\frac{\pi}{L}\right)^2 [k^2 + a_l^\pm(q) + 2q]. \quad (9)$$

Since in the subsequent discussion of the density response function we focus on the singlet excitations in particular, we write the singlet wave functions in a slightly different form for the purpose of a better interpretation. By multiplying the spatial wave function of Eq. (6) with its singlet spin function, the full space-spin function can be written as

$$\Psi_{kl}(x_1\sigma_1, x_2\sigma_2) = \Phi_k(x_1\sigma_1, x_2\sigma_2) \sqrt{2} C_l\left[\frac{\pi}{L}(x_1 - x_2)\right], \quad (10)$$

where we defined the Slater determinant

$$\Phi_k(x_1\sigma_1, x_2\sigma_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{k/2}(x_1)\delta_{\sigma_1\uparrow} & \phi_{k/2}(x_1)\delta_{\sigma_1\downarrow} \\ \phi_{k/2}(x_2)\delta_{\sigma_2\uparrow} & \phi_{k/2}(x_2)\delta_{\sigma_2\downarrow} \end{vmatrix}$$

and we further defined the spatial normalized orbital by $\phi_k(x) = e^{2\pi i k x/L}/\sqrt{L}$ which corresponds to a periodic single-particle wave function of a free particle on the quantum ring. Let us consider the excitation from the ground state to another singlet state with $l = 0$, which requires that the excited state is characterized by an even k value. In that case, $\phi_{k/2}$ in the Slater determinant above is a proper periodic wave function as $k/2$ is an integer. According to Eq. (9) the excitation energy is

$$\Delta E_{k0}^+ = E_{k0}^+ - E_{00}^+ = \left(\frac{\pi k}{L}\right)^2, \quad (11)$$

which is independent of the interaction strength q as the excited state has the same relative wave function as the ground state. For the case that $q = 0$, we have $C_0(z; q = 0) = 1/\sqrt{2}$ and the ground and excited states both become pure Slater determinants. The excitation then represents a promotion of two electrons from a doubly occupied $k = 0$ state to a doubly occupied state with a one-particle quantum number $k/2$, which is commonly called a double excitation. When q is nonzero, this language is not accurate anymore as also the relative wave function becomes relevant. If the interaction strength becomes very large, the energy required to excite to a state with nonzero l becomes very large too and the excitations with energy ΔE_{k0}^+ give the dominant contribution to the density response function, as we will see later.

B. The strong interaction expansion of the exact solution

As the interaction strength q increases, the electronic repulsion becomes more important and the electrons tend to stay in opposite positions on the ring. This physically intuitive picture can be analyzed in more detail using the Mathieu equation. According to Eqs. (6) and (7), the square of the spatial wave function is given by

$$|\psi_{kl}^\pm(R, z; q)|^2 = \frac{2}{L^2} M_l^2(z; q),$$

where $M_l(z; q)$ is either a Mathieu cosine C_l or a Mathieu sine S_l depending on whether the wave function is a singlet or a triplet one. We therefore see that the probability to find a given electron at x_2 given an electron at x_1 only depends on the relative coordinate $x_1 - x_2$, as one would expect on the basis of the symmetry of the system. This probability distribution is given by the square of the Mathieu function M_l .

Let us analyze the properties of this function in the large interaction limit which according to Eq. (3) satisfies a single-particle Schrödinger type of equation in a potential of the form $V(z) = 2q \cos(2z)$. For large values of q , we can see that the relative wave function described by M_l becomes localized in the minimum of the potential at $z = \pi/2$, which corresponds to a relative distance of the particles of $L/2$. We can expand the potential around this minimum to obtain

$$2q \cos(2z) = -2q + 4q \left(z - \frac{\pi}{2}\right)^2 + \dots$$

This potential describes (apart from a shift of the minimum) a harmonic oscillator with frequency $\Omega = 2\sqrt{q}$. The eigenfunctions of the harmonic oscillator are well known to consist of Gaussians of width proportional to $1/\sqrt{\Omega} = 1/(\sqrt{2}q^{1/4})$. In the limit of large q , the harmonic frequency increases and the wave functions become localized around $z = \pi/2$. This behavior is illustrated in Fig. 1. The eigenenergies ϵ_l of the harmonic oscillator are well known and given by $\epsilon_l = -q + \Omega(l + 1/2) = a/2$. This also immediately provides an asymptotic formula for the characteristic value of the Mathieu equation for large values of q :

$$a_l^\pm(q) = -2q + 2\sqrt{q}(2l + 1) + \dots$$

and consequently also an asymptotic expansion for the eigenenergies of the quantum ring from Eq. (9).

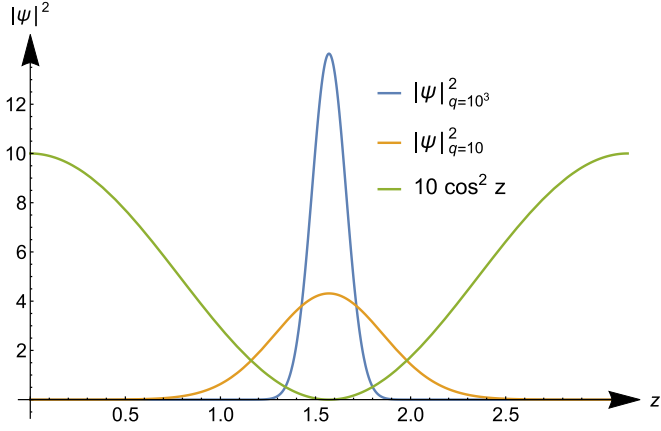


FIG. 1. The squared ground-state wave function $|\psi_{00}|^2$ for two values of the interaction strength q , and the interaction $\cos^2 z$ using a suitable scaling for showing it in the same plot. For large q , the wave function localizes around $z = \pi/2$ where $\cos^2 z$ is almost parabolic and $|\psi_{00}|^2$ then tends to a sharp Gaussian.

A more rigorous connection to the harmonic oscillator wave functions can be made on the basis of the substitution $u(z) = \sqrt{2}q^{1/4} \cos z$ which transforms the Mathieu equation (3) to the new form

$$\left[-\frac{1}{2} \left(1 - \frac{u^2}{2\sqrt{q}} \right) \frac{d^2}{du^2} + \frac{u}{4\sqrt{q}} \frac{d}{du} + \frac{u^2}{2} \right] \mathcal{M}(u) = \epsilon \mathcal{M}(u),$$

where we defined $\epsilon = (a + 2q)/(4\sqrt{q})$ and $\mathcal{M}(u(z)) = M(z; q)$. In the large q limit, this equation attains the form of the Schrödinger equation for the harmonic oscillator. Its eigenfunctions are well known and, apart from a normalization, are given by the parabolic cylinder functions $\mathcal{D}_m(u)$ defined by

$$\begin{aligned} \mathcal{D}_m(u) &= \frac{(-1)^m}{2^{m/2}} e^{u^2/2} \frac{d^m}{du^m} e^{-u^2} \\ &= \frac{1}{2^{m/2}} e^{-u^2/2} H_m(u), \end{aligned} \quad (12)$$

where $H_m(u)$ are the Hermite polynomials. On the basis of this analysis, we may suspect that it is possible to find an asymptotic large- q expansion of the Mathieu functions in terms of harmonic oscillator functions \mathcal{D}_m of argument u . Sips [44–47] already derived such an expansion on the basis of the transformed Mathieu equation. For reference, in the next section we briefly outline its main features for the case of the Mathieu cosine, which is relevant for the discussion of singlet states. The general form of the Sips expansion is given by

$$C_l(z; q) = \sum_{n=-\infty}^{\infty} c_{2n,l}(q) \mathcal{D}_{l+2n}[u(z)], \quad (13)$$

in which we defined $\mathcal{D}_{m<0} = 0$. The specific form of the coefficients $c_{2n,l}(q)$ is given in the work of Sips [44–46], who outlined a systematic procedure to obtain them. In general they can be obtained from a recursion relation [47] and we refer to Appendix B for a more detailed discussion.

In Eq. (13) we see that for odd values of l the Mathieu cosine is expanded in functions \mathcal{D}_m with only odd values of m while for even l it is expanded in functions \mathcal{D}_m with only

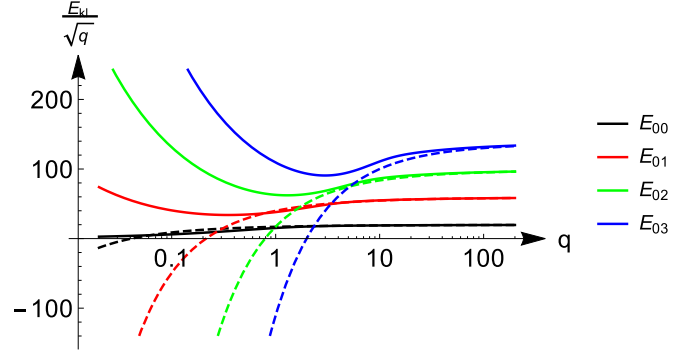


FIG. 2. The ground-state ($l = 0$) and excited-state ($l = 1, 2, 3$) energies divided by \sqrt{q} for $k = 0$ as function of the interaction strength q in units of L^{-2} . We plot the exact energies (solid lines) vs the approximate energies (dashed lines) from the expansion in Eq. (14).

even values of m . This follows directly from the derivation by Sips [44] but we see with hindsight that this condition is necessary to make the Mathieu cosine satisfy $C_l(z + \pi; q) = (-1)^l C_l(z; q)$. Namely, if we replace z by $z + \pi$ then the variable u changes to $-u$, yielding this desired property for a series of the form (13) since $\mathcal{D}_m(-u) = (-1)^m \mathcal{D}_m(u)$. The Sips expansion, Eq. (13), will be used in the next section to determine the large interaction expansion of the density response function.

We conclude the section with a remark on the eigenenergies of the quantum ring. We can obtain an asymptotic expansion for them as the work of Sips also derives the large q behavior of the Mathieu characteristic values in terms of an asymptotic series expansion in power of $q^{1/2}$ (see Appendix B). Taking the first few leading orders, we obtain the following expression for the eigenenergies of the quantum ring:

$$\begin{aligned} E_{kl}^{\pm} &= \left(\frac{\pi}{L} \right)^2 \left[k^2 + 2\sqrt{q}(2l+1) - \frac{1}{4}(2l^2 + 2l + 1) \right. \\ &\quad \left. + \frac{(2l+1)}{128\sqrt{q}} [(2l+1)^2 + 3] \right] + O(q^{-1}). \end{aligned} \quad (14)$$

The asymptotic expansion is the same for the singlet and triplet energies as their difference becomes exponentially small in the large q limit (see Appendix B). To illustrate the q dependence of the eigenenergies, we present in Fig. 2 some of the lowest eigenvalues and their asymptotic expansion from Eq. (14) as a function of q . We see that the asymptotic expansion converges more slowly for higher values of l , and for these l we need high values of q in order to have a reliable estimate.

III. DENSITY RESPONSE OF STRONGLY INTERACTING ELECTRONS

After having discussed the two-particle wave function and energy spectrum of the system, let us now move to its response properties. Particularly relevant to TDDFT is the induced density change $\delta n(\mathbf{r}, t)$ when a small time-dependent external potential $\delta v(\mathbf{r}, t)$ is applied. They are related by the retarded

density response function $\chi(\mathbf{r}t, \mathbf{r}'t')$ as follows:

$$\delta n(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \chi(\mathbf{r}t, \mathbf{r}'t') \delta v(\mathbf{r}', t'), \quad (15)$$

where χ is defined via

$$\begin{aligned} \chi(\mathbf{r}t, \mathbf{r}'t') &= \frac{\delta n(\mathbf{r}, t)}{\delta v(\mathbf{r}', t')} \\ &= -i\theta(t - t') \langle \Psi_0 | [\hat{n}_H(\mathbf{r}, t), \hat{n}_H(\mathbf{r}', t')] | \Psi_0 \rangle, \end{aligned} \quad (16)$$

where \hat{n}_H is the density operator in the Heisenberg picture and Ψ_0 is the ground state of the system. Since the unperturbed system is time independent, the density response function is a function of the relative time $\tau = t - t'$ only and we can Fourier transform it with respect to τ :

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \int d\tau \chi(\mathbf{r}, \mathbf{r}', \tau) e^{i\omega\tau}.$$

Before addressing in greater detail the properties of χ of the quantum ring in the large interaction limit, let us first make some considerations about the static density response function in a more general context.

A. Static density response in the strong interaction limit

Let us consider an interacting many-electron system in its ground state. The Hamiltonian consists of a kinetic energy operator, an external potential $v(\mathbf{r})$, and a two-body interaction. If we consider a small variation $\delta v(\mathbf{r})$ in the static external potential, the ground-state density will vary by an amount $\delta n(\mathbf{r})$, which can be expressed as

$$\delta n(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}'), \quad (17)$$

where $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}, \mathbf{r}', \omega = 0)$ is the static density response function. Let us now consider a shifted potential $v'(\mathbf{r}) = v(\mathbf{r} + \mathbf{R})$. The ground-state density for this new potential is given by $n'(\mathbf{r}) = n(\mathbf{r} + \mathbf{R})$. For small translations, we can write that $\delta n(\mathbf{r}) = n'(\mathbf{r}) - n(\mathbf{r}) = \mathbf{R} \cdot \nabla n(\mathbf{r})$ and similarly $\delta v(\mathbf{r}) = v'(\mathbf{r}) - v(\mathbf{r}) = \mathbf{R} \cdot \nabla v(\mathbf{r})$. Since this is valid for all small vectors \mathbf{R} , we find from Eq. (17) that

$$\nabla n(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \nabla v(\mathbf{r}'). \quad (18)$$

This equation relates the gradient of the external potential to the gradient of the ground-state density, and amounts to the static limit of an equation derived for the dynamic density response function by Vignale [48].

Let us now consider a system in which we scale the two-body interaction with a parameter λ and let us choose the external potential $v_\lambda(\mathbf{r})$ in such a way that the density $n(\mathbf{r})$ is the same for all values of λ . According to the Hohenberg-Kohn theorem [49], such a potential is unique when it exists. For such a system, the density response function will depend on λ as well and Eq. (18) becomes

$$\nabla n(\mathbf{r}) = \int d\mathbf{r}' \chi_\lambda(\mathbf{r}, \mathbf{r}') \nabla v_\lambda(\mathbf{r}'). \quad (19)$$

Let us now consider the limit of very large values of λ . One can show, for a general inhomogeneous system, that

asymptotically $v_\lambda(\mathbf{r}) = \lambda u(\mathbf{r}) + \dots$, where $u(\mathbf{r})$ is the so-called strictly correlated electron potential [32,33,50]. The result is intuitively clear as the linearly growing repulsive two-body interaction must be compensated by a linearly growing attractive one-body potential in order to keep the density profile constant. This has consequences for the behavior of χ_λ . We consider two cases. Let us first assume that for $\lambda \rightarrow \infty$ the response function χ_λ attains a finite value $\alpha(\mathbf{r}, \mathbf{r}')$. Because the left-hand side of Eq. (19) is independent of λ , this implies that

$$\mathbf{0} = \int d\mathbf{r}' \alpha(\mathbf{r}, \mathbf{r}') \nabla u(\mathbf{r}'), \quad (20)$$

which means that the three vector components of ∇u must be eigenfunctions of α with zero eigenvalue. Since the density response function reaches a finite limit, the system does not become rigid even when the interaction becomes infinitely large. This is a possible situation in systems in which the Hamiltonian by a coordinate transformation can be separated in two parts, in which one of the parts is weakly dependent on the interaction strength. That such inhomogeneous systems exist is demonstrated for the harmonic model system described in Appendix A and for which we demonstrate that Eq. (20) is indeed valid.

A probably more common situation is that such a separation is either not possible or that both parts of such a Hamiltonian are still strongly λ dependent. In this case, one would expect that the energy required to excite the system grows with λ , and as such the density response function would vanish for large λ . If this is the case, it is to be expected that χ_λ in Eq. (19) asymptotically behaves as

$$\chi_\lambda(\mathbf{r}, \mathbf{r}') = \frac{1}{\lambda} \beta(\mathbf{r}, \mathbf{r}') + \dots, \quad (21)$$

where β is a λ -independent function and the terms that follow decay faster than $1/\lambda$. This means that for a given perturbation $\delta v(\mathbf{r})$, the density response $\delta n(\mathbf{r})$ decays as $1/\lambda$ and therefore the strong interaction makes the system more rigid and suppresses density variations. In such a case, Eq. (19) reduces to

$$\nabla n(\mathbf{r}) = \int d\mathbf{r}' \beta(\mathbf{r}, \mathbf{r}') \nabla u(\mathbf{r}'), \quad (22)$$

which is an exact equation for the leading order in λ .

When we finally consider systems in which the ground-state density and external potential are spatially constant, the reasoning that we carried out does not apply anymore since the gradients in Eq. (19) are identically zero. However, such systems are homogeneous, which implies that the center of mass can be separated off and we can therefore expect the response function to attain a finite value in the large interaction limit. This is exactly the case of our quantum ring model. Indeed, we saw in Eq. (11) that the quantum ring admits excitation energies that are independent of the interaction strength and these correspond to excitations that only change the center-of-mass wave function and do not affect the relative probability distribution of the particles. As we will see in more detail below, such excitations give a contribution to the density response function that survives in the large interaction limit, while the remaining excitations give a contribution which behaves as in Eq. (21).

It is interesting to connect this analysis to the f -sum rule for the dynamic density response function. In a system where the density is kept independent of λ with $v_\lambda(\mathbf{r})$, the f -sum rule attains the form [51]

$$\frac{1}{\pi} \int d\omega \omega \chi_\lambda(\mathbf{r}, \mathbf{r}', \omega) = \nabla[n(\mathbf{r})\nabla\delta(\mathbf{r} - \mathbf{r}')]. \quad (23)$$

We therefore see that the frequency integration removes the λ dependence. This is not in contradiction with Eq. (21). Although the density response function itself can become very small for large λ , the integrand in Eq. (23) can remain finite as it is weighted by the frequency ω . As a consequence the integral gets contributions proportional to the excitation energies, which grow with increasing interaction strength.

B. Exact density response of the quantum ring

After having discussed the general static case, we now turn our attention to the exact dynamical density response function of the quantum ring. Inserting a complete set of eigenstates of the Hamiltonian \hat{H} from Eq. (1) into the one-dimensional analog of Eq. (16), we find the Lehmann representation [51] of the retarded response function

$$\chi(x, x', \omega) = \sum_{k, l, p = \pm} \left[\frac{\langle \Psi_{00}^+ | \hat{n}(x) | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x') | \Psi_{00}^+ \rangle}{\omega - \Delta E_{kl}^p(q) + i\eta} - \frac{\langle \Psi_{00}^+ | \hat{n}(x') | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x) | \Psi_{00}^+ \rangle}{\omega + \Delta E_{kl}^p(q) + i\eta} \right], \quad (24)$$

where we defined the excitation energies as $\Delta E_{kl}^p(q) = E_{kl}^p(q) - E_{00}^+(q)$. The expression contains an infinitesimal parameter $\eta > 0$ that arises from the Fourier transform of the Heaviside function and the limit $\eta \rightarrow 0$ is implied after the evaluation of all terms. Furthermore, $\hat{n}(x)$ is the density operator in the Schrödinger picture and $p = \pm$ labels the singlet or triplet eigenstates. The label k runs over all positive and negative integers while l runs over non-negative integers, with the condition that both are even or both are odd. The expression in Eq. (24) is simplified by the fact that the triplet terms vanish because the triplet spin function is orthogonal to the singlet spin function of the ground state, which yields $\langle \Psi_{00}^+ | \hat{n}(x) | \Psi_{kl}^- \rangle = 0$. The remaining nonzero terms can be evaluated as

$$\begin{aligned} \langle \Psi_{00}^+ | \hat{n}(x_1) | \Psi_{kl}^+ \rangle &= 2 \int_0^L dx_2 \psi_{00}^{+*}(x_1, x_2) \psi_{kl}^+(x_1, x_2) \\ &= \frac{2}{L} e^{2\pi i k x_1 / L} D_{kl}(q), \end{aligned} \quad (25)$$

where ψ_{kl}^+ denotes the spatial part of the singlet wave function of Eq. (6) expressed in the original coordinates and the excitation amplitudes $D_{kl}(q)$ read

$$D_{kl}(q) = \frac{2}{\pi} \int_0^\pi dz C_0(z; q) C_l(z; q) e^{-ikz}. \quad (26)$$

The amplitude $D_{kl}(q)$ has a number of properties directly related to properties of the Mathieu functions. Since $C_l(z; q)$ is real, $D_{kl}^*(q) = D_{(-k)l}(q)$, and as a consequence of the orthogonality of the Mathieu functions, $D_{0l}(q) = \delta_{l0}$. Moreover, the fact that $C_l(z + \pi; q) = (-1)^l C_l(z; q)$ and that these functions

are even in z leads to $D_{kl}(q) = (-1)^{k+l} D_{kl}^*(q)$. Making use of the symmetry properties of $D_{kl}(q)$ described, combined with $\Delta E_{kl}^+(q) = \Delta E_{(-k)l}^+(q)$, yields the following expansion of the response function:

$$\chi(x, x', \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} \chi(k, \omega) e^{2\pi i k(x-x')/L}, \quad (27)$$

where

$$\begin{aligned} \chi(k, \omega) &= \frac{4}{L} \sum_l \left[\frac{|D_{kl}(q)|^2}{\omega - \Delta E_{kl}^+(q) + i\eta} - \frac{|D_{kl}(q)|^2}{\omega + \Delta E_{kl}^+(q) + i\eta} \right] \\ &= \frac{8}{L} \sum_l \frac{\Delta E_{kl}^+(q) |D_{kl}(q)|^2}{(\omega + i\eta)^2 - [\Delta E_{kl}^+(q)]^2}, \end{aligned} \quad (28)$$

in which the sum runs over even values of l for k even and over odd values of l for k odd. We see from Eq. (27) that $\chi(k, \omega)$ can be regarded as the discrete Fourier transform of $\chi(x, x', \omega)$ with respect to the relative spatial coordinate $x - x'$ as was to be expected on the basis of the symmetry of the system. It will be now convenient to define the spatially discrete and temporally continuous Fourier transform of a function $f(x, t)$ and its inverse as

$$f(k, \omega) = \int_0^L dx e^{-\frac{2\pi i k}{L} x} \int_{-\infty}^{\infty} dt e^{i\omega t} f(x, t), \quad (29)$$

$$f(x, t) = \frac{1}{L} \sum_{k=-\infty}^{\infty} e^{\frac{2\pi i k}{L} x} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} f(k, \omega). \quad (30)$$

By using this Fourier transformation in Eq. (15) we rewrite the density response as

$$\delta n(k, \omega) = \chi(k, \omega) \delta v(k, \omega), \quad (31)$$

in which k is an integer and ω is a continuous variable. We will make use of this relation below. We have now obtained an explicit form of the density response function that allows for an analytical analysis in the strong interaction limit.

However, before moving to that, we briefly give the form of the response function for the noninteracting system, i.e., $q = 0$, which in the density functional context will be the same as the Kohn-Sham response function, since the system has the same density for all values of q . For the noninteracting case, the Mathieu characteristic value is $a_l^+(0) = l^2$ and the Mathieu cosine functions are given by $C_0(z; 0) = 1/\sqrt{2}$ and $C_l(z; 0) = \cos(lz)$ for $l \geq 1$. The excitation energies are given by Eq. (9),

$$E_{kl}^+(0) = \left(\frac{\pi}{L} \right)^2 [k^2 + l^2],$$

while the eigenstates are given by Eq. (6) as

$$\psi_{kl}^+(x_1, x_2) = \frac{1}{\sqrt{2}} [\phi_{\frac{k+l}{2}}(x_1) \phi_{\frac{k-l}{2}}(x_2) + \phi_{\frac{k-l}{2}}(x_2) \phi_{\frac{k+l}{2}}(x_1)], \quad (32)$$

in which $k \pm l$ is always even. Note that $l \neq |k|$ yields a doubly excited state. The corresponding excitation amplitude can be calculated from Eq. (26). Apart from the amplitude $D_{00}(0) = 1$, which does not contribute to the Lehmann sum

since $\Delta E_{00}^+ = 0$, for $(kl) \neq (00)$ we have that

$$D_{kl}(0) = \begin{cases} 1/\sqrt{2} & \text{if } l = |k| \\ \frac{\sqrt{2}}{\pi} \frac{ik}{k^2 - l^2} [(-1)^{k+l} - 1] & \text{if } l \neq |k|. \end{cases} \quad (33)$$

Since only terms where $k + l$ is even contribute, we see that the only nonzero excitation amplitudes are the ones with $l = |k|$. This implies the absence of double excitations in the density-response function, a well-known property of noninteracting systems [4,52]. Inserting Eq. (33) into Eq. (28) we find that the noninteracting response function $\chi_s(k, \omega)$ is given by

$$\chi_s(k, \omega) = \frac{4}{L} \frac{\Delta E_{kk}^+(0)}{(\omega + i\eta)^2 - [\Delta E_{kk}^+(0)]^2} \quad (34)$$

with $\Delta E_{kk}^+(0) = 2(\pi k/L)^2$. We note that in k space, χ_s has only a single pole for $\omega > 0$ and no zeros.

Having determined the noninteracting response function, it now remains to study the density response function in the complementary limit of very strong interactions. For this purpose, we need to study the excitation energies $\Delta E_{kl}^+(q)$ and excitation amplitudes $D_{kl}(q)$ in the limit of large q . This is the topic of the next section.

C. Strong interaction expansion of the dynamic density response function

Let us focus on the excitation energies $\Delta E_{kl}^+(q)$ and the excitation amplitudes $D_{kl}(q)$ for large q . Because for $\Delta E_{kl}(q)$, explicit asymptotic expansions are known (see Appendix B), and this leaves us with the determination of $D_{kl}(q)$ defined by Eq. (26). We start by inserting the Sips expansion of Eq. (13) into Eq. (26), which gives

$$D_{kl}(q) = \frac{2}{\pi} \sum_{n_1, n_2 = -\infty}^{\infty} c_{2n_1, 0}(q) c_{2n_2, l}(q) \mathcal{J}_{kl}^{n_1 n_2}(q), \quad (35)$$

where we defined

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \int_0^\pi dz e^{-ikz} \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u), \quad (36)$$

where $u(z) = \sqrt{2} q^{1/4} \cos z$. Since the coefficients $c_{2n, l}(q)$ are known (see Appendix B for explicit expressions), it remains to evaluate $\mathcal{J}_{kl}^{n_1 n_2}(q)$. Changing the integration variable to u and

defining $b = \sqrt{2} q^{1/4}$ gives the expression

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \frac{1}{b} \int_{-b}^b du f_k\left(\frac{u}{b}\right) \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u), \quad (37)$$

where we defined the function

$$f_k(x) = \frac{e^{-ik \arccos(x)}}{\sqrt{1-x^2}} = \sum_{r=0}^{\infty} a_r(k) x^r \quad (38)$$

and its Taylor coefficients $a_r(k)$. Inserting this Taylor series into Eq. (37) then gives the expansion

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \sum_{r=0}^{\infty} \frac{a_r(k)}{b^{r+1}} \int_{-b}^b du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u),$$

where the interchange of integral and sum is allowed as we have an absolutely convergent series. Due to the Gaussian decay of the functions $\mathcal{D}_n(u)$, in the limit $q \rightarrow \infty$, we make an error which, as a function of q , decays faster than any polynomial function if we replace b in the limits of the integral by infinity. We therefore obtain the asymptotic expansion

$$\mathcal{J}_{kl}^{n_1 n_2}(q) = \sum_{r=0}^{\infty} \frac{a_r(k) I_{n_1 n_2, r}^l}{(\sqrt{2} q^{1/4})^{r+1}}, \quad (39)$$

where we introduced coefficients of the form

$$I_{n_1 n_2, r}^l = \int_{-\infty}^{\infty} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u). \quad (40)$$

This integral can be computed analytically, and the explicit expression is given in Appendix C. Also note that due to the parity properties of the integrand $I_{n_1 n_2, r}^l$ vanishes unless r and l are both even or both odd. Therefore, depending on whether l is even or odd, the summation index r in Eq. (39) can be taken to run only over even or only over odd values.

Expression (39) together with Eq. (35) gives an explicit procedure to calculate the large q expansion of the excitation amplitudes. The asymptotic expansions of $D_{kl}(q)$ and of $|D_{kl}(q)|^2$ are given in Appendix C in Eqs. (C5) and (C6) respectively. Together with the asymptotic expansion for the excitation energies, Eq. (B4), inserted into Eq. (28), we find that the asymptotic expansion of the density response function is given by

$$\chi(k, \omega) = \begin{cases} \frac{8}{L} \frac{(\pi k/L)^2}{(\omega + i\eta)^2 - (\frac{\pi k}{L})^4} \left[1 - \frac{k^2}{4\sqrt{q}} + \frac{k^2(k^2-2)}{32q} \right] + O(q^{-3/2}) & \text{if } k \text{ is even} \\ \frac{L}{2\pi^2} \left\{ -\frac{k^2}{q} + \frac{k^2(k^2-1)}{2q^{3/2}} - \frac{k^2}{q^2} \left[\frac{368k^4 - 928k^2 + 947}{2304} + \frac{1}{16} \left(\frac{L}{\pi}\right)^4 \omega^2 \right] \right\} + O(q^{-5/2}) & \text{if } k \text{ is odd.} \end{cases} \quad (41)$$

From this expression, we can draw a number of interesting conclusions. We find that the response function behaves quite differently for even and odd Fourier coefficients in the strong interaction regime. If we apply a potential with general coefficients $\delta v(k, \omega)$ to the system, the density change $\delta n(k, \omega)$ is strongly suppressed for odd k as $\chi(k, \omega)$ becomes very small. In this limit it will therefore mainly have even Fourier coefficients, which implies that $\delta n(x, t) = \delta n(x + \frac{L}{2}, t)$, i.e., the density change at antipodal points of the ring is the same. If we, however, apply a potential with only odd Fourier coefficients, the density change has the symmetry $\delta n(x, t) =$

$-\delta n(x + \frac{L}{2}, t)$ and is therefore opposite in antipodal points of the ring. From Eq. (41) we find that the leading term in real space in this case is given by

$$\delta n(x, t) = \frac{n_0}{q} \left(\frac{L}{2\pi}\right)^4 \partial_x^2 \delta v(x, t). \quad (42)$$

We can understand the dependence on q as follows. The generation of an antisymmetric antipodal density requires excitation to states with an odd number of nodes in the relative wave function, which requires a large energy in the strong interaction limit and therefore the density response is

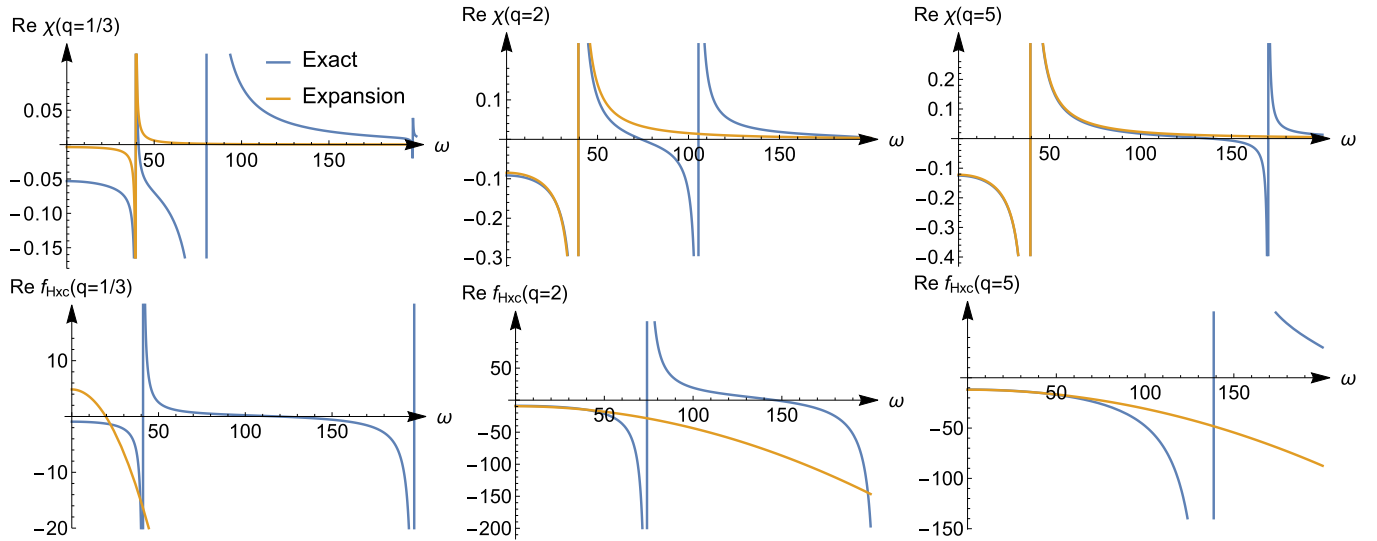


FIG. 3. The real part of $\chi(k=2, \omega)$ in units of L (top) and $f_{\text{Hxc}}(k=2, \omega)$ in units of L^{-1} (bottom) for different values of the interaction strength q . The exact results are obtained by numerical integration, and the expansion of χ and f_{Hxc} is taken up to the same order as shown in Eqs. (41) and (52).

suppressed for large interaction strength. From Eq. (42) we also see that the density increases instantaneously around the points where the potential has positive curvature. The instantaneous nature of the response has a simple explanation. If we perturb the system with a potential $\delta v(k, \omega)$ which is only nonzero for frequencies ω well below the first excitation energy, the temporal variation of the perturbation is much slower than a typical time scale of the free evolution of the system and the density response can be regarded as instantaneous. Since the excitation energies ΔE_{kl}^+ for odd k (which must have odd l as well) increase proportionally to \sqrt{q} , the density response function in this case is well approximated by a frequency-independent function for $\omega \ll \sqrt{q}$, which explains the instantaneous dependence of the density variation on the perturbation in Eq. (42).

For even values of k , the density response function has a more interesting frequency dependence. In the strong interaction limit

$$\lim_{q \rightarrow \infty} \chi(k, \omega) = \frac{8}{L} \frac{(\pi k/L)^2}{(\omega + i\eta)^2 - (\pi k/L)^4}. \quad (43)$$

The poles of this response function correspond to the center-of-mass excitations of Eq. (11). Being independent of q , they are not shifted towards infinity when we increase the interaction strength. This is a peculiarity of the quantum ring system as the Hamiltonian is separable in a λ -dependent and a λ -independent part. This happens also for some other homogeneous systems such as the three-dimensional electron gas with periodic boundary conditions or for electrons restricted to the surface of a sphere [53]. The analysis based on Eq. (19) shows that such a separation is usually not possible in inhomogeneous systems. When it is possible, both parts will generally still depend on λ (see Appendix A for an example).

To illustrate the accuracy of the expansion in Eq. (41) we display the exact response function and the expanded one in the top panels of Fig. 3 for $k=2$ and for some values of the interaction strength. For small interactions ($q=1/3$), the

exact response function has two poles; one is approximately at the same location as the Kohn-Sham response function ($\omega = 2(\pi k/L)^2$), while a new pole with a small weight appears at the center-of-mass excitation energy at $\omega = (\pi k/L)^2$. The expansion captures this pole, albeit with a very different weight. When we increase the interaction strength, the pole originally at the Kohn-Sham energy will shift to higher energies to a position proportional to \sqrt{q} , while the pole corresponding to the center-of-mass excitation stays fixed and increases in weight. Already at $q=5$, the asymptotic expansion yields good results for this k value. We thus see that the expansion is accurate for frequencies that are small compared to \sqrt{q} . This result was to be expected since in the expansion of Eq. (41) we treated the frequency ω as a constant that is small compared \sqrt{q} .

Having obtained the exact response function, we have obtained all information needed to study the xc kernel of TDDFT, which will be the topic of the next section.

IV. TDDFT IN THE STRONG INTERACTION LIMIT

A. The exchange-correlation kernel

In TDDFT an effective noninteracting system, known as the Kohn-Sham system, is constructed in such a way as to have exactly the same density as the interacting many-particle system of interest. The external potential in this system, $v_s([n]; \mathbf{r}t)$, is a functional of the density [6,41] and is often written as follows

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + \int d\mathbf{r}' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}', t) + v_{\text{xc}}(\mathbf{r}t). \quad (44)$$

Here $v(\mathbf{r}t)$ is the external potential of the interacting system of interest and $w(\mathbf{r}, \mathbf{r}')$ is the two-particle interaction of that system. The second term in Eq. (44) is the Hartree potential and the last one is the exchange-correlation (xc) potential. Taking the functional derivative of Eq. (44) with respect to the density, one obtains

$$\chi_s^{-1}(\mathbf{r}t, \mathbf{r}'t') = \chi^{-1}(\mathbf{r}t, \mathbf{r}'t') + f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t'). \quad (45)$$

Here χ_s^{-1} is the inverse of the Kohn-Sham density response function whereas χ^{-1} is the inverse of the density response function of the interacting system and f_{Hxc} , the Hartree-xc kernel, is defined as

$$f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{\text{Hxc}}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}, \quad (46)$$

where v_{Hxc} is the sum of the Hartree and the xc potential. Equation (45) is commonly used to calculate χ from the knowledge of χ_s at the price of approximating f_{Hxc} .

For the discussion in the next section, it is important to note that the functional derivative is not a uniquely defined function [41,54] due to the fact that for a system with a fixed number of particles the density change must integrate to zero at any time, i.e.,

$$0 = \int d\mathbf{r} \delta n(\mathbf{r}t). \quad (47)$$

Let us define a new function

$$\tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') + g(\mathbf{r}, t, t') + h(\mathbf{r}', t, t') \quad (48)$$

with g and h arbitrary functions. The change in the Hartree-xc potential produced by the kernel of Eq. (48) due to a density change δn is given by

$$\begin{aligned} \delta \tilde{v}_{\text{Hxc}}(\mathbf{r}t) &= \int d\mathbf{r}' dt' \tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t') \\ &= \int d\mathbf{r}' dt' f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t') \end{aligned}$$

$$f_{\text{Hxc}}(k, \omega) = \begin{cases} -\frac{3\pi^2 k^2}{8L} - \frac{1}{\sqrt{\lambda}} \frac{L^2}{\sqrt{V_0}} \frac{1}{16\pi} [\omega^2 - (\frac{\pi k}{L})^4] + \frac{1}{\lambda} \frac{L}{V_0} \frac{k^2+2}{64} [\omega^2 - (\frac{\pi k}{L})^4] + O(\lambda^{-3/2}) & \text{if } k \text{ is even} \\ \lambda \frac{V_0 L}{2k^2} + \sqrt{\lambda} \frac{\sqrt{V_0} \pi (k^2-1)}{2k^2} - \frac{\pi^2 (368k^4 + 224k^2 + 371)}{1152k^2 L} + O(\lambda^{-1/2}) & \text{if } k \text{ is odd} \end{cases} \quad (52)$$

where we have reintroduced the variable λ rather than q as the λ notation is commonly used in the density functional context, which will be central for the discussion in the next section. Since these quantities only differ by a numerical prefactor [see Eq. (4)] we will refer to the large interaction regime as the regime in which either of these two variables tends to infinity.

To illustrate the accuracy of the expansion in Eq. (52) we display the exact f_{Hxc} kernel and the expanded one in the bottom panels of Fig. 3 for $k=2$ and some values of the interaction strength. We see that the corresponding asymptotic expansion for f_{Hxc} is accurate up to the lowest excitation energy corresponding to a change in the relative wave function. In this energy region f_{Hxc} has a pole at an energy corresponding to a zero in χ , as a consequence of Eq. (51). It is worth noticing that since the noninteracting response function has no zeros, there is no pole in f_{Hxc} originating from the first term in Eq. (51). This is peculiar to our quantum ring system for which the noninteracting response function has only a single pole for $\omega > 0$. Instead, for a general system, the Kohn-Sham response function will have multiple poles and zeros which implies that, to order λ^0 , f_{Hxc} is frequency dependent, causing the adiabatic approximation to fail in this order. In our system,

$$\begin{aligned} &+ \int d\mathbf{r}' dt' [g(\mathbf{r}, t, t') + h(\mathbf{r}', t, t')] \delta n(\mathbf{r}'t') \\ &= \delta v_{\text{Hxc}}(\mathbf{r}t) + C(t), \end{aligned} \quad (49)$$

where the integral over g integrates to zero as a consequence of Eq. (47) and the integral over h yields a function $C(t)$ of time t only, which is merely a gauge of the potential. We therefore see that \tilde{f}_{Hxc} and f_{Hxc} are physically equivalent integral kernels. The quantity that is defined unambiguously¹ is the mixed spatial derivative

$$\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \tilde{f}_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t') = \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} f_{\text{Hxc}}(\mathbf{r}t, \mathbf{r}'t'), \quad (50)$$

a property that will be used below.

Let us turn to the specific case of the quantum ring. The density response function is diagonal in the momentum-energy representation and for the Fourier components the following relation holds:

$$f_{\text{Hxc}}(k, \omega) = \frac{1}{\chi_s(k, \omega)} - \frac{1}{\chi(k, \omega)}. \quad (51)$$

By Fourier transforming the kernel f_{Hxc} we impose a dependence on the relative coordinate in real space, which reduces the ambiguity of Eq. (48) to that of adding an arbitrary spatially constant function. In Eq. (51) this freedom is reflected in the fact that the kernel is well defined for all k values except for $k=0$, since in this case both the response functions vanish. For the homogeneous quantum ring, the Kohn-Sham response function coincides with the response function of truly noninteracting electrons of Eq. (34). Using this equation, together with the expansion of Eq. (41), we obtain an explicit expression for f_{Hxc} in the strong interaction limit:

f_{Hxc} for even k tends to a frequency-independent function for all ω when the interaction strength approaches infinity. Its static value, given by $f_{\text{Hxc}} = -\frac{3L}{8} (\frac{\pi k}{L})^2 = \chi_s^{-1}[k, \omega = (\frac{\pi k}{L})^2]$, is the value needed to shift the Kohn-Sham pole to the $q \rightarrow \infty$ pole.

For the odd k values (not shown here), all poles in the response function shift to infinity as $q \rightarrow \infty$. The asymptotic expansion for f_{Hxc} captures this, and the kernel becomes frequency independent in this limit. In fact, for odd values of k in Eq. (52), all the leading terms up to order λ^0 are frequency independent. However, frequency-dependent terms will appear to order $\lambda^{-1/2}$ (not presented here) as is also the case for even k .

For the discussion in the next section it is useful to recast the kernel in real space. The expressions in Eq. (52) are sufficient to calculate this quantity to order λ^0 in real space using the

¹Note that Ref. [31] did not discuss the possible addition of arbitrary functions of one spatial variable to the kernel.

Fourier transform of Eq. (53)

$$f_{\text{Hxc}}(r, \omega) = \frac{1}{L} \sum_{k=-\infty}^{\infty} f_{\text{Hxc}}(k, \omega) e^{\frac{2\pi i k r}{L}} \quad (53)$$

and $r = x - x'$ is the relative distance between the points x and x' , which are the one-dimensional counterparts of the spatial points in Eq. (46). Since x and x' are both in the interval from 0 to L we have that $r \in [-L, L]$. We find that

$$f_{\text{Hxc}}(r, \omega) = \lambda f_1(r) + \sqrt{\lambda} f_2(r) + f_3(r) + O(\lambda^{-1/2}). \quad (54)$$

The leading term is given explicitly by

$$f_1(r) = \frac{V_0 \pi^2}{2L} \left[-|r| + \left| r + \frac{L}{2} \right| + \left| r - \frac{L}{2} \right| - \frac{3L}{4} \right] \quad (55)$$

in which we choose the arbitrary constant function [see the discussion below Eq. (51)] such that the Fourier coefficient of f_1 becomes zero for $k = 0$. For f_2 we find (up to a constant) that

$$f_2(r) = \frac{\sqrt{V_0} \pi}{4} \left[\delta(r) - \delta\left(r + \frac{L}{2}\right) - \delta\left(r - \frac{L}{2}\right) \right] - \frac{\sqrt{V_0} \pi^3}{2L^2} \left[-|r| + \left| r + \frac{L}{2} \right| + \left| r - \frac{L}{2} \right| - \frac{3L}{4} \right]. \quad (56)$$

Since in the next section we will focus mostly on f_1 and f_2 , we do not report here the real space representation of f_3 . In the next section, we will show how f_1 and f_2 can be calculated in an alternative manner using the SCE theory in the adiabatic approximation.

B. Expanding the xc kernel in the theory of strictly correlated electrons

To date, no good and reliable approximations for electrons in the strong correlation regime have been developed within TDDFT. A ground-state theory of so-called strictly correlated electrons (SCE) [32,50] has been constructed and applied within the adiabatic approximation to calculate the xc kernel to the leading order in the interaction strength. In this section, we will first benchmark this approximation against the exact solution for the quantum ring model and then derive and compare the next order.

Let us begin with a brief overview of the ingredients of SCE theory that we will use. The Hartree-xc energy for a system with interaction strength λ can be written as [55]

$$E_{\text{Hxc}}^\lambda = \int_0^\lambda d\lambda' W_{\lambda'}[n], \quad (57)$$

where we defined

$$W_\lambda[n] = \langle \Psi_\lambda[n] | \hat{W} | \Psi_\lambda[n] \rangle. \quad (58)$$

In this expression, \hat{W} is the two-particle interaction and $\Psi_\lambda[n]$ is the ground-state wave function of a system with a local external potential, interaction $\lambda \hat{W}$, and ground-state density n .

In the strong interaction limit, $W_\lambda[n]$ can be expanded as [33]²

$$W_\lambda[n] = V_{\text{SCE}}[n] + \frac{V_{\text{ZPE}}[n]}{\sqrt{\lambda}} + O(\lambda^{-3/2}), \quad (59)$$

where the first term is the SCE energy, which has the explicit form

$$V_{\text{SCE}}[n] = \frac{1}{2} \sum_{i=2}^N \int d\mathbf{r} n(\mathbf{r}) w(|\mathbf{r} - \mathbf{f}_i([n]; \mathbf{r})|), \quad (60)$$

where w is the two-particle interaction which we assume to depend only on the distance between the particles. The functions $\mathbf{f}_i([n]; \mathbf{r})$ are the so-called comotion functions, which specify the position of $N - 1$ electrons given the position of one electron at \mathbf{r} . The second term in Eq. (59) contains the so-called zero-point energy (ZPE), which describes the vibrations of the electrons around their equilibrium positions and is given explicitly as

$$V_{\text{ZPE}}[n] = \frac{1}{2} \int d\mathbf{r} \frac{n(\mathbf{r})}{N} \sum_{n=1}^{D(N-1)} \frac{\omega_n(\mathbf{r})}{2}, \quad (61)$$

where D is the spatial dimensionality of the system and ω_n are the harmonic frequencies. Inserting Eq. (59) into Eq. (57), we find the large λ expansion of the Hartree-xc energy to be

$$E_{\text{Hxc}}^\lambda = \lambda V_{\text{SCE}}[n] + 2\sqrt{\lambda} V_{\text{ZPE}}[n] + O(\lambda^0). \quad (62)$$

The ground-state theory can be used in the adiabatic approximation [31] to find an approximate exchange-correlation kernel from

$$f_{\text{Hxc}}^{\text{A}}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta^2 E_{\text{Hxc}}^\lambda}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \delta(t - t'), \quad (63)$$

where we added the superscript A to indicate that we make the adiabatic approximation. This approximation yields a frequency-independent Hartree-xc kernel when transformed to frequency space, which we denote as $f_{\text{Hxc}}^{\text{A}}(\mathbf{r}, \mathbf{r}')$. The second-order variation of Eq. (62) with respect to the density gives an expansion in orders of $\sqrt{\lambda}$ for the Hartree-xc kernel:

$$f_{\text{Hxc}}^{\text{A}}(\mathbf{r}, \mathbf{r}') = \lambda f^{\text{ASCE}}(\mathbf{r}, \mathbf{r}') + \sqrt{\lambda} f^{\text{AZPE}}(\mathbf{r}, \mathbf{r}') + O(\lambda^0), \quad (64)$$

where we defined the adiabatic SCE and ZPE kernels as

$$f^{\text{ASCE}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 V_{\text{SCE}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}, \quad (65)$$

$$f^{\text{AZPE}}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta^2 V_{\text{ZPE}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}. \quad (66)$$

Let us now turn again to the case of the quantum ring. In this case, there are two electrons and just one simple comotion

²Strictly speaking, the absence of a term of order λ^{-1} in this expansion has only been shown for a Coulomb system but we find it to be true in our model as well.

function $f : [0, L] \rightarrow [0, L]$ given by

$$f(x) = \begin{cases} x + \frac{L}{2} & \text{if } x \in [0, \frac{L}{2}) \\ x - \frac{L}{2} & \text{if } x \in [\frac{L}{2}, L]. \end{cases} \quad (67)$$

If one electron is at x , this function simply puts the other electron at the antipodal point of the quantum ring. From this comotion function, it is straightforward to calculate the SCE energy. Since $|x - f(x)| = L/2$, we have from our interaction $w(x) = V_0 \cos^2(\pi x/L)$ in Hamiltonian (1) that $w(|x - f(x)|) = 0$ and therefore $V_{\text{SCE}} = 0$ for our density. Physically this means that the electrons are simply localized at the bottom of a potential well with zero energy.

To next order, oscillations around these equilibrium positions start to appear. These zero-point oscillations give an energy contribution which can be calculated using Eq. (61). For a one-dimensional two-electron system there is only one nonzero harmonic frequency given by [56]

$$\omega_1(x) = \sqrt{w''(|x - f(x)|) \left(\frac{n(x)}{n[f(x)]} + \frac{n[f(x)]}{n(x)} \right)}, \quad (68)$$

where $w''(x) = \partial_x^2 w(x)$. If we calculate this frequency for our quantum ring, we find $\omega_1(x) = 2\pi\sqrt{V_0}/L$ and $V_{\text{ZPE}} = \pi\sqrt{V_0}/(2L)$. We can verify that this is in accordance with the exact strong interaction expansion of the Hartree-xc energy. Since the Kohn-Sham kinetic energy as well as the external potential is zero for the quantum ring system, E_{Hxc}^λ simply coincides with the total energy, which is known in the strong interaction limit from the large- q expansion of the lowest Mathieu characteristic value (see Appendix B). This gives

$$E_{\text{Hxc}}^\lambda = \frac{\pi\sqrt{V_0}}{L}\sqrt{\lambda} - \frac{\pi^2}{4L^2} - \frac{\pi^3}{16L^3\sqrt{V_0}\sqrt{\lambda}} + O(\lambda^{-1}), \quad (69)$$

where the leading coefficient indeed exactly gives $2V_{\text{ZPE}}$. The expansion of W_λ can be calculated from Eq. (57) to give

$$W_\lambda = \frac{dE_{\text{Hxc}}^\lambda}{d\lambda} = \frac{\pi\sqrt{V_0}}{2L}\frac{1}{\sqrt{\lambda}} + \frac{\pi^3}{32L^3\sqrt{V_0}}\frac{1}{\lambda^{3/2}} + O(\lambda^{-2}). \quad (70)$$

This result agrees with a direct calculation of W_λ using the Sips expansion of the Mathieu functions and indeed has the structure of the expansion in Eq. (59) in which we also included the term to order $\lambda^{-3/2}$.

Let us turn to the calculation of the kernels of Eqs. (65) and (66).

The ASCE kernel is obtained from the expression derived in Ref. [31] and reads

$$\begin{aligned} f^{\text{ASCE}}(x, x') &= - \int_0^x dy \frac{w''(|y - f(y)|)}{n[f(y)]} \\ &\quad \times [\theta(y - x') - \theta(f(y) - x')] \\ &= f_1(x - x') - f_1(x) - f_1(x') + f_1(0), \end{aligned} \quad (71)$$

where f_1 is the function given in Eq. (55). Because of the freedom in Eq. (48) f^{ASCE} is physically equivalent to the kernel $f_1(x - x')$ and agrees with the leading term in the expansion of Eq. (54) in the strong interaction limit. Both kernels are shown in Fig. 4. Since $f_1(x - x')$ has a simpler shape, we will restrict ourselves to this function. The kernel describes how a

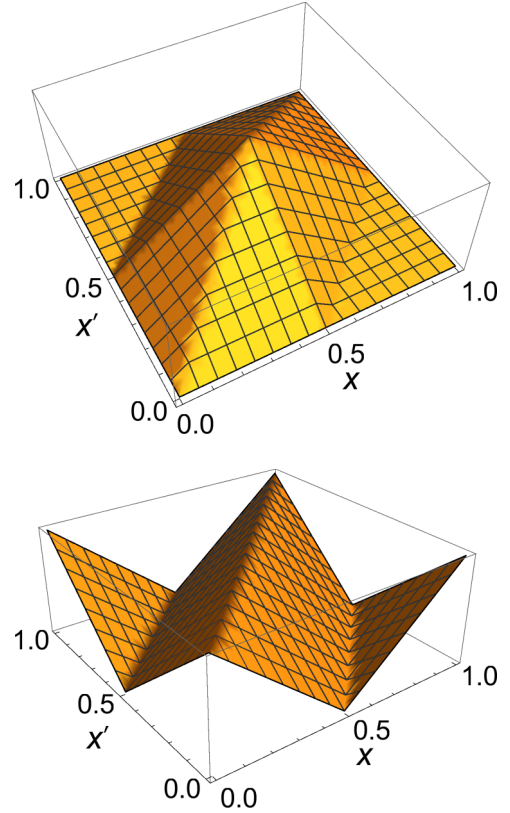


FIG. 4. Top: The Hxc kernel $f^{\text{ASCE}}(x, x')$ of Eq. (71). Bottom: The physically equivalent Hxc kernel $f_1(x - x')$ of Eq. (55). The x and x' axes are in units of L and f_{Hxc} is given in arbitrary units.

density variation induces a change in v_{Hxc} . To leading order in λ we have

$$\delta v_{\text{Hxc}}(x, t) = \lambda \int dx' f_1(x - x') \delta n(x', t).$$

By taking the second derivative of this equation, we obtain

$$\begin{aligned} \partial_x^2 \delta v_{\text{Hxc}}(x, t) &= \lambda \frac{V_0 \pi^2}{L} [-\delta n(x, t) + \delta n(x + L/2, t) \\ &\quad + \delta n(x - L/2, t)], \end{aligned} \quad (72)$$

where we stress that $\delta n(x, t)$ is periodic with L . Since $f_1(x - x')$ is linear everywhere except at the kinks at $x - x' = 0, \pm L/2$, the second derivatives yield δ functions at these points. Also note that the sign of the density change yields the curvature of the induced potential. Equation (72) has some interesting consequences. If we make a localized density variation $\delta n(x, t)$ in a very small interval of the ring, there will not only be a change δv_{Hxc} in the same interval, but at the same time a similar change in the potential with opposite sign in an antipodal interval. This shows very clearly that the Hxc-potential depends nonlocally, but instantaneously, on the density.

Let us analyze the next orders in the strong interaction expansion. The calculation of f^{AZPE} allows for a comparison with the next leading term in Eq. (54), which is proportional to $\sqrt{\lambda}$. The kernel f^{AZPE} was obtained by taking the second functional derivative of the one-dimensional counterpart of Eq. (61), using Eq. (68) and the functional derivative of the

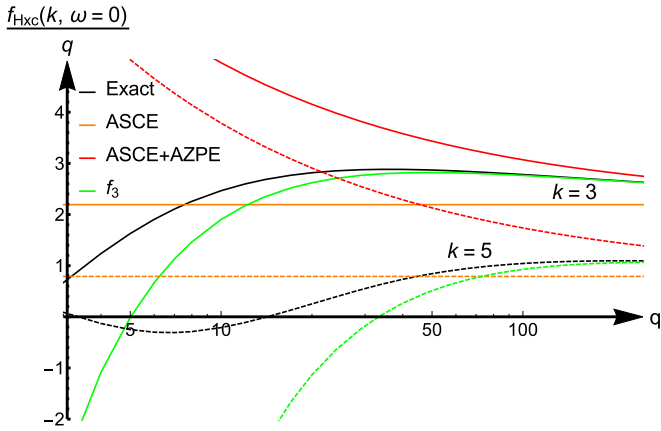


FIG. 5. The static $f_{\text{Hxc}}(k, \omega = 0)/q$ as function of q , for $k = 3$ (solid lines) and $k = 5$ (dashed lines) in units of L^{-1} . We show the exact kernel obtained by numerical integration, and compare ASCE, ASCE+AZPE, and ASCE+AZPE+ f_3 (denoted by f_3 in the figure) coming from Eq. (54). Note that we plot the kernel as function of q instead of λ [see Eq. (4)] in order to be consistent with the previous figures.

comotion functions (derived already in Ref. [31]). We also find agreement between this expression and that of the next leading term in Eq. (56), i.e., $f^{\text{AZPE}}(x, x') = f_2(x - x')$ modulo the addition of arbitrary functions of x and x' separately [see again Eq. (48)]. We observe that the first two leading terms of the expansion of the Hartree-xc kernel from the adiabatic SCE theory agree with the exact results for the quantum ring. An interpretation of this fact will be presented below.

We have thus seen that, in this model, the ASCE and AZPE terms agree with the terms f_1 and f_2 respectively of the exact asymptotic expansion. To better elucidate their role in the strong interaction limit, we show in Fig. 5 the first three terms contributing to f_{Hxc} , all scaled by λ , and compare them with the expression for the exact kernel, in Fourier space for $k = 3$ and $k = 5$. As was pointed out earlier, the accuracy of the expansion depends on the value of k : high k values require higher λ values to achieve better accuracy. The first term, that is the ASCE, is constant, while the second one, that is the AZPE, only improves on it for large λ values and worsens it for smaller ones, as one would expect for an asymptotic expansion. The third term, beyond the AZPE, also exhibits a non-negligible contribution in the small- λ regime.

We will now offer a physical interpretation of the above terms and make some considerations about their properties in the case of more general systems than the quantum ring model. In the (infinitely) strong interaction limit, a given system behaves very rigidly, since the position of the reference electron determines the positions of all the remaining electrons. Upon application of a perturbation, the response of the system is instantaneous, or adiabatic, while maintaining its rigidity, unless special symmetries are present. This behavior is likely to apply to a wider class of systems, both with a uniform (such as the quantum ring) and a nonuniform density. On the other hand, it is unclear whether the frequency independence of f_2 is equally general as we already move away from the strictly correlated electron limit by introducing zero-point vibrations: Thus the adiabaticity of f_2 for general systems is still an open

issue. Finally, as already noted before, the third term f_3 of the expansion will be nonadiabatic for general systems.

V. CONCLUSIONS

In this work, we have considered an exactly solvable model consisting of two interacting electrons on a quantum ring. We focused on the response properties and calculated the energy spectrum, the excitation amplitudes, the density response function, and the exchange-correlation kernel of time-dependent density functional theory. In the limit of strong interaction, we derived the asymptotic expansion in powers of the square root of the interaction strength for the response function and kernel. For the kernel, we found that its leading terms are local in time but nonlocal in space. This already shows that the commonly used adiabatic local-density, or semilocal, approximations will fail for such strongly correlated systems, since they are local both in time and space. We compared the expansion for the kernel to a similar one obtained from the adiabatic-SCE formalism [31] which has the spatial nonlocality built in. The leading term of the exact expansion was found to coincide with the adiabatic-SCE kernel derived in Ref. [31]. After working out the next order term, the so-called zero-point energy contribution, we found that it also coincided with the exact next-to-leading term. For our model, the subsequent term in the expansion is still adiabatic, but we showed that in general systems this term will be nonadiabatic.

The agreement with our exact results puts the adiabatic-SCE and the adiabatic-ZPE approximations on firmer ground and gives confidence in employing the formalism of strictly correlated electrons in the adiabatic approximation for calculating response properties of strongly correlated systems.

ACKNOWLEDGMENTS

L.C., D.K., and R.v.L. acknowledge the Academy of Finland for support under Project No. 267839. G.L. acknowledges the Université Pierre et Marie Curie through an ATER position.

APPENDIX A: RESPONSE FUNCTION OF A HARMONIC MODEL SYSTEM

To illustrate some properties of the response function in the large interaction limit for an inhomogeneous system, let us analyze a model system of two harmonically confined electrons in three dimensions with a harmonic repulsion [57]. The Hamiltonian of the system is given by

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}\omega_\lambda^2(|\mathbf{r}_1|^2 + |\mathbf{r}_2|^2) - \frac{\lambda}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2, \quad (\text{A1})$$

in which the harmonic frequency ω_λ is chosen in such a way that the density is independent of λ . Using the coordinate transformation $\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}$ and $\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2}$, the Hamiltonian can be written as that of two independent harmonic oscillators

$$\hat{H} = -\frac{1}{2}(\nabla_s^2 + \nabla_r^2) + \frac{1}{2}\omega_\lambda^2|\mathbf{s}|^2 + \frac{1}{2}\nu_\lambda^2|\mathbf{r}|^2, \quad (\text{A2})$$

where $v_\lambda^2 = \omega_\lambda^2 - 2\lambda$. The eigenfunctions and eigenvalues of this Hamiltonian are well known. The normalized eigenfunctions are given by

$$\Psi_{\mathbf{nm}}(\mathbf{s}, \mathbf{r}) = (\omega_\lambda v_\lambda)^{3/4} \Phi_{\mathbf{n}}(\sqrt{\omega_\lambda} \mathbf{s}) \Phi_{\mathbf{m}}(\sqrt{v_\lambda} \mathbf{r}), \quad (\text{A3})$$

where we defined the triplet of non-negative integers $\mathbf{n} = (n_1, n_2, n_3)$ and $\mathbf{m} = (m_1, m_2, m_3)$ and the functions

$$\Phi_{\mathbf{n}}(\mathbf{x}) = \mathcal{H}_{\mathbf{n}}(\mathbf{x}) \frac{e^{-|\mathbf{x}|^2/2}}{\pi^{3/4}}$$

in which we denoted

$$\mathcal{H}_{\mathbf{n}}(\mathbf{x}) = \frac{H_{n_1}(x_1)H_{n_2}(x_2)H_{n_3}(x_3)}{\sqrt{2^{|\mathbf{n}|} n_1! n_2! n_3!}}, \quad (\text{A4})$$

where $|\mathbf{n}| = n_1 + n_2 + n_3$ and $H_n(x)$ is the Hermite polynomial of order n . The energy eigenvalues are given by

$$E_{\mathbf{nm}} = \omega_\lambda (|\mathbf{n}| + \frac{3}{2}) + v_\lambda (|\mathbf{m}| + \frac{3}{2}). \quad (\text{A5})$$

The ground-state wave function $\Psi_0 = \Psi_{\mathbf{00}}$ has the explicit form

$$\Psi_0(\mathbf{s}, \mathbf{r}) = \left[\frac{\omega_\lambda v_\lambda}{\pi^2} \right]^{3/4} e^{-\omega_\lambda |\mathbf{s}|^2/2 - v_\lambda |\mathbf{r}|^2/2}. \quad (\text{A6})$$

From this function, the density is readily obtained as

$$n(\mathbf{x}) = 2 \left[\frac{\beta}{\pi} \right]^{3/2} e^{-\beta |\mathbf{x}|^2}, \quad (\text{A7})$$

where we defined

$$\beta = \frac{2\omega_\lambda v_\lambda}{\omega_\lambda + v_\lambda}. \quad (\text{A8})$$

If we insert $v_\lambda = \sqrt{\omega_\lambda^2 - 2\lambda}$ into this relation, we can determine the λ dependence of ω_λ as β is independent of λ . We find

$$\omega_\lambda = \sqrt{\frac{\lambda}{2}} \left(y + \frac{1}{y} \right), \quad (\text{A9})$$

$$v_\lambda = \sqrt{\frac{\lambda}{2}} \left(y - \frac{1}{y} \right), \quad (\text{A10})$$

where y solves the quartic equation

$$y^4 - \beta \sqrt{\frac{2}{\lambda}} y^3 - 1 = 0. \quad (\text{A11})$$

In the limit of large interaction, we find that $y = 1 + \beta/(2\sqrt{2\lambda}) + O(\lambda^{-1})$ such that

$$\omega_\lambda = \sqrt{2\lambda} + O(1) \quad (\text{A12})$$

$$v_\lambda = \beta/2 + O(\lambda^{-1}). \quad (\text{A13})$$

We see that the harmonic frequency of the center-of-mass mode approaches infinity, whereas the one of the relative mode approaches a finite value. This has interesting consequences for the excitation spectrum. For the excitation energies of the relative mode, it implies that

$$\lim_{\lambda \rightarrow \infty} (E_{\mathbf{0m}} - E_{\mathbf{00}}) = \frac{\beta}{2} |\mathbf{m}| \quad (\text{A14})$$

while all other excitation energies diverge to infinite values at large interaction strength. The latter correspond to excitations of the center-of-mass mode. In contrast to the quantum ring, only the excitation energies of the relative mode remain finite in the large interaction limit, which is due to the very different nature of the two-body interaction.

Let us turn our attention to the density response function. In the response function, only the singlet excitations contribute. This means that the spatial wave functions that we need to consider are symmetric in the interchange of the particle positions. For this to be true, the relative wave functions need to be even and we have to require that $|\mathbf{m}|$ only attains even values. The response function therefore has the form

$$\chi(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\mathbf{n}, \mathbf{m}} \left[\frac{D_{\mathbf{nm}}(\mathbf{r}_1) D_{\mathbf{nm}}^*(\mathbf{r}_2)}{\omega - \Delta E_{\mathbf{nm}} + i\eta} - \frac{D_{\mathbf{nm}}(\mathbf{r}_2) D_{\mathbf{nm}}^*(\mathbf{r}_1)}{\omega + \Delta E_{\mathbf{nm}} + i\eta} \right], \quad (\text{A15})$$

where $\Delta E_{\mathbf{nm}} = E_{\mathbf{nm}} - E_{\mathbf{00}}$ are the excitation energies and we further put the restriction that we sum over all \mathbf{m} such that $|\mathbf{m}|$ is even. The excitation amplitudes corresponding to these excitations are given by

$$\begin{aligned} D_{\mathbf{nm}}(\mathbf{r}_1) &= \langle \Psi_0 | \hat{n}(\mathbf{r}_1) | \Psi_{\mathbf{nm}} \rangle \\ &= 2 \int d\mathbf{r}_2 \Psi_{\mathbf{00}}^*(\mathbf{r}_1, \mathbf{r}_2) \Psi_{\mathbf{nm}}(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (\text{A16})$$

where we rewrote the eigenfunctions in terms of the original coordinates. Let us now consider the large interaction limit $\lambda \rightarrow \infty$ of the response function. Since only the excitation energies of the form $\Delta E_{\mathbf{0m}}$ remain finite in this limit, we only need to consider the excitation amplitudes of the form

$$\begin{aligned} D_{\mathbf{0m}}(\mathbf{r}_1) &= 2 \left[\frac{\omega_\lambda v_\lambda}{\pi^2} \right]^{3/2} \int d\mathbf{r}_2 \mathcal{H}_{\mathbf{m}}(\sqrt{v_\lambda/2}(\mathbf{r}_1 - \mathbf{r}_2)) \\ &\quad \times e^{-\frac{\omega_\lambda}{2}(\mathbf{r}_1 + \mathbf{r}_2)^2 - \frac{v_\lambda}{2}(\mathbf{r}_1 - \mathbf{r}_2)^2}. \end{aligned} \quad (\text{A17})$$

If we now use that

$$\lim_{\lambda \rightarrow \infty} \left[\frac{\omega_\lambda}{2\pi} \right]^{3/2} e^{-\frac{\omega_\lambda}{2}(\mathbf{r}_1 + \mathbf{r}_2)^2} = \delta(\mathbf{r}_1 + \mathbf{r}_2) \quad (\text{A18})$$

is a limit representation for the delta distribution and the fact that $v_\lambda \rightarrow \beta/2$ in the large interaction limit, we find that

$$\lim_{\lambda \rightarrow \infty} D_{\mathbf{0m}}(\mathbf{r}_1) = 2 \left(\frac{\beta}{\pi} \right)^{3/2} \mathcal{H}_{\mathbf{m}}(\sqrt{\beta} \mathbf{r}_1) e^{-\beta |\mathbf{r}_1|^2}. \quad (\text{A19})$$

For the response function in the large interaction limit, we therefore obtain

$$\begin{aligned} \alpha(\mathbf{r}_1, \mathbf{r}_2, \omega) &= \lim_{\lambda \rightarrow \infty} \chi(\mathbf{r}_1, \mathbf{r}_2, \omega) \\ &= n(\mathbf{r}_1) n(\mathbf{r}_2) \sum_{\mathbf{m}} \mathcal{H}_{\mathbf{m}}(\sqrt{\beta} \mathbf{r}_1) \mathcal{H}_{\mathbf{m}}(\sqrt{\beta} \mathbf{r}_2) \\ &\quad \times \left[\frac{1}{\omega - \frac{\beta}{2} |\mathbf{m}| + i\eta} - \frac{1}{\omega + \frac{\beta}{2} |\mathbf{m}| + i\eta} \right], \end{aligned} \quad (\text{A20})$$

where the sum runs over \mathbf{m} values such that $|\mathbf{m}|$ is even. We see that in the large interaction limit it is still possible to excite the relative modes of the system.

Let us now have a look at the external potential in the strong interaction limit

$$v_\lambda(\mathbf{r}) = \frac{1}{2}\omega_\lambda^2|\mathbf{r}|^2 = \lambda|\mathbf{r}|^2 + O(\sqrt{\lambda}), \quad (\text{A21})$$

which implies $\nabla v_\lambda(\mathbf{r}) = 2\lambda\mathbf{r} + O(\sqrt{\lambda})$. Since the response function does not vanish in the large interaction limit, Eq. (20) tells us that

$$\mathbf{0} = \int d\mathbf{r}_2 \alpha(\mathbf{r}_1, \mathbf{r}_2; \omega = 0) \mathbf{r}_2$$

must hold, where we took the static limit of the response function of Eq. (A20). Since the polynomial functions in Eq. (A20) are all even (since $|\mathbf{m}|$ is even), and \mathbf{r}_2 is an odd function, we find that this relation is indeed satisfied.

APPENDIX B: SIPS'S EXPANSION OF THE MATHIEU FUNCTION

In this appendix we describe the details of the expansion of the Mathieu functions for large q . A recent general discussion is given by Frenkel and Portugal [47], who give an overview of various expansions for the Mathieu functions for large and small values of q in different regions of their domain and recursion formulas to determine the expansion coefficients. The expansion that we are interested in for this work is the large q expansion for the Mathieu cosine function $C_l(z; q)$ in the region enclosing the value $z = \pi/2$. Such an expansion was derived originally by Sips [43–46], who developed a systematic theory. For the Mathieu cosine, this expansion is of the form of Eq. (13). We here give the explicit expressions for the coefficients $c_{2n,l}(q)$ in Eq. (13), and for this it will be convenient to define new coefficients $g_{2n,l}(q)$

$$c_{2n,l}(q) = C_l(q) g_{2n,l}(q), \quad (\text{B1})$$

which only differ from the coefficients $c_{2n,l}(q)$ by a prefactor $C_l(q)$. This is done to ensure that $g_{0,l}(q) = 1$, which is convenient for a recursive calculation of the remaining coefficients $g_{2n,l}(q)$ as is done in Refs. [46,47]. The prefactor $C_l(q)$ is chosen such that the Mathieu cosine satisfies the normalization of Eq. (8). It has the explicit asymptotic expansion [44,46,47]

$$C_l(q) = \left(\frac{\pi\sqrt{q}}{2(l!)^2} \left(1 + \frac{2l+1}{8\sqrt{q}} + \frac{l^4 + 2l^3 + 263l^2 + 262l + 108}{2048q} + \dots \right) \right)^{-1/2}. \quad (\text{B2})$$

In terms of the new coefficients $g_{2n,l}(q)$, the Sips expansion of Eq. (13) becomes [46]

$$C_l(z; q) = C_l(q) \sum_{n=-\infty}^{\infty} g_{2n,l}(q) \mathcal{D}_{2n+l}(u), \quad (\text{B3})$$

where the functions $\mathcal{D}_l(u)$ are defined in Eq. (12) and $u = \sqrt{2}q^{1/4} \cos z$. Note that the expansion here differs in the choice of argument u compared to that of Ref. [43] by a factor of $\sqrt{2}$ as we preferred to use the physicists' convention for the Hermite polynomials appearing in the harmonic oscillator functions \mathcal{D}_l . We prefer here to avoid a general discussion on

the determination of $g_{2n,l}(q)$ and refer the interested reader to Refs. [46,47] for details. Instead, we give the explicit forms of the coefficients $g_{2n,l}(q)$ up to order $1/q$, which is sufficient for this work:

$$\begin{aligned} g_{-8,l}(q) &= \frac{1}{2^{13}q} 8! \binom{l}{8}, \\ g_{-6,l}(q) &= -\frac{1}{2^{10}q} 6! \binom{l}{6}, \\ g_{-4,l}(q) &= \left[\frac{1}{2^6\sqrt{q}} + \frac{(l-1)}{2^8q} \right] 4! \binom{l}{4}, \\ g_{-2,l}(q) &= -\left[\frac{1}{2^4\sqrt{q}} + \frac{(l^2 + 27l - 10)}{2^{10}q} \right] l(l-1), \\ g_{0,l}(q) &= 1, \\ g_{2,l}(q) &= \left[-\frac{1}{2^4\sqrt{q}} + \frac{(l^2 - 25l - 36)}{2^{10}q} \right], \\ g_{4,l}(q) &= \left[-\frac{1}{2^6\sqrt{q}} - \frac{(l+2)}{2^8q} \right], \\ g_{6,l}(q) &= \frac{1}{2^{10}q}, \quad g_{8,l}(q) = \frac{1}{2^{13}q}, \end{aligned}$$

where we define $\binom{n}{m} = 0$ if $n < m$. From the formulas given in Ref. [47], it is readily seen that to know the Sips expansion to order $q^{-k/2}$ we need to know the coefficients $g_{2n,l}(q)$ for $n \in \{-2k, \dots, 2k\}$. For example, the knowledge of the next order $q^{-3/2}$ would need the knowledge of the coefficients from $g_{-12,l}(q)$ up to $g_{12,l}(q)$; see, for example, Ref. [46].

To show the accuracy of the Sips expansion we display in Fig. 6 the Mathieu cosine $C_l(q; z)$ for $l = 0$ and $l = 3$ for $q = 1$ and $q = 10$ and compare them to the Sips expansion using the coefficients $g_{2n,l}(q)$ given explicitly above. We see that already at $q = 10$ the Sips expansion performs very well. In general, we find that for higher values of l more terms in the expansion need to be taken into account for high accuracy.

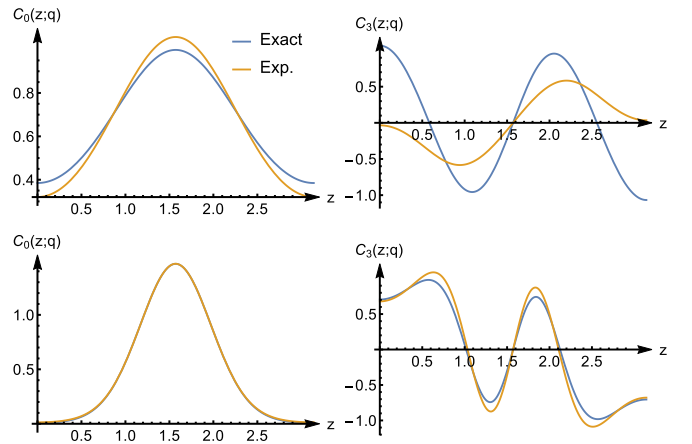


FIG. 6. Comparison of the exact Mathieu functions to the expansion Eq. (B3) for the large q limit in which the expansion coefficients $g_{2n,l}(q)$ that contain terms up to order $1/q$ were used. The upper (lower) panels have $q = 1$ ($q = 10$), while the left (right) panels have $l = 0$ ($l = 3$). The accuracy of the expansion converges to the exact case more quickly for lower values of l .

It remains to give the asymptotic values of the Mathieu characteristic value. The characteristic values $a_l^+(q)$ and $a_l^-(q)$ have the same asymptotic expansion of the form [47]

$$a_l^\pm(q) = -2q + 2(2l+1)\sqrt{q} - \frac{1}{4}(2l^2 + 2l + 1) - \frac{(2l+1)}{128\sqrt{q}}[(2l+1)^2 + 3] + O(q^{-1}), \quad (\text{B4})$$

while the difference $a_l^+(q) - a_l^-(q)$ is exponentially small in the large q limit [43].

APPENDIX C: EXPANSION OF THE EXCITATION AMPLITUDES

Here we further outline some general features of the expansion of the excitation amplitudes $D_{kl}(q)$. If we rewrite the expansion of Eq. (35) using the coefficients of Eq. (B1), we have the expression

$$D_{kl}(q) = \frac{2}{\pi} C_0(q) C_l(q) \sum_{n_1, n_2 = -\infty}^{\infty} g_{2n_1, 0}(q) \times g_{2n_2, l}(q) \mathcal{J}_{kl}^{n_1 n_2}(q). \quad (\text{C1})$$

For the products of the prefactors we can write

$$C_0(q) C_l(q) = q^{1/4} F_l(q), \quad (\text{C2})$$

where $F_l(q)$ has an expansion in powers of $q^{-1/2}$, i.e.,

$$F_l(q) = \frac{1}{l!} \sqrt{\frac{\pi}{2}} \left[1 - \frac{l+1}{8\sqrt{q}} + O(q^{-1}) \right] \quad (\text{C3})$$

and higher powers can be calculated from expression (B2). With these definitions and Eq. (39) we can rewrite the expansion of Eq. (C1) as

$$D_{kl}(q) = \frac{2}{\pi} F_l(q) \sum_{n_1, n_2 = -\infty}^{\infty} g_{2n_1, 0}(q) g_{2n_2, l}(q) \times \sum_{r=0}^{\infty} \frac{a_r(k) I_{n_1 n_2, r}^l}{(\sqrt{2})^{r+1} q^{r/4}}, \quad (\text{C4})$$

where the factor $q^{1/4}$ from Eq. (C2) has been absorbed in the last sum. The function $F_l(q)$ and the coefficients $g_{2n, l}(q)$ have an expansion in powers of $q^{-1/2}$. Now since the coefficients $I_{n_1 n_2, r}^l$ vanish unless k and l are both even or both odd, we conclude that $D_{kl}(q)$ has an expansion only in odd powers of $q^{-1/4}$ if l is odd and only in even powers of $q^{-1/4}$ otherwise. The explicit expression for $I_{n_1 n_2, r}^l$ is given by

$$I_{n_1 n_2, r}^l = \int_{-\infty}^{\infty} du u^r \mathcal{D}_{2n_1}(u) \mathcal{D}_{2n_2+l}(u) = \begin{cases} 0 & \text{If } r+l \text{ odd} \\ \frac{r!}{2^r} \sqrt{\pi} 2^{n_1+n_2+\frac{l}{2}} \sum_{p=\max(0, -s)}^{\min(2n_1, 2n_2+l)} \binom{2n_1}{p} \binom{2n_2+l}{p} \frac{p!}{2^{r(s+p)!}} & \text{otherwise} \end{cases}$$

where we defined $s = r/2 - n_1 - n_2 - l/2$ [58]. Finally the coefficients $a_r(k)$ can be obtained from a Taylor expansion of the function $f_k(x)$ defined in Eq. (38). Taking all these terms together, we find the following expansion of the excitation amplitude:

$$D_{kl}(q) = (-i)^k \left[1 - \frac{k^2}{8\sqrt{q}} + \frac{k^2(k^2-4)}{128q} - \frac{k^2(k^4-14k^2+46)}{3072q^{3/2}} + O(q^{-2}) \right] \delta_{l0} + (-i)^{k+1} \left[-\frac{k}{2q^{1/4}} + \frac{k(k^2-1)}{16q^{3/4}} - \frac{k(2k^4-16k^2+13)}{512q^{5/4}} + O(q^{-7/4}) \right] \delta_{l1} + (-i)^k \left[-\frac{k^2}{4\sqrt{2}\sqrt{q}} + \frac{k^2(2k^2-5)}{64\sqrt{2}q} + O(q^{-3/2}) \right] \delta_{l2} + (-i)^{k+1} \left[\frac{k(2k^2+1)}{16\sqrt{6}q^{3/4}} + O(q^{-5/4}) \right] \delta_{l3}. \quad (\text{C5})$$

The excitation amplitude indeed has an expansion in odd powers of $q^{-1/4}$ for odd l and in even powers of $q^{-1/4}$ for even l , as we demonstrated above. This implies that $|D_{kl}(q)|^2$ has an expansion in powers of $q^{-1/2}$. The expansion derived here has been checked numerically to ensure the correctness of the derivations. As a further check on the result, we see that the excitation amplitude satisfies $D_{kl}(q) = (-1)^{k+l} D_{kl}^*(q)$ as well as $D_{0l}(q) = \delta_{l0}$.

The order for $D_{kl}(q)$ given in Eq. (C5) is enough to yield the following asymptotic expansion for the absolute value squared of the excitation amplitudes to order $q^{-3/2}$:

$$|D_{kl}(q)|^2 = \left[1 - \frac{k^2}{4\sqrt{q}} + \frac{k^2(k^2-2)}{32q} - \frac{k^2(2k^4-13k^2+23)}{768q^{3/2}} \right] \delta_{l0} + \left[\frac{k^2}{4\sqrt{q}} + \frac{k^2(1-k^2)}{16q} + \frac{k^2(4k^4-20k^2+15)}{512q^{3/2}} \right] \delta_{l1} + \left[\frac{k^4}{32q} - \frac{k^4(2k^2-5)}{256q^{3/2}} \right] \delta_{l2} + \left[\frac{k^2(4k^4+4k^2+1)}{1536q^{3/2}} \right] \delta_{l3} + O(q^{-2}). \quad (\text{C6})$$

We compare the expansion of $|D_{kl}(q)|^2$ to the exact values obtained by numerically integrating Eq. (26) in Fig. 7. We see from this figure that higher values of k require higher values

of q to make the expansion accurate. This was to be expected since larger k values imply a more oscillatory integrand in Eq. (26), while a larger value of q makes the Mathieu functions

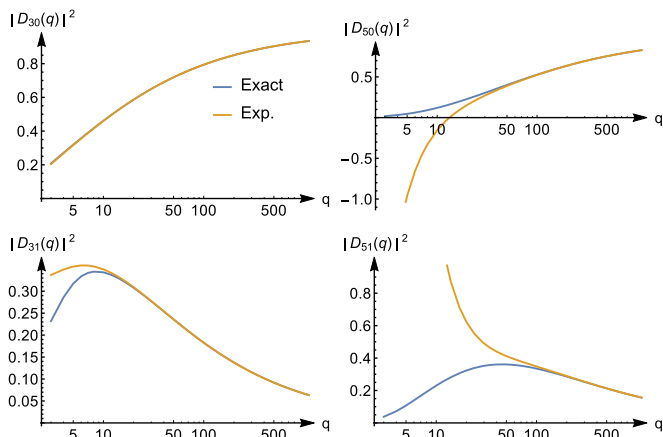


FIG. 7. Square $|D_{kl}(q)|^2$ of the excitation amplitudes for $l = 0$ (top) and $l = 1$ (bottom) for $k = 3$ (left) and $k = 5$ (right) as function of q . We compare the square of Eq. (26) (denoted by Exact) to the expansion of Eq. (C6) (denoted by Exp.).

more localized and thereby makes the expansion of Eq. (38) used in the integrand more accurate.

We finally note that the frequency-sum rule, Eq. (23), can be used to check the validity of some of the terms of Eq. (C6). If we insert the explicit form of Eq. (28) into the one-dimensional equivalent of Eq. (23) for the frequency sum rule, we can derive that

$$\sum_l (k^2 + [a_l^+(q) - a_0^+(q)]) |D_{kl}(q)|^2 = k^2, \quad (\text{C7})$$

where the sum runs over even l if k is even and over odd l when k is odd. The right-hand side is independent of the interaction strength q ; thus in the sum on the left-hand side the q dependence in the excitation amplitudes has to be compensated by the q dependence of the Mathieu characteristic values to give a result independent of the interaction strength.

- [1] E. K. U. Gross, J. F. Dobson, and M. Petersilka, Density functional theory of time-dependent phenomena, in *Density Functional Theory II: Relativistic and Time Dependent Extensions*, edited by R. F. Nalewajski (Springer, Berlin, 1996), pp. 81–172.
- [2] K. Burke, J. Werschnik, and E. K. U. Gross, Time-dependent density functional theory: Past, present, and future, *J. Chem. Phys.* **123**, 062206 (2005).
- [3] R. van Leeuwen, Key concepts in time-dependent density-functional theory, *Int. J. Mod. Phys. B* **15**, 1969 (2001).
- [4] C. A. Ullrich, *Time-Dependent Density-Functional Theory* (Oxford University Press, Oxford, UK, 2012).
- [5] M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio, (eds.), *Fundamentals of Time-Dependent Density Functional Theory*, Lecture Notes in Physics Vol. 837 (Springer, Berlin, 2012).
- [6] M. Ruggenthaler, M. Penz, and R. van Leeuwen, Existence, uniqueness, and construction of the density-potential mapping in time-dependent density-functional theory, *J. Phys.: Condens. Matter* **27**, 203202 (2015).
- [7] N. T. Maitra, Perspective: Fundamental aspects of time-dependent density functional theory, *J. Chem. Phys.* **144**, 220901 (2016).
- [8] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Excitation Energies from Time-Dependent Density-Functional Theory, *Phys. Rev. Lett.* **76**, 1212 (1996).
- [9] T. Stein, L. Kronik, and R. Baer, Reliable prediction of charge transfer excitations in molecular complexes using time-dependent density functional theory, *J. Am. Chem. Soc.* **131**, 2818 (2009).
- [10] O. Gritsenko and E. J. Baerends, Asymptotic correction of the exchange-correlation kernel of time-dependent density functional theory for long-range charge-transfer excitations, *J. Chem. Phys.* **121**, 655 (2004).
- [11] N. T. Maitra, Undoing static correlation: Long-range charge transfer in time-dependent density-functional theory, *J. Chem. Phys.* **122**, 234104 (2005).
- [12] J. Autschbach, Charge-transfer excitations and time-dependent density functional theory: Problems and some proposed solutions, *ChemPhysChem* **10**, 1757 (2009).
- [13] O. V. Gritsenko, S. J. A. van Gisbergen, A. Görling, and E. J. Baerends, Excitation energies of dissociating H₂: A problematic case for the adiabatic approximation of time-dependent density functional theory, *J. Chem. Phys.* **113**, 8478 (2000).
- [14] W. Hieringer and A. Görling, Failure of time-dependent density functional methods for excitations in spatially separated systems, *Chem. Phys. Lett.* **419**, 557 (2006).
- [15] K. J. H. Giesbertz and E. J. Baerends, Failure of time-dependent density functional theory for excited state surfaces in case of homolytic bond dissociation, *Chem. Phys. Lett.* **461**, 338 (2008).
- [16] S. Botti, F. Sottile, N. Vast, V. Olevano, L. Reining, H.-C. Weissker, A. Rubio, G. Onida, R. Del Sole, and R. W. Godby, Long-range contribution to the exchange-correlation kernel of time-dependent density functional theory, *Phys. Rev. B* **69**, 155112 (2004).
- [17] A. Dreuw, J. L. Weisman, and M. Head-Gordon, Long-range charge-transfer excited states in time-dependent density functional theory require non-local exchange, *J. Chem. Phys.* **119**, 2943 (2003).
- [18] D. Hofmann, T. Körzdörfer, and S. Kümmel, Kohn-Sham Self-Interaction Correction in Real Time, *Phys. Rev. Lett.* **108**, 146401 (2012).
- [19] M. Dierksen and S. Grimme, The vibronic structure of electronic absorption spectra of large molecules: A time-dependent density functional study on the influence of “exact” Hartree-Fock exchange, *J. Phys. Chem. A* **108**, 10225 (2004).
- [20] M. J. G. Peach, P. Benfield, T. Helgaker, and D. J. Tozer, Excitation energies in density functional theory: An evaluation and a diagnostic test, *J. Chem. Phys.* **128**, 044118 (2008).
- [21] A. Görling, Exact exchange-correlation kernel for dynamic response properties and excitation energies in density-functional theory, *Phys. Rev. A* **57**, 3433 (1998).

- [22] I. V. Tokatly and O. Pankratov, Many-Body Diagrammatic Expansion in a Kohn-Sham Basis: Implications for Time-Dependent Density Functional Theory of Excited States, *Phys. Rev. Lett.* **86**, 2078 (2001).
- [23] U. von Barth, N. E. Dahlen, R. van Leeuwen, and G. Stefanucci, Conserving approximations in time-dependent density functional theory, *Phys. Rev. B* **72**, 235109 (2005).
- [24] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, Describing static correlation in bond dissociation by Kohn-Sham density functional theory, *J. Chem. Phys.* **122**, 094116 (2005).
- [25] M. Hellgren and U. von Barth, Exact-exchange kernel of time-dependent density functional theory: Frequency dependence and photoabsorption spectra of atoms, *J. Chem. Phys.* **131**, 044110 (2009).
- [26] M. Hellgren and U. von Barth, Correlation energy functional and potential from time-dependent exact-exchange theory, *J. Chem. Phys.* **132**, 044101 (2010).
- [27] A. Heßelmann and A. Görling, Correct Description of the Bond Dissociation Limit without Breaking Spin Symmetry by a Random-Phase-Approximation Correlation Functional, *Phys. Rev. Lett.* **106**, 093001 (2011).
- [28] A. Heßelmann and A. Görling, Efficient exact-exchange time-dependent density-functional theory methods and their relation to time-dependent Hartree-Fock, *J. Chem. Phys.* **134**, 034120 (2011).
- [29] J. E. Bates and F. Furche, Random phase approximation renormalized many-body perturbation theory, *J. Chem. Phys.* **139**, 171103 (2013).
- [30] J. Erhard, P. Bleiziffer, and A. Görling, Power Series Approximation for the Correlation Kernel Leading to Kohn-Sham Methods Combining Accuracy, Computational Efficiency, and General Applicability, *Phys. Rev. Lett.* **117**, 143002 (2016).
- [31] G. Lani, S. Di Marino, A. Gerolin, R. van Leeuwen, and P. Gori-Giorgi, The adiabatic strictly-correlated-electrons functional: Kernel and exact properties, *Phys. Chem. Chem. Phys.* **18**, 21092 (2016).
- [32] M. Seidl, Strong-interaction limit of density-functional theory, *Phys. Rev. A* **60**, 4387 (1999).
- [33] P. Gori-Giorgi, G. Vignale, and M. Seidl, Electronic zero-point oscillations in the strong-interaction limit of density functional theory, *J. Chem. Theory Comput.* **5**, 743 (2009).
- [34] F. Malet and P. Gori-Giorgi, Strong Correlation in Kohn-Sham Density Functional Theory, *Phys. Rev. Lett.* **109**, 246402 (2012).
- [35] M. Mundt, S. Kümmel, R. van Leeuwen, and P.-G. Reinhard, Violation of the zero-force theorem in the time-dependent Krieger-Li-Iafrate approximation, *Phys. Rev. A* **75**, 050501 (2007).
- [36] G. Vignale, Center of Mass and Relative Motion in Time Dependent Density Functional Theory, *Phys. Rev. Lett.* **74**, 3233 (1995).
- [37] J. F. Dobson, Harmonic-Potential Theorem: Implications for Approximate Many-Body Theories, *Phys. Rev. Lett.* **73**, 2244 (1994).
- [38] S. Viefers, P. Koskinen, P. Singha Deo, and M. Manninen, Quantum rings for beginners: Energy spectra and persistent currents, *Phys. E (Amsterdam, Neth.)* **21**, 1 (2004).
- [39] M. Ruggenthaler, K. J. H. Giesbertz, M. Penz, and R. van Leeuwen, Density-potential mappings in quantum dynamics, *Phys. Rev. A* **85**, 052504 (2012).
- [40] P.-F. Loos and P. M. W. Gill, Exact Wave Functions of Two-Electron Quantum Rings, *Phys. Rev. Lett.* **108**, 083002 (2012).
- [41] M. Ruggenthaler, S. E. B. Nielsen, and R. van Leeuwen, Analytic density functionals with initial-state dependence and memory, *Phys. Rev. A* **88**, 022512 (2013).
- [42] F. M. Arscott, I. N. Sneddon, M. Stark, and S. Ulam, *Periodic Differential Equations: An Introduction to Mathieu, Lamé, and Allied Functions* (MacMillan, New York, 1964).
- [43] Edited by F. W. J. Olver, A. B. Olde Daalhuis, D. W. Lozier, B. I. Schneider, R. F. Boisvert, C. W. Clark, B. R. Miller and B. V. Saunders, DLMF, NIST Digital Library of Mathematical Functions, <http://dlmf.nist.gov/28.8>.
- [44] R. Sips, Représentation asymptotique des fonctions de Mathieu et des fonctions d'onde sphéroïdales, *Trans. Amer. Math. Soc.* **66**, 93 (1949).
- [45] R. Sips, Représentation asymptotique des fonctions de Mathieu et des fonctions sphéroïdales. II, *Trans. Amer. Math. Soc.* **90**, 340 (1959).
- [46] G. Blanch, The asymptotic expansions for the odd periodic Mathieu functions, *Trans. Amer. Math. Soc.* **97**, 357 (1960).
- [47] D. Frenkel and R. Portugal, Algebraic methods to compute Mathieu functions, *J. Phys. A: Math. Gen.* **34**, 3541 (2001).
- [48] G. Vignale, Sum rule for the linear density response of a driven electronic system, *Phys. Lett. A* **209**, 206 (1995).
- [49] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [50] M. Seidl, P. Gori-Giorgi, and A. Savin, Strictly correlated electrons in density-functional theory: A general formulation with applications to spherical densities, *Phys. Rev. A* **75**, 042511 (2007).
- [51] G. Stefanucci and R. van Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction* (Cambridge University Press, Cambridge, UK, 2013).
- [52] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, Double excitations within time-dependent density functional theory linear response, *J. Chem. Phys.* **120**, 5932 (2004).
- [53] M. Seidl, Adiabatic connection in density-functional theory: Two electrons on the surface of a sphere, *Phys. Rev. A* **75**, 062506 (2007).
- [54] M. Hellgren and E. K. U. Gross, Discontinuities of the exchange-correlation kernel and charge-transfer excitations in time-dependent density-functional theory, *Phys. Rev. A* **85**, 022514 (2012).
- [55] D. C. Langreth and J. P. Perdew, The exchange-correlation energy of a metallic surface, *Solid State Commun.* **17**, 1425 (1975).
- [56] F. Malet, A. Mirtschink, K. J. H. Giesbertz, L. O. Wagner, and P. Gori-Giorgi, Exchange–correlation functionals from the strong interaction limit of DFT: applications to model chemical systems, *Phys. Chem. Chem. Phys.* **16**, 14551 (2014).
- [57] M. Moshinsky, O. Novaro, and A. Calles, The pseudo-atom: A soluble many body problem, *J. Phys. Colloques* **31**, C4-125 (1970).
- [58] E. W. Weisstein, Hermite Polynomial, <http://mathworld.wolfram.com/HermitePolynomial.html>.

Article II

Strictly-correlated-electron approach to excitation energies of dissociating moleculesLuis Cort,¹ Soeren Ersbak Bang Nielsen,² and Robert van Leeuwen¹¹*Department of Physics, Nanoscience Center P.O. Box 35 FI-40014 University of Jyväskylä, Finland*²*Max Planck Institute for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany*

(Received 14 December 2018; published 4 February 2019)

In this work we consider a numerically solvable model of a two-electron diatomic molecule to study a recently proposed approximation based on the density functional theory of so-called strictly correlated electrons (SCE). We map out the full two-particle wave function for a wide range of bond distances and interaction strengths and obtain analytic results for the two-particle states and eigenenergies in various limits of strong and weak interactions, and in the limit of large bond distance. We then study the so-called Hartree-exchange-correlation (Hxc) kernel of time-dependent density functional theory which is a key ingredient in calculating excitation energies. We study an approximation based on adiabatic SCE (ASCE) theory which was shown to display a particular feature of the exact Hxc kernel, namely, a spatial divergence as function of the bond distance. This makes the ASCE kernel a candidate for correcting a notorious failure of the commonly used adiabatic local density approximation (ALDA) in the calculation of excitation energies of dissociating molecules. Unlike the ALDA, we obtain nonzero excitation energies from the ASCE kernel in the dissociation regime but they do not correspond to those of the true spectrum unless the interaction strength is taken to be very large such that the SCE theory has the right regime of validity, in which case the excitation energies become exact and represent the so-called zero-point oscillations of the strictly correlated electrons. The commonly studied physical dissociation regime, namely, large molecular separation at intermediate interaction strength, therefore remains a challenge for density functional approximations based on SCE theory.

DOI: [10.1103/PhysRevA.99.022501](https://doi.org/10.1103/PhysRevA.99.022501)**I. INTRODUCTION**

Density functional theory (DFT) is a commonly used electronic structure method. Its ground-state version is mainly used to calculate energies and structures of electronic systems [1], while its time-dependent (TD) counterpart TDDFT also allows for the calculation of dynamic properties and excitation energies [2]. Virtually all density functional calculations are based on the Kohn-Sham (KS) system, a non-interacting system that produces the same electronic density as the true system of interest. The KS system provides a considerable simplification of the many-body problem which is advantageous for numerical implementations. However, all the complications of the true many-body system are hidden in the effective potential of the KS system. This KS potential is typically expressed as a sum of the external potential of the interacting system of interest and the Hartree-exchange-correlation (Hxc) potential containing implicitly the many-body effects of the interacting system. The KS formalism is equally applicable in ground-state and time-dependent DFT, but in this work we will focus on the calculation of excitation energies which are obtained in TDDFT using a linear response formalism. For this purpose, it is enough to know the functional derivative of the Hxc potential with respect to the density which yields a quantity known as the Hxc kernel. The simplest possible approximation for the Hxc kernel is the adiabatic local density approximation (ALDA), for which the kernel is local in space and time. Although this approximation has been used successfully [2], it has a number

of important deficiencies, such as the inability to reproduce Born-Oppenheimer surfaces of excited states in dissociating molecules [3,4].

When a molecule separates into fragments, its excitation energies should approach those of the separate fragments. This behavior is not reproduced by the ALDA since upon dissociation the gap between the bonding and antibonding KS eigenvalues decreases exponentially fast with the bond distance, and the ALDA kernel is unable to correct for this thereby rendering many of the excitation energies to become zero in the dissociation limit. To correct for this, asymptotic corrections have been devised [3,4] that introduce exponentially growing terms in the kernel that compensate for the closing of the bonding-antibonding gap. Although such corrections can reproduce the main features of the exact bonding curve for the lowest excited state [3,4], there is no systematic way to construct such functionals. Other more systematic approximations often rely on perturbative expansions, which makes them questionable in the multiconfiguration regime required to describe molecular dissociation.

In recent work [5], an approximate kernel was derived within the framework of so-called strictly correlated electrons (SCE). This is a ground-state DFT formalism that becomes exact in the limit of very large two-body interactions. When the simplest approximation within this formalism is applied within the adiabatic approximation, an approximate Hxc kernel can be derived. This so-called adiabatic SCE (ASCE) kernel was shown to have a number of desirable features. It was shown to obey the so-called zero-force theorem [2,6]

and it was shown that in the case of molecular dissociation, it exhibits an exponential growth with the bond distance [5]. The kernel therefore displays a very nonlocal spatial behavior that has the potential to cure the deficiency of the ALDA kernel for molecular dissociation. We recently investigated the ASCE kernel [7] in a model system for which the exchange-correlation kernel can be obtained exactly for various two-body interaction strengths. It was found that the leading order and the next to leading order of the asymptotic expansion for the exact Hxc kernel in terms of the interaction strength agreed with that one predicted by the adiabatic SCE formalism. This result shows that the SCE formalism is a promising method for describing the linear response properties in the strong interaction limit. Moreover, these terms were also shown to be frequency independent in the exact theory such that the adiabatic approximation in this limit is in fact exact. In view of these favorable properties of the ASCE kernel, the natural question arises as to whether this kernel can be used to correctly predict the excitation energies of dissociating molecules. Answering this question is the main aim of this work.

To attack this problem, we developed a simplified one-dimensional model of a diatomic molecule having the main physical characteristics of a real three-dimensional hydrogen molecule and for which we can perform analytical and numerical calculations for arbitrary bond distance and interaction strength. In particular, the KS orbitals and eigenvalues are known analytically, a feature that is very desirable as it provides an analytic expression for the KS gap upon dissociation. The model is used to benchmark the performance of the ASCE kernel as well as to discuss many features of the SCE formalism in the limit of large interactions.

The paper is organized as follows: In Sec. II we give a brief introduction to the main elements of SCE theory that we need. In Sec. III we introduce the model system and discuss its properties. In Sec. IV we discuss the ASCE kernel for our model density and obtain the excitation energies. In Sec. V we present our conclusions.

II. DENSITY FUNCTIONAL THEORY IN THE LARGE INTERACTION LIMIT

The main motivation of this work is to benchmark the recently proposed approximations for the exchange-correlation (xc) potential and xc kernel based on the so-called theory of strictly correlated electrons [5,7]. To provide a self-contained minimal background for the reader, we briefly review some basic aspects of DFT. Our starting point is the time-independent N -body Hamiltonian of a system which we write as [1]

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{W}, \quad (1)$$

where \hat{T} is the kinetic energy and \hat{W} the two-body interaction, the strength of which is regulated by a real parameter λ . Finally, \hat{V}_λ represents the external potential and is the sum of one-body potentials $v_\lambda(\mathbf{r})$. The latter potential depends on the interaction strength λ via the requirement that for each value of λ , the same electronic density $n(\mathbf{r})$ is obtained from the ground state of Eq. (1). This makes v_λ a functional of the density via the Hohenberg-Kohn theorem [8] and we

will therefore sometimes write $v_\lambda[n]$ to stress this fact when necessary.

Typically, the Hamiltonian is given at $\lambda = 1$ with a known external potential and the key many-body problem is to solve for its eigenstates. However, consideration of the full λ dependence is useful in formal derivations in DFT and is particularly relevant for this work. An important limit is obtained by taking $\lambda = 0$, in which case the system becomes noninteracting while retaining the density of the interacting system. This system is denoted as the Kohn-Sham (KS) system and its external potential is commonly denoted by $v_s(\mathbf{r})$. The ground state of the KS system is a Slater determinant consisting of KS orbitals φ_i satisfying

$$\left(-\frac{1}{2}\nabla^2 + v_s[n](\mathbf{r})\right)\varphi_i(\mathbf{r}, \sigma) = \epsilon_i \varphi_i(\mathbf{r}, \sigma), \quad (2)$$

where σ is a spin index. The KS equations are a device for obtaining the density of the interacting system by solving one-particle equations. However, to make the procedure useful, we need to make a connection to the interacting system which we will take at a general interaction strength λ . To do this, we define the Hxc potential as

$$v_{\text{Hxc}}^\lambda[n](\mathbf{r}) = v_s[n](\mathbf{r}) - v_\lambda[n](\mathbf{r}). \quad (3)$$

A given approximation for this quantity allows us to obtain the density of the interacting system by using the potential $v_{\text{KS}}[n, v_\lambda] = v_\lambda + v_{\text{Hxc}}^\lambda[n]$ in Eq. (2) instead of $v_s[n]$ where v_λ is a given and known potential of the interacting system at interaction strength λ (which is commonly taken to be $\lambda = 1$ but we would like here to use a general interaction strength for the discussion below) [9]. The central object of DFT is therefore the Hxc potential. This quantity in turn is given by the functional derivative of the Hxc energy with respect to the density $v_{\text{Hxc}}^\lambda(\mathbf{r}) = \delta E_{\text{Hxc}}^\lambda / \delta n(\mathbf{r})$. The Hxc energy can be obtained from

$$E_{\text{Hxc}}^\lambda[n] = \int_0^\lambda d\lambda' W_{\lambda'}[n], \quad (4)$$

where we defined

$$W_\lambda[n] = \langle \Psi_\lambda[n] | \hat{W} | \Psi_\lambda[n] \rangle, \quad (5)$$

where $\Psi_\lambda[n]$ is the ground state of Hamiltonian (1). The quantity W_λ has been studied in limiting cases. For small values of λ it is accessible via perturbation theory, while in the limit of large values of λ there is an asymptotic expansion that is derived from SCE theory. This expansion has the form [10]

$$W_\lambda[n] = V_{\text{SCE}}[n] + \frac{V_{\text{ZPE}}[n]}{\sqrt{\lambda}} + O(\lambda^{-3/2}), \quad (6)$$

where the leading term is the interaction energy of the strictly correlated electrons and the next term arises from their zero-point energy (ZPE) in vibrations around their equilibrium positions. Correspondingly, the asymptotic expansion of the Hxc energy for large λ is given by

$$E_{\text{Hxc}}^\lambda[n] = \lambda V_{\text{SCE}}[n] + 2\sqrt{\lambda} V_{\text{ZPE}}[n] + E_2[n] + O(\lambda^{-1/2}), \quad (7)$$

as can be checked by differentiation with respect to λ and comparison to Eq. (6). This expression further introduces

a density functional $E_2[n]$, the relevance of which will become clear later. The functional derivative with respect to the density gives an expansion of the Hxc potential in powers of $\sqrt{\lambda}$:

$$v_{\text{Hxc}}^\lambda(\mathbf{r}) = \lambda v_{\text{SCE}}(\mathbf{r}) + \sqrt{\lambda} v_{\text{ZPE}}(\mathbf{r}) + v_2(\mathbf{r}) + O(\lambda^{-1/2}) \quad (8)$$

which is valid for large value of λ . A very interesting point is that, at least for one-dimensional many-electron systems, the two leading terms are explicitly known functionals of the density and can be calculated explicitly in a rather simple way from so-called co-motion functions [11]. Before we discuss the applicability of this expansion, let us further define the adiabatic Hxc kernel by

$$f_{\text{Hxc}}^\lambda(\mathbf{r}, \mathbf{r}') = \frac{\delta v_{\text{Hxc}}^\lambda(\mathbf{r})}{\delta n(\mathbf{r}')} \quad (9)$$

which according to Eq. (8) has the expansion

$$f_{\text{Hxc}}^\lambda(\mathbf{r}, \mathbf{r}') = \lambda \frac{\delta v_{\text{SCE}}(\mathbf{r})}{\delta n(\mathbf{r}')} + O(\sqrt{\lambda}). \quad (10)$$

The first term on the right-hand side represents the so-called adiabatic SCE kernel $\lambda f_{\text{Hxc}}^{\text{ASCE}}$ which has been studied in detail in Refs. [5,7] which we refer to for more details. So far, our discussion has been very general and, apart from the adiabatic approximation to the time-dependent kernel of TDDFT in Eq. (10), no approximations have been used. The main question is, however, how reliable the asymptotic expansions in Eqs. (7) and (8) are for values close to the physically relevant interaction strength $\lambda = 1$. Since the expansion is asymptotic, retaining higher-order terms typically worsen the approximation unless we increase the value of λ . This means that for values of λ close to one, the best approximation may be obtained by only retaining the term v_{SCE} . Indeed, it was pointed out in Ref. [12] that in this interaction regime adding the ZPE contribution generally will give a worsening of the result. It was found that at the lowest SCE level for a model one-dimensional diatomic molecule the bonding curve is correct at large separation but inaccurate at equilibrium separation, while adding the ZPE contribution gives an overall worse result for the bonding curve. The asymptotic expansion can therefore not be applied as such and, consequently, Ref. [12] considers various amendments. A similar conclusion was obtained from our previous work on the model system of a quantum ring [7] where we found the ZPE contribution to worsen the results at smaller interaction strengths. This work was done for a homogeneous system in which we mainly studied the properties of the kernel itself. In this work, we extend that work to an inhomogeneous model system in which again the kernel will be at the focus of attention. The equations derived in the present section will be referenced in later sections.

III. MOLECULAR MODEL

A. Definition of the model

For our description of the simplified molecular model, we consider two electrons with spatial coordinates x_1 and x_2 both in the domain $[-\frac{L}{2}, \frac{L}{2}]$ on a ring of length L . The Hamiltonian

of our system is given by

$$\hat{H}_\lambda = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + v_\lambda(x_1) + v_\lambda(x_2) + \lambda \cos^2\left[\frac{\pi}{L}(x_1 - x_2)\right], \quad (11)$$

where the first two terms are the kinetic energy of each electron, v_λ is the one-body external potential, and $w(x) = \lambda \cos^2(\pi x/L)$ is the electron-electron repulsion. We impose periodic boundary conditions such that the particles effectively move on a ring which is commonly referred to as a quantum ring (QR) system [9]. The strength of the interaction λ is a parameter which we will take to be positive. The interaction tends to keep particles on opposing parts of the ring and has a convenient form for numerical considerations. In accordance with Eq. (1), the potential v_λ is chosen in such a way that for each value of λ the same ground-state density is produced. For our model, it turns out to be useful to specify the external potential at $\lambda = 0$ which corresponds to the KS potential. In this way, we can choose the potential in such a way that we obtain an analytic solution for the KS orbitals. The potential at all other interaction strengths, including the physically relevant case $\lambda = 1$, is subsequently determined by the constraint that the density is the same for all values of λ as we will discuss in more detail later.

B. Kohn-Sham system

The KS system is obtained from Eq. (11) by taking $\lambda = 0$ and we adopt the common notation of denoting the KS potential by v_s , i.e., $v_s = v_{\lambda=0}$. In this limit, the Hamiltonian of Eq. (11), which we now denote by \hat{H}_s , attains the form

$$\hat{H}_s = -\frac{1}{2}(\partial_{x_1}^2 + \partial_{x_2}^2) + v_s(x_1) + v_s(x_2). \quad (12)$$

We now specify an explicit choice for v_s which we take to be

$$v_s(x) = V_0 \left[1 + \cos\left(\frac{4\pi x}{L}\right)\right], \quad (13)$$

where V_0 is a constant with units of energy. This potential has two minima located at $x_0 = \pm L/4$ where $v_s(x_0) = 0$ and is positive everywhere else. The ground-state density has two maxima at the potential minima and therefore represents a simple model of a diatomic molecule in which the atoms are separated by a bond distance $L/2$. We want to use this model to describe molecular dissociation and therefore vary the bond length L . While doing this we want to guarantee that the width of each atomic density remains fixed upon separation, which can be achieved by requiring that the curvature of the potential at $x_0 = \pm L/4$ is independent of L . This condition reads as

$$v_s''(x_0) = \left(\frac{4\pi}{L}\right)^2 V_0 = \alpha, \quad (14)$$

where α is length independent which gives $V_0 = \alpha(L/(4\pi))^2$ for an arbitrary α (in this paper we will always take $\alpha = 1$). The KS orbitals of our system satisfy the eigenvalue equation

$$\left[-\frac{1}{2}\partial_x^2 + v_s(x)\right]\varphi_l^\pm(x) = \varepsilon_l^\pm \varphi_l^\pm(x), \quad (15)$$

where we added a symmetry label \pm for orbitals that are even or odd with respect to reflection in the origin, i.e.,

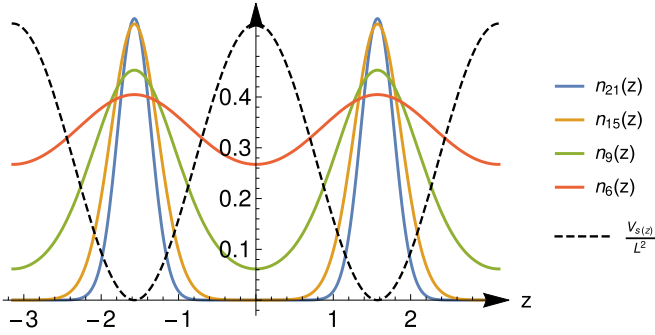


FIG. 1. The ground-state density n as a function of the dimensionless coordinate $z = 2\pi x/L$. The densities for various L values are denoted by n_L in the plot. The corresponding KS potential v_s/L^2 [Eq. (13)] is plotted in arbitrary units for comparison and indicated by a dashed line. For large L , we obtain two peaks of fixed width while for small L the system becomes homogeneous.

$\varphi_l^\pm(-x) = \pm\varphi_l^\pm(x)$. These equations must be solved together with the boundary conditions $\varphi_l(-L/2) = \varphi_l(L/2)$ and the same for their first derivatives. It is convenient to define the dimensionless coordinate $z = 2\pi x/L$ and use the explicit form of the potential to rewrite Eq. (15) as

$$[-\partial_z^2 + 2v \cos(2z)]M_l^\pm(z) = a_l^\pm(v)M_l^\pm(z), \quad (16)$$

where we have defined the following constants:

$$a_l^\pm(v) = 2\left(\frac{L}{2\pi}\right)^2 (\varepsilon_l^\pm - V_0), \quad (17)$$

$$v(L) = \frac{\alpha}{4}\left(\frac{L}{2\pi}\right)^4. \quad (18)$$

We recover the KS orbitals from $\varphi_l^\pm(x) = M_l^\pm(2\pi x/L)$. Equation (16) is the well-known Mathieu equation and its eigenfunctions and eigenvalues have been intensively studied [13]. The functions M_l^+ and M_l^- are commonly denoted as the Mathieu-cosine C_l and the Mathieu-sine S_l functions, respectively, while the values a_l^\pm are called the Mathieu characteristic values. The convention is that the label of the even states start at $l = 0$ whereas the labels of the odd states start at $l = 1$. The Mathieu functions satisfy $M_l^\pm(z + \pi) = (-1)^l M_l^\pm(z)$ and are therefore 2π periodic. They are commonly normalized as follows:

$$\int_{-\pi}^{\pi} dz (M_l^\pm(z))^2 = \pi. \quad (19)$$

Correspondingly, the normalized (to one) KS orbitals are expressed in terms of Mathieu functions as

$$\varphi_l^+(x) = \sqrt{\frac{2}{L}} C_l\left(\frac{2\pi x}{L}; v\right), \quad (20)$$

$$\varphi_l^-(x) = \sqrt{\frac{2}{L}} S_l\left(\frac{2\pi x}{L}; v\right), \quad (21)$$

while the Kohn-Sham eigenenergies can be recovered from the Mathieu characteristic values by means of Eq. (17). In Fig. 1 we plot the KS potential and the ground-state density for different bond distances to illustrate the main features that we mentioned, in particular, the fact that the width of the

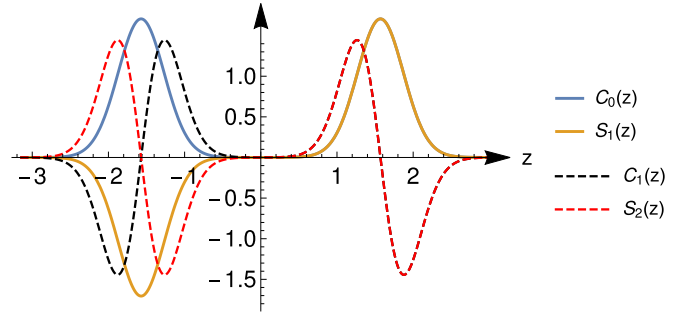


FIG. 2. Selected KS orbitals as a function of the dimensionless coordinate $z = 2\pi x/L \in [-\pi, \pi]$ plotted for the bond distance $L/2 = 10.5$. We display the ground state and first few excited states corresponding to the bonding and antibonding orbital pairs represented by the pair of Mathieu functions C_0 and S_1 as well as the pair C_1 and S_2 . For this bond distance, the bonding and antibonding orbitals coincide for positive z .

maxima becomes independent of the bond distance for large L . Although we are not particularly interested in the case of very short bond distances, we note that in the limit $L \rightarrow 0$ the parameter v becomes equal to zero and the ground-state KS orbital is given by the constant function $\varphi_0(x) = 1/\sqrt{L}$ representing a system of constant density. We will not investigate this limit in detail; a homogenous QR at various interaction strength has been studied in detail in Ref. [7].

In Fig. 2 we plot the ground state and the first few excited-state KS orbitals. Of particular interest for our later discussion of the Hxc kernel is the lowest pair of bonding and antibonding states represented by the pair of Mathieu functions C_0 and S_1 . The corresponding energy gap between the KS eigenvalues closes exponentially fast with increasing bond distance:

$$\varepsilon_1^- - \varepsilon_0^+ = \frac{2\pi^2}{L^2} [a_1^-(v) - a_0^+(v)] \quad (22)$$

$$= \frac{32}{L^2} (2\pi)^{3/2} v^{3/4} e^{-4\sqrt{v}} \xrightarrow{L \rightarrow \infty} 0, \quad (23)$$

where we used the asymptotic expansion for the Mathieu characteristic value given in Appendix A. We remind the reader that v is an increasing function of L given by Eq. (18). The density in the bond midpoint has a similar exponential decay [see Eq. (A6) in Appendix A] given by

$$n(0) = \frac{16}{L} (2\pi)^{1/2} v^{1/4} e^{-4\sqrt{v}} \quad (L \rightarrow \infty). \quad (24)$$

The knowledge of this precise behavior of the KS gap as well as the density in the bond midpoint will facilitate considerably the calculation of the excitation energy from the ASCE kernel in Sec. IV.

C. Exact solution of the model

After having considered the model in the KS limit, we will now consider the case of finite interaction strength λ . The potential v_λ in Eq. (11) can not be obtained analytically except in some limiting cases that we will discuss below. We therefore obtain v_λ directly from the constraint that the density is independent of λ using the numerical algorithm outlined in Ref. [14]. In our case, the density is given by the ground-state

KS orbital from Eq. (20) to be

$$n(x) = 2|\varphi_0^+(x)|^2 = \frac{4}{L} C_0^2 \left(\frac{2\pi x}{L}; \nu \right) \quad (25)$$

for all λ where we remind the reader that ν depends on L via Eq. (18). Therefore, for a given value of L we have the numerical task to find ν_λ for a range of interaction strengths of interest. The ground state is a spin-singlet state and, consequently, we will mostly be interested in the singlet excited states. The singlet wave function has the structure

$$\Psi(x_1\sigma_1, x_2\sigma_2) = \psi(x_1, x_2) \frac{1}{\sqrt{2}} (\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}),$$

where σ_i for $i = 1, 2$ are spin variables and where the spatial part of the wave function is symmetric $\psi(x_1, x_2) = \psi(x_2, x_1)$ to ensure antisymmetry of the full space-spin wave function. To obtain deeper insight in the results, we will also derive analytic results in the regime of large bond distance $L/2$ for fixed interaction strength λ , which is the common molecular dissociation regime, and the complementary regime of large interaction strength λ for fixed bond distance $L/2$, which is the SCE regime. We will start in the next subsection with the first regime.

1. Large bond distance for fixed interaction strength

We first consider the regime of large bond distance $L/2$ at fixed values of λ . In this regime, the molecule is typically dissociated in two one-electron atoms (unless the interacting strength λ is very small such that there are contributions from the ionic states with two or zero electrons on each atom). For a one-electron atom, the KS potential is equal to the true external potential and therefore we have $\nu_\lambda(x) = \nu_s(x)$ for x in the neighborhood of each atom at large separation. The ground-state atomic orbitals $A(x)$ and $B(x)$ on atoms A and B are localized around $x = \pm L/4$ and can be expressed in terms of the first bonding and antibonding molecular KS orbitals as $A(x) = [\varphi_0^+(x) + \varphi_1^-(x)]/\sqrt{2}$ and $B(x) = [\varphi_0^+(x) - \varphi_1^-(x)]/\sqrt{2}$ (see, for example, Fig. 2). The exact ground-state (GS) wave function for the large bond distance limit is the well-known Heitler-London (HL) wave function

$$\begin{aligned} \Psi_\lambda^{\text{GS}}(x_1, x_2) &= \frac{1}{\sqrt{2}} [A(x_1)B(x_2) + B(x_1)A(x_2)] \\ &= \frac{1}{\sqrt{2}} [\varphi_0^+(x_1)\varphi_0^+(x_2) - \varphi_1^-(x_1)\varphi_1^-(x_2)]. \end{aligned} \quad (26)$$

The ground-state energy is given by

$$E_\lambda^{\text{GS}} = 2\varepsilon_0^+ = \sqrt{\alpha} - \frac{\pi^2}{L^2} + O(L^{-4}) \quad (L \rightarrow \infty), \quad (27)$$

where we used that $\varepsilon_0^+ = \varepsilon_1^-$ in the large- L limit and the asymptotic expansion of the Mathieu characteristic values in Appendix A. This result is easy to understand. Since at the atomic positions $x_0 = \pm L/4$ we have that $\nu_s''(x_0) = \alpha$ the potential around each atom is given by $\nu_s(x) = \alpha(x - x_0)^2/2$ which corresponds to a harmonic well with harmonic frequency $\sqrt{\alpha}$. Each atomic oscillator has ground-state energy $\sqrt{\alpha}/2$, thereby adding up to the molecular ground-state energy $\sqrt{\alpha}$.

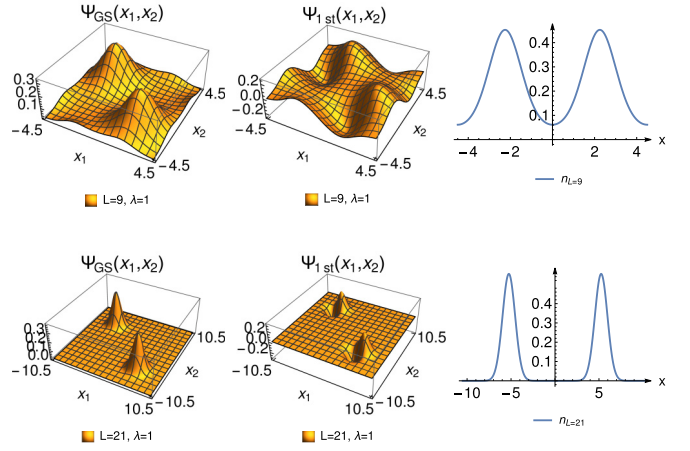


FIG. 3. The ground- and first-excited-state wave functions for interaction strength $\lambda = 1$ plotted for $L = 9$ and 21 . The rightmost panels display the corresponding ground-state densities.

Let us now consider the first excited state which in the large- L limit is given by

$$\begin{aligned} \Psi_\lambda^{(1)}(x_1, x_2) &= \frac{1}{2} [\varphi_1^+(x_1)\varphi_1^-(x_2) + \varphi_1^-(x_1)\varphi_1^+(x_2) \\ &\quad - \varphi_0^+(x_1)\varphi_2^-(x_2) - \varphi_2^-(x_1)\varphi_0^+(x_2)]. \end{aligned} \quad (28)$$

The orbitals used in this expression are displayed in Fig. 2. For large L the states φ_0^+ and φ_1^- become degenerate and the same is true for the states φ_1^+ and φ_2^- . These orbitals can be used to construct localized ground- and excited-state atomic orbitals from the combinations $\varphi_0^+ \pm \varphi_1^-$ and $\varphi_1^+ \pm \varphi_2^-$ if desired. The energy of the two-particle state of Eq. (28) is given by

$$E_\lambda^{(1)} = \varepsilon_0^+ + \varepsilon_1^+ = 2\sqrt{\alpha} - \frac{3\pi^2}{L^2} + O(L^{-4}) \quad (L \rightarrow \infty). \quad (29)$$

Again, it is straightforward to interpret the energy. The system is a superposition of two states in which one atom is a ground-state oscillator with energy $\sqrt{\alpha}/2$ and the other one a first excited oscillator with energy $3\sqrt{\alpha}/2$ giving a total molecular energy of $2\sqrt{\alpha}$.

To judge the accuracy of these limiting wave functions, we plot the exact ψ_λ for $\lambda = 1$ and $L = 9$ and 21 (corresponding to bond lengths 4.5 and 10.5) in Fig. 3. We see that for $L = 21$ the wave functions (26) and (28) are a good approximation to the true wave functions (as we also checked numerically). At $L = 9$ the system still has a considerable density at the bond midpoint and the HL-type wave functions are a less good approximation.

Finally, we compare in Fig. 4 the exact external potential ν_λ to ν_s . We see that around the atoms both potentials agree, but that around the bond midpoint there is a considerable deviation. This amounts to a peak in the Hxc potential $\nu_{\text{Hxc}}^\lambda = \nu_s - \nu_\lambda$ at the bond midpoint. This is a well-known feature of the Hxc potential [15] and is related to the so-called left-right correlation in the system. We refer to the cited reference for a more in-depth discussion.

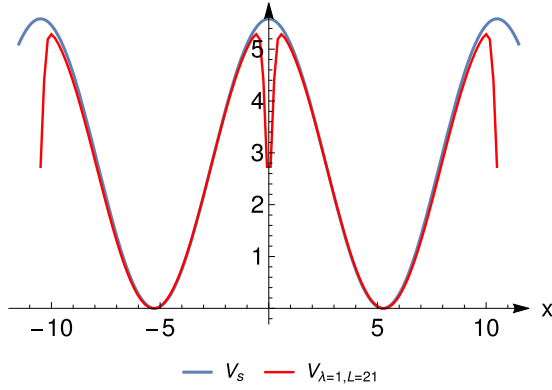


FIG. 4. The potential v_λ for $\lambda = 1$ for $L = 21$ compared to v_s .

2. Large interaction strength at fixed bond distance

We now turn our attention to the complementary regime of larger interaction strength λ for fixed bond distance. This is the regime in which SCE become exact. From our numerical work we find that in this limit the two-particle wave function localizes in a region where $|x_1 - x_2| \approx L/2$ as displayed in Fig. 5. This is in accordance with SCE theory which tells that in the very strong interaction limit, the position of a single electron determines the positions of the remaining electrons uniquely. For this reason, it is convenient to introduce the center of mass $R = (x_1 + x_2)/2$ and relative coordinate $r = x_1 - x_2$, where $R \in [-L/2, L/2]$ and $r \in [-L, L]$. The Hamiltonian (11) in the new coordinates attains the form

$$\hat{H}_\lambda = -\frac{1}{4}\partial_R^2 - \partial_r^2 + v_\lambda\left(R + \frac{r}{2}\right) + v_\lambda\left(R - \frac{r}{2}\right) + \lambda \cos^2\left(\frac{\pi r}{L}\right). \quad (30)$$

We want to give an explicit approximate expression of the Hamiltonian (11) for the limit $\lambda \rightarrow \infty$ for any fixed bond distance $L/2$. Since the wave function is localized around the

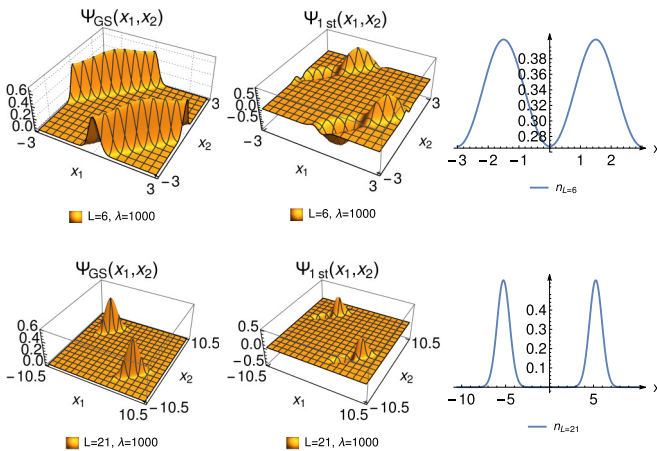


FIG. 5. The ground- and excited-state wave functions at large interaction strength $\lambda = 1000$ for the bond distances $L/2 = 3$ and 10.5 . We note that the wave function localizes in narrow strips along the lines $|x_1 - x_2| = L/2$. The rightmost panels display the corresponding ground-state densities.

lines $r = \pm L/2$, it is natural to expand the external potential v_λ around these values. For example, for $r = L/2$ we have to second order

$$v_\lambda\left(R + \frac{r}{2}\right) + v_\lambda\left(R - \frac{r}{2}\right) = \bar{v}_\lambda(R) + \beta_\lambda(R)\left(r - \frac{L}{2}\right)^2, \quad (31)$$

where we defined

$$\bar{v}_\lambda(R) = 2v_\lambda\left(R + \frac{L}{4}\right), \quad (32)$$

$$\beta_\lambda(R) = \left.\frac{\partial^2 v_\lambda(R \pm r/2)}{\partial r^2}\right|_{r=L/2} \quad (33)$$

with an essentially identical result for the expansion around $r = -L/2$, and where we used the property $v_\lambda(x) = v_\lambda(x + L/2)$ in the definitions of \bar{v}_λ and β_λ and in the cancellation of the linear term. With the expansion of Eq. (31), the Hamiltonian becomes

$$\hat{H}_\lambda = -\frac{1}{4}\partial_R^2 - \partial_r^2 + \bar{v}_\lambda(R) + \beta_\lambda(R)\left(r - \frac{L}{2}\right)^2 + \lambda \cos^2\left(\frac{\pi r}{L}\right) \quad (34)$$

with a similar expansion around $r = -L/2$. We see that this Hamiltonian becomes separable when we neglect the term β_λ . However, the two-body interaction has form $w(r) = \lambda(\pi/L)^2(r - L/2)^2$ around $r = L/2$ and the question is therefore whether we can neglect β_λ compared to $\lambda(\pi/L)^2$. From our calculation we find that v_λ and therefore also β_λ converge to a finite value for large λ . Therefore, for fixed L and large enough λ we can neglect β_λ and the system becomes approximately separable. If we write the wave function in this limit as $\Psi_\lambda(r, R) = \chi_\lambda(r)\varphi_\lambda(R)$, then its factors are determined from the equations

$$\left[-\frac{1}{4}\partial_R^2 + 2v_\lambda\left(R + \frac{L}{4}\right)\right]\varphi_\lambda(R) = \epsilon\varphi_\lambda(R), \quad (35)$$

$$\left[-\partial_r^2 + \lambda \cos^2\left(\frac{\pi r}{L}\right)\right]\chi_\lambda(r) = \tilde{\epsilon}\chi_\lambda(r). \quad (36)$$

These equations determine all the eigenstates in the large- λ limit. Let us, however, focus on the ground state and take χ_λ and φ_λ to be ground states of their corresponding Hamiltonians. The ground-state density is then obtained from

$$n(x_1) = 2 \int_{-L/2}^{L/2} dx_2 \left| \varphi_\lambda\left(\frac{x_1 + x_2}{2}\right) \right|^2 |\chi_\lambda(x_1 - x_2)|^2. \quad (37)$$

The function $|\chi_\lambda(r)|^2$ becomes very narrowly peaked around $r = \pm L/2$ as λ becomes very large. We can therefore normalize it such that for the limit that $\lambda \rightarrow \infty$,

$$|\chi_\lambda(r)|^2 \rightarrow \delta\left(r - \frac{L}{2}\right) + \delta\left(r + \frac{L}{2}\right) \quad (38)$$

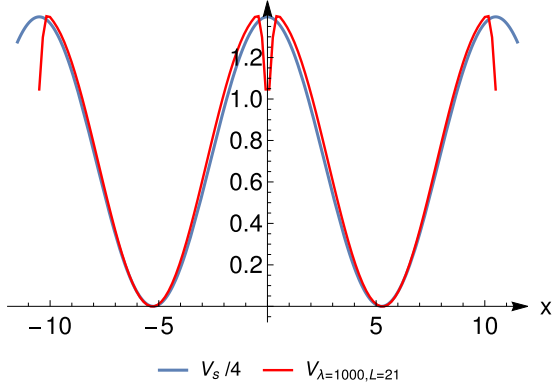


FIG. 6. The potential v_λ for $\lambda = 1000$ for $L = 21$ compared to $v_s/4$.

from which we obtain, using Eq. (37), that for large interaction strength

$$\begin{aligned} n(x) &= 2 \left[\left| \varphi_\lambda \left(x + \frac{L}{4} \right) \right|^2 + \left| \varphi_\lambda \left(x - \frac{L}{4} \right) \right|^2 \right] \\ &= 4 \left| \varphi_\lambda \left(x - \frac{L}{4} \right) \right|^2. \end{aligned} \quad (39)$$

The ground-state density is also given by $n(x) = 2|\varphi_0^+(x)|^2$ in which $\varphi_0^+(x)$ solves Eq. (15). Comparison of this equation to Eq. (35) then immediately yields that

$$v_\lambda(x) = \frac{v_s(x)}{4} = \frac{V_0}{4} \left[1 + \cos \left(\frac{4\pi x}{L} \right) \right] \quad (40)$$

and $\varphi_0^+(x) = \sqrt{2} \varphi_\lambda(x - L/4)$. From our derivation we therefore deduce that in our system

$$\lim_{\lambda \rightarrow \infty} v_\lambda(x) = \frac{v_s(x)}{4}. \quad (41)$$

A comparison with the general Eq. (8) from SCE theory shows that in our case v_{SCE} and v_{ZPE} are zero and that $v_2(x) = v_s - v_\lambda = 3v_s(x)/4$. The fact that v_{SCE} and v_{ZPE} vanish can also be directly derived from SCE theory and is a consequence of the symmetry of our system. In Fig. 6 we compare v_λ to $v_s/4$ for various large values of λ and note a good agreement between them with the exception of some deviations around the bond midpoint. This discrepancy becomes smaller for higher values of λ .

Let us now consider the energies of the system. The eigenenergies of the two-particle state are given by $E = \epsilon + \tilde{\epsilon}$ where ϵ and $\tilde{\epsilon}$ are the eigenvalues of the Hamiltonians in Eqs. (35) and (36). From the fact that $v_\lambda = v_s/4$ in Eq. (35) we see that the eigenvalues ϵ are half of the KS eigenvalues of Eq. (15). These eigenvalues correspond to an excitation which only involves a change of the center-of-mass wave function without changing the relative wave function. The eigenvalues $\tilde{\epsilon}$ are calculated from Eq. (36). The transformation $z = \pi r/L$ transforms this Hamiltonian to

$$\left[-\partial_z^2 + 2q \cos(2z) \right] M(z) = a(q)M(z), \quad (42)$$

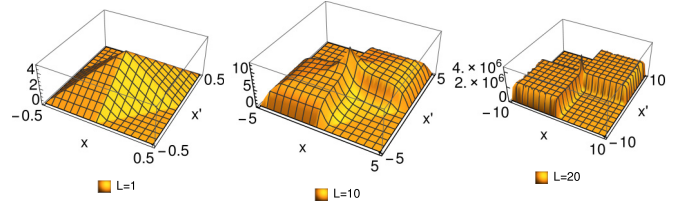


FIG. 7. The ASCE kernel for $L = 1, 10, 20$. We see that with growing L plateaus develop the heights of which grow exponentially with L .

where

$$q = \lambda \left(\frac{L}{2\pi} \right)^2, \quad (43)$$

$$a(q) = \frac{L^2}{\pi^2} \tilde{\epsilon} - 2q. \quad (44)$$

Equation (42) is again the Mathieu equation with this time a parameter q that depends on the interaction strength. The eigenvalues in the limit of large interactions have the form

$$\tilde{\epsilon}_l = \frac{\pi^2}{L^2} [2q + a_l^+(q)] = \left(l + \frac{1}{2} \right) \frac{2\pi}{L} \sqrt{\lambda} \quad (\lambda \rightarrow \infty), \quad (45)$$

which is a harmonic spectrum with harmonic frequency $\omega_\lambda = 2\pi\sqrt{\lambda}/L$. These excitations involve a change of the relative wave function and represent the zero-point vibrations of the strictly correlated electrons of SCE theory. The lowest excitation energy for this mode is therefore ω_λ . This will be relevant of our discussion of the excitation energy obtained from the ASCE kernel.

IV. ADIABATIC SCE KERNEL

A. Definition and properties

We have studied in detail the excitation properties of our model system in two different regimes. We will now investigate the adiabatic SCE kernel (Fig. 7). As was discussed below Eq. (10), the ASCE kernel is defined as

$$f^{\text{ASCE}}(x, x') = \frac{\delta v_{\text{SCE}}(x)}{\delta n(x')}. \quad (46)$$

The SCE potential vanishes for our system, but its functional derivative does not. As was discussed in detail in Refs. [5,7], it is explicitly given by the expression

$$\begin{aligned} f^{\text{ASCE}}(x, x') &= \int_{-L/2}^x dy \frac{w''[y - f(y)]}{n(f(y))} \\ &\times \{ \theta(y - x') - \theta[f(y) - x'] \}, \end{aligned} \quad (47)$$

where θ is the usual Heaviside function and $w(x)$ the two-body interaction. The function $f(x)$ is the so-called comotion function which specifies the position of another electron given the position of a reference electron. For our system, the comotion function attains the simple form

$$f(x) = \begin{cases} x - \frac{L}{2} & \text{if } x > 0, \\ x + \frac{L}{2} & \text{if } x \leq 0. \end{cases} \quad (49)$$

If we define the function $\mathcal{P}(x)$ to be

$$\mathcal{P}(x) = \int_{-L/2}^x dy \frac{w''[y - f(y)]}{n(f(y))}, \quad (50)$$

then the integrand contains $d\mathcal{P}/dx$ and we can obtain f^{ASCE} by partial integration while usefully manipulating the results using the fact that $\mathcal{P}(x) - \mathcal{P}(0)$ is an odd function. In the quadrant $x, x' > 0$ we obtain

$$f^{\text{ASCE}}(x, x') = \mathcal{P}(-x)\theta(x - x') + \mathcal{P}(-x')\theta(x' - x), \quad (51)$$

while in the quadrant $x < 0, x' > 0$ we have

$$f^{\text{ASCE}}(x, x') = [\mathcal{P}(x) - \mathcal{P}(x') + \mathcal{P}(0)]\theta[f(x) - x']. \quad (52)$$

The function in the remaining quadrants is determined from the symmetry $f^{\text{ASCE}}(x, x') = f^{\text{ASCE}}(-x, -x')$. For our system, the function $\mathcal{P}(x)$ can be written more explicitly as

$$\mathcal{P}(x) = w''\left(\frac{L}{2}\right) \int_{-L/2}^x \frac{dy}{n(y)}, \quad (53)$$

where for our two-body potential $w''(L/2) = 2\pi^2/L^2$. In Appendix B we show that

$$\lim_{L \rightarrow \infty} \mathcal{P}(x) = \mathcal{P}(0) \left[\frac{1}{2} + \theta(x) \right] \quad (54)$$

for $x \neq 0$. This equation implies that for large values of L , the kernel assumes the form

$$f^{\text{ASCE}}(x, x') = \frac{1}{2}\mathcal{P}(0)[\theta(x)\theta(x') + \theta(-x)\theta(-x')] \quad (55)$$

for $x, x' \neq 0$. The function exhibits plateaus of height $\mathcal{P}(0)$ in the quadrants in which both coordinates have the same sign and is zero otherwise. In Appendix B we show that this height grows exponentially fast with L according to

$$\mathcal{P}(0) = w''\left(\frac{L}{2}\right) \frac{L^2}{16(2\pi)^{3/2} \nu^{3/4}} e^{4\sqrt{\nu}} \quad (L \rightarrow \infty) \quad (56)$$

[we remind the reader that ν depends on L according to Eq. (18)]. With these results we are ready to calculate excitation energies from the ASCE kernel.

Lowest excitation energy

We now address the issue of calculating the excitation energy of the system. To make our point, it is sufficient to restrict ourselves to the so-called small matrix approximation [2] in which the singlet excitation energy Ω from an occupied state i to an unoccupied state a is given by

$$\Omega^2 = \omega_{ia}^2 + 4\omega_{ia}K_{ia,ia}, \quad (57)$$

where $\omega_{ia} = \epsilon_a - \epsilon_i$ is the difference in KS energies, and

$$K_{ia,ia} = \int dx dx' \Phi_{ia}(x) f_{\text{Hxc}}(x, x') \Phi_{ia}(x'), \quad (58)$$

where $\Phi_{ia}(x) = \varphi_i(x)\varphi_a(x)$ is an excitation function (in which we take the orbitals to be real for simplicity) and f_{Hxc} the Hxc kernel which we took in an adiabatic approximation relevant to the discussion below. In our particular case we consider the excitation from the lowest KS orbital φ_0^+ to φ_1^- . For ease of notation and to be in accordance with adopted language we

denote the orbitals by the gerade and ungerade sigma orbitals $\sigma_g(x)$ and $\sigma_u(x)$ and their eigenvalues by ϵ_g and ϵ_u . We know that in the dissociation limit, the KS gap ω_{gu} vanishes. The excitation energy is therefore given by

$$\Omega^2 = \lim_{L \rightarrow \infty} 4\omega_{gu}K_{gu,gu}. \quad (59)$$

In the ALDA this expression vanishes as the kernel can not compensate for the decay of the KS gap. However, as we will show now, the ASCE kernel [we remind the reader of Eq. (10)] will lead to a finite contribution. The matrix element in the large separation limit is readily calculated from Eq. (55) to be

$$K_{gu,gu} = \frac{\lambda}{4}\mathcal{P}(0), \quad (60)$$

where we used the symmetry and normalization of the KS orbitals. If we use this in Eq. (59), we find that in the large- L limit

$$\Omega^2 = \lambda(\epsilon_u - \epsilon_g)\mathcal{P}(0) = 2\lambda w''\left(\frac{L}{2}\right) \quad (L \rightarrow \infty). \quad (61)$$

For our system we have $w''(L/2) = 2\pi^2/L^2$ and we obtain $\Omega = 2\pi\sqrt{\lambda}/L$ which is exactly the harmonic frequency of the zero-point oscillation of Eq. (45). We therefore deduce that the excitations that we recover from the ASCE kernel are exactly the ones that correspond to the zero-point oscillations. With hindsight, this may not be surprising as, after all, the zero-point oscillations represent an always present set of excitations in SCE theory. Note that in the derivation of Eq. (61), it is important to consider a fixed but arbitrary large L and then take the limit $\lambda \rightarrow \infty$, i.e., the standard SCE regime, and not the other way around otherwise $\Omega = 2\pi\sqrt{\lambda}/L \rightarrow 0$.

B. ASCE kernel in the conventional molecular dissociation regime

In the previous subsection we found that in the limit that the interaction strength λ becomes very large at fixed bond distance $L/2$, the lowest excitation energy is that of the lowest zero-point oscillation of the strictly correlated electrons, and in that regime the ASCE kernel gives an exact result. Let us now see how the ASCE kernel performs in the opposite regime in which the bond distance becomes large at fixed interaction strength, in particular for the chemically relevant case of interaction strength $\lambda = 1$. This is the conventional dissociation regime as commonly studied in bond breaking in chemistry. Note that we now apply the ASCE kernel outside its formal range of applicability and, therefore, the approximation becomes uncontrolled. The consideration is nevertheless illuminating as it illustrates the reasons for the breakdown of the approximation. For $\lambda = 1$, the matrix element (60) of the ASCE kernel is given by $\mathcal{P}(0)/4$ and we have for the lowest excitation energy

$$\Omega^{\text{ASCE}} = \left[2w''\left(\frac{L}{2}\right) \right]^{\frac{1}{2}} \quad (L \rightarrow \infty). \quad (62)$$

Let us compare this to the exact excitation energy

$$\Omega^{\text{exact}} = \sqrt{\alpha} \quad (L \rightarrow \infty) \quad (63)$$

as follows directly from Eqs. (27) and (29). We remind the reader that the parameter α [see Eq. (14)] is given by the curvature of the external potential at its minima (as v_s becomes the true external potential around the atoms in the dissociation limit). Since upon dissociation the separate atoms become independent single-particle oscillators, Eq. (63) is a natural result. If we consider the ASCE approximation, on the other hand, we see that according to Eq. (62) the lowest excitation energy is determined solely by the curvature of the interaction potential $w''(L/2)$. This is because, by using the ASCE kernel, we pretend that the separated atoms still behave as strictly correlated electrons with an excitation energy determined by the zero-point oscillations. This is the wrong physical picture in this regime and, therefore, the ASCE approximation fails to describe the right physics. In fact, in our system $w''(L/2) = 2\pi^2/L^2 \rightarrow 0$ for $L \rightarrow \infty$ and therefore the ASCE excitation energy becomes zero in the dissociation limit. For other forms of the two-body interaction this may not be the case, but this does not change our conclusion regarding the physical picture. The ASCE approximation is therefore not an improvement over the ALDA in the dissociation regime. Both approximations attain the wrong dissociation limit; in the case of the ALDA the excitation energy becomes zero, whereas in the case of the ASCE approximation the excitation energy is determined by the two-body interaction potential rather than by the external potential of the separated atoms. This result is not surprising as we have used the ASCE kernel outside its regime of applicability. The ASCE kernel is therefore not of use if one is interested in the regime of large bond length at intermediate interaction strength, which is the relevant case for bond breaking in most common chemical applications. To correct these problems within the present formalism, a natural way to proceed would be include ZPE and higher-order kernels in the expansion of the Hxc kernel as was done in Ref. [7]. However, that work showed that the extra terms lead to worse approximation than just the ASCE approximation for low interaction strengths, as is typical for an asymptotic expansion. The description of the conventional dissociation regime using density functional methods therefore remains a challenging task.

V. CONCLUSIONS

In this work, we studied the properties of an approximate adiabatic Hxc kernel based on the theory of strictly correlated electrons. To benchmark this approximation, we studied a numerically and analytically solvable system which is able to simulate the main features of a dissociating molecule. We studied in detail the two-particle eigenstates in various limits and calculated the excitation spectrum in the limit of large interaction strength. The ASCE kernel was shown to reproduce the so-called zero-point oscillation part of the spectrum. The attainment of this exact result shows that the ASCE kernel becomes exact in this regime as we also concluded from earlier work [7]. However, most current interest in molecular dissociation in chemistry is devoted to the complementary regime of large bond distance at intermediate interaction strength. In this regime, the ASCE kernel is not suitable for obtaining the excitation spectrum. We conclude that the description of molecular dissociation based on

functionals founded on SCE theory remains a challenge for the future.

APPENDIX A: PROPERTIES OF MATHIEU FUNCTIONS

In this Appendix we describe a few useful properties of the Mathieu functions and their characteristic values that we use in the main text. Many properties of these functions can be found in Ref. [13]. The Mathieu characteristic values have the following expansion for large q (where q is the parameter in the Mathieu equation):

$$a_l^+(q), a_{l+1}^-(q) = -2q + 2(2l+1)\sqrt{q} - \frac{1}{4}(2l^2 + 2l + 1) + \frac{(2l+1)}{128\sqrt{q}}[(2l+1)^2 + 3] + O(q^{-1}). \quad (\text{A1})$$

The difference $a_{l+1}^-(q) - a_l^+(q)$ is exponentially small in the large- q limit [13]

$$a_{l+1}^-(q) - a_l^+(q) = \frac{2^{4l+5}}{l!} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} q^{\frac{l}{2} + \frac{3}{4}} e^{-4\sqrt{q}} \times \left[1 - \frac{6l^2 + 14l + 7}{32\sqrt{q}} + O(q^{-1})\right]. \quad (\text{A2})$$

We note that in our previous work [7] we denoted a_{l+1}^- by a_l^- in the asymptotic formula (A1) which amounts to a different labeling convention for the characteristic values. Here, we stick to a more common convention.

For this work we need an accurate representation of $C_0(z; q)$ for small values of z . A representation that is valid for large q in the interval $|z| < \pi/2$ is given by

$$C_0(z, q) = \frac{C_0(0, q)}{\sqrt{2}} \times \frac{e^{2\sqrt{q}\sin(z)} \cos\left(\frac{z}{2} + \frac{\pi}{4}\right) + e^{-2\sqrt{q}\sin(z)} \sin\left(\frac{z}{2} + \frac{\pi}{4}\right)}{\cos z}. \quad (\text{A3})$$

To determine this function, we also need to know its prefactor $C_0(0; q)$ which is given by [16]

$$C_0(0, q) = C_0\left(\frac{\pi}{2}; q\right) 2^{3/2} e^{-2\sqrt{q}} \left[1 + \frac{1}{16q^{1/2}} + \frac{9}{256q}\right]. \quad (\text{A4})$$

This equation involves yet another prefactor which is obtainable from Sips' expansion [7] and given in leading order in q to be

$$C_0\left(\frac{\pi}{2}; q\right) = \left(\frac{\pi\sqrt{q}}{2}\right)^{1/4} \left(1 + \frac{1}{8\sqrt{q}} + \frac{27}{512q} + \dots\right)^{-1/2}. \quad (\text{A5})$$

In particular, we find that

$$C_0^2(0, q) = 4(2\pi)^{1/2} q^{1/4} e^{-4\sqrt{q}} \quad (q \rightarrow \infty) \quad (\text{A6})$$

from which we obtain the density in the bond midpoint of Eq. (24).

APPENDIX B: ANALYSIS OF THE FUNCTION $\mathcal{P}(x)$

We study here the properties of the function $\mathcal{P}(x)$ defined in Eq. (53) which we rewrite here as

$$\begin{aligned} \mathcal{P}(x) &= w''\left(\frac{L}{2}\right) \frac{L}{4} \int_{-L/2}^x \frac{dy}{C_0^2(2\pi y/L; \nu)} \\ &= \gamma \int_{-\pi}^{2\pi x/L} f(t, \nu) dt, \end{aligned} \quad (\text{B1})$$

where we used the explicit form of the density and we defined

$$\begin{aligned} f(z, \nu) &= \frac{C_0^2(0, \nu)}{C_0^2(z, \nu)}, \\ \gamma &= \frac{L^2 w''\left(\frac{L}{2}\right)}{8\pi C_0^2(0; \nu)}. \end{aligned} \quad (\text{B2})$$

It will be convenient to further introduce the functions

$$\mathcal{I}(z, \nu) = \int_0^z dt f(t; \nu) \quad (\text{B3})$$

and $\mathcal{J}(\nu) = \mathcal{I}(\pi/2, \nu)$ such that we can write

$$\mathcal{P}(x) = \gamma \left[2\mathcal{J}(\nu) + \mathcal{I}\left(\frac{2\pi x}{L}, \nu\right) \right], \quad (\text{B4})$$

where we used the symmetry of the integrand. Using then the asymptotic expansion of Mathieu functions functions (A3), the $f(t; \nu)$ reads as

$$f(z, \nu) = \frac{2 \cos^2 z}{\left[e^{2\sqrt{\nu} \sin(z)} \cos\left(\frac{z}{2} + \frac{\pi}{4}\right) + e^{-2\sqrt{\nu} \sin(z)} \sin\left(\frac{z}{2} + \frac{\pi}{4}\right) \right]^2}. \quad (\text{B5})$$

For ν very large this function has its main contributions from $z = 0$ and we can approximate

$$f(z, \nu) = \frac{\cos z}{\cosh^2(2\sqrt{\nu} \sin z)} \quad (\text{B6})$$

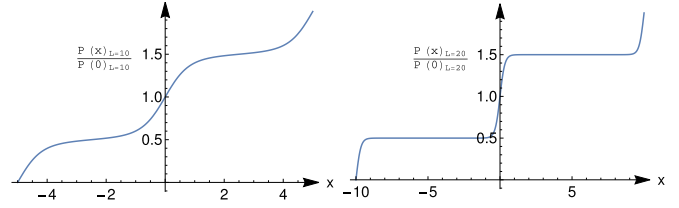


FIG. 8. The function $\mathcal{P}(x)/\mathcal{P}(0)$ for $L = 10$ (left panel) and $L = 20$ (right panel) where we clearly see a step structure appearing for increasing L .

which inserted into Eq. (B3) gives

$$I(z, \nu) = \frac{\tanh(2\sqrt{\nu} \sin z)}{2\sqrt{\nu}} \quad (\text{B7})$$

and, consequently,

$$\mathcal{J}(\nu) = \frac{\tanh(2\sqrt{\nu})}{2\sqrt{\nu}} = \frac{1}{2\sqrt{\nu}} \quad (\nu \rightarrow \infty). \quad (\text{B8})$$

From this we can evaluate $\mathcal{P}(0)$. Using Eqs. (A6) and (B2), we find

$$\mathcal{P}(0) = 2\gamma \mathcal{J}(\nu) = w''\left(\frac{L}{2}\right) \frac{L^2}{16(2\pi)^{3/2} \nu^{3/4}} e^{4\sqrt{\nu}} \quad (L \rightarrow \infty), \quad (\text{B9})$$

which yields Eq. (56). Finally, we consider the quantity

$$\begin{aligned} \frac{\mathcal{P}(x) - \mathcal{P}(0)}{\mathcal{P}(0)} &= \frac{\mathcal{I}(2\pi x/L, \nu)}{2\mathcal{J}(\nu)} \\ &= \frac{\tanh(2\sqrt{\nu} \sin(2\pi x/L))}{2 \tanh(2\sqrt{\nu})} \\ &= \theta(x) - \frac{1}{2} \quad (L \rightarrow \infty) \end{aligned} \quad (\text{B10})$$

and, therefore,

$$\mathcal{P}(x) = \mathcal{P}(0) \left[\frac{1}{2} + \theta(x) \right] \quad (L \rightarrow \infty). \quad (\text{B11})$$

This behavior of the function $\mathcal{P}(x)$ is illustrated in Fig. 8 where we plotted $\mathcal{P}(x)/\mathcal{P}(0)$. In this figure, we clearly see the step appearing with increasing L .

- [1] U. von Barth, Basic density-functional theory - an overview, *Phys. Scr. T* **109**, 9 (2004).
- [2] C. A. Ullrich, *Time-dependent Density-Functional Theory: Concepts and Applications* (Oxford University Press, Oxford, UK, 2012).
- [3] O. V. Gritsenko, S. J. A. van Gisbergen, A. Görling, and E. J. Baerends, Excitation energies of dissociating H_2 : A problematic case for the adiabatic approximation of time-dependent density functional theory, *J. Chem. Phys.* **113**, 8478 (2000).
- [4] O. Gritsenko and E. J. Baerends, Asymptotic correction of the exchange-correlation kernel of time-dependent density functional theory for long-range charge-transfer excitations, *J. Chem. Phys.* **121**, 655 (2004).

- [5] G. Lani, S. Di Marino, A. Gerolin, R. van Leeuwen, and P. Gori-Giorgi, The adiabatic strictly-correlated electrons functional: Kernel and exact properties, *Phys. Chem. Chem. Phys.* **18**, 21092 (2016).
- [6] M. Mundt, S. Kümmel, R. van Leeuwen, and P.-G. Reinhard, Violation of the zero-force theorem in the time-dependent Krieger-Li-Iafrate approximation, *Phys. Rev. A* **75**, 050501(R) (2007).
- [7] L. Cort, D. Karlsson, G. Lani, and R. van Leeuwen, Time-dependent density-functional theory for strongly interacting electrons, *Phys. Rev. A* **95**, 042505 (2017).
- [8] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).

- [9] M. Ruggenthaler, S. E. B. Nielsen, and R. van Leeuwen, Analytic density functionals with initial-state dependence and memory, *Phys. Rev. A* **88**, 022512 (2013).
- [10] P. Gori-Giorgi, G. Vignale, and M. Seidl, Electronic zero-point oscillations in the strong-interaction limit of density functional theory, *J. Chem. Theory Comput.* **5**, 743 (2009).
- [11] M. Seidl, Strong-interaction limit of density-functional theory, *Phys. Rev. A* **60**, 4387 (1999).
- [12] F. Malet, A. Mirtschink, K. J. H. Giesbertz, L. O. Wagner, and P. Gori-Giorgi, Exchange-correlation functionals from the strong interaction limit of DFT: Applications to model chemical systems, *Phys. Chem. Chem. Phys.* **16**, 14551 (2014).
- [13] NIST Digital Library of Mathematical Functions, <https://dlmf.nist.gov/28.8>, Release 1.0.21 of 2018-12-15, edited by F. W. J. Olver, A. B. Olde Daalhuis, D. W. Lozier, B. I. Schneider, R. F. Boisvert, C. W. Clark, B. R. Miller, and B. V. Saunders.
- [14] S. E. B. Nielsen, M. Ruggenthaler, and R. van Leeuwen, Numerical construction of the density-potential mapping, *Eur. Phys. J. B* **91**, 235 (2018).
- [15] M. A. Buijse, E. J. Baerends, and J. G. Snijders, Analysis of correlation in terms of exact local potentials: Applications to two-electron systems, *Phys. Rev. A* **40**, 4190 (1989).
- [16] G. Blanch, The asymptotic expansions for the odd periodic mathieu functions, *Trans. Amer. Math. Soc.* **97**, 357 (1960).