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Peer reviewed|Thesis/dissertation

# UNIVERSITY OF CALIFORNIA, IRVINE

Developing Thermal Density Functional Theory Using the Asymmetric Hubbard Dimer

#### DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

#### DOCTOR OF PHILOSOPHY

in Physics

by

Justin Clifford Smith

Dissertation Committee: Professor Kieron Burke, Chair Professor Steven White Professor Siddharth Parameswaran

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# DEDICATION

This dissertation is dedicated in memory of my father Terrance Clifford Smith.

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Exact conditions on the temperature dependence of density functionals Physical Review B	2016
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Dirac Point Degenerate with Massive Bands at a Topological Quantum Critical Point Physical Review Letters	2011
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Review of Interacting Electrons Theory and Computational Approaches by R M. Martin, L. Reining, and D. M. Ceperley American Journal of Physics (to appear)	2017

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of materials under extreme conditions	
APS March Meeting	New Orleans, LA
Thermal Corrections to Density Functional Simulations of	March 2016
Warm Dense Matter	
APS March Meeting	Baltimore, MD
The Hubbard Dimer: A density functional case study of a	March 2015
many-body problem	
APS March Meeting	San Antonio, TX
Density Functional Treatment of the Hubbard Dimer	March 2014
APS March Meeting	Denver, CO

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Digging deep into physics and science policy	November 2016
GPS-BIOMED Elevator Pitch Competition	Irvine, CA
Understanding Density Functional Theory Through the Lens	December 2015
of a Simple Model	
Brews and Brains	Irvine, CA

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# ABSTRACT OF THE DISSERTATION

Developing Thermal Density Functional Theory Using the Asymmetric Hubbard Dimer

By

Justin Clifford Smith

Doctor of Philosophy in Physics University of California, Irvine, 2017

Professor Kieron Burke, Chair

In this dissertation, I introduce both ground-state and thermal density functional theory. Throughout I use the asymmetric two-site Hubbard model, called the Hubbard dimer for short, to better understand and/or develop these theories. This model is used because it can be solved analytically and it contains all the necessary physics while still being conceptually simple enough to tease apart the various aspects of density functional theory. Ground-state density functional theory has seen broad use in many disciplines including physics, chemistry, geology, and material science and has led to a number of important physical and technological successes. In the first two chapters I elucidate the behavior of the ground-state theory using the Hubbard dimer. The simplicity of the model allows me to showcase aspects of the theory that are common points of confusion within the electronic structure community, e.g. the fundamental gap problem. The next two chapters focus on thermal density functional theory which has been coming to prominence as the study of warm dense matter has become a growing interest at the national laboratories and in the astronomical body community. The Hubbard dimer allows me to do the first ever exact thermal density functional theory calculation. In this work I am better able to understand the approximations used in thermal density functional theory and can point to why they succeed and fail. This also allows me to illustrate old conditions and derive new ones. I conclude with an overview of the work and a few different directions in which the asymmetric Hubbard dimer could be used further.

# Chapter 1

# The Hubbard Dimer: A density functional case study of a many-body problem (part 1)

This chapter, and the next, is entirely from Ref. [47] with its corrigendum incorporated. This work was co-authored with Diego Carrascal (first), Jaime Ferrer (second), and Kieron Burke (fourth). I was third author and contributed writing, proof reading, additional calculations and derivations, and verification of all results.

This first chapter consists of the first portions of the paper that lay out the foundation of DFT, the Hubbard dimer, and Site-Occupation Functional Theory.

# 1.1 Abstract

This review explains the relationship between density functional theory and strongly correlated models using the simplest possible example, the two-site Hubbard model. The relationship to traditional quantum chemistry is included. Even in this elementary example, where the exact ground-state energy and site occupations can be found analytically, there is much to be explained in terms of the underlying logic and aims of Density Functional Theory. Although the usual solution is analytic, the density functional is given only implicitly. We overcome this difficulty using the Levy-Lieb construction to create a parametrization of the exact function with negligible errors. The symmetric case is most commonly studied, but we find a rich variation in behavior by including asymmetry, as strong correlation physics vies with charge-transfer effects. We explore the behavior of the gap and the many-body Green's function, demonstrating the 'failure' of the Kohn-Sham method to reproduce the fundamental gap. We perform benchmark calculations of the occupation and components of the KS potentials, the correlation kinetic energies, and the adiabatic connection. We test several approximate functionals (restricted and unrestricted Hartree-Fock and Bethe Ansatz Local Density Approximation) to show their successes and limitations. We also discuss and illustrate the concept of the derivative discontinuity. Useful appendices include analytic expressions for Density Functional energy components, several limits of the exact functional (weak- and strong-coupling, symmetric and asymmetric), various adiabatic connection results, proofs of exact conditions for this model, and the origin of the Hubbard model from a minimal basis model for stretched  $H_2$ .

### **1.2** Introduction

In condensed matter, the world of electronic structure theory can be divided into two camps: the weakly and the strongly correlated. Weakly correlated solids are almost always treated with density-functional methods as a starting point for ground-state properties[67, 147, 42, 33, 37]. Many-body (MB) approximations such as GW might then be applied to find properties of the quasi-particle spectrum, such as the gap[297, 231, 15]. This approach is 'firstprinciples', in the sense that it uses the real-space Hamiltonian for the electrons in the field of the nuclei, and produces a converged result that is independent of the basis set, once a sufficiently large basis set is used. Density functional theory (DFT) is known to be exact in principle, but the usual approximations often fail when correlations become strong[56].

On the other hand, strongly correlated systems are most often treated via lattice Hamiltonians with relatively few parameters[150, 59]. These simplified Hamiltonians can be easier to deal with, especially when correlations are strong[75, 59]. Even approximate solutions to such Hamiltonians can yield insight into the physics, especially for extended systems[278]. However, such Hamiltonians can rarely be unambiguously derived from a first-principles starting point, making it difficult (if not impossible) to say how accurate such solutions are quantitatively or to improve on that accuracy. Moreover, methods that yield approximate Green's functions are often more focused on response properties or thermal properties rather than on total energies in the ground-state.

On the other hand, the ground-state energy of electrons plays a much more crucial role in chemical and material science applications [190, 211]. Very small energy differences determine geometries and sometimes qualitative properties, such as the nature of a transition state in a chemical reaction [164, 117, 78] or where a molecule is adsorbed on a surface [20, 210]. An error of 0.05 eV changes a reaction rate by a factor of 5 at room temperature. Thus quantum chemical development has focused on extracting extremely accurate energies for the ground and other eigenstates [306, 115, 88, 255, 321]. This is routinely achieved for molecules using coupled-cluster methods (CCSD(T)) and reasonable basis sets [237, 280]. Such methods are called *ab initio*, but are not yet widespread for solids, where quantum Monte Carlo (QMC) is more often used [84, 294]. DFT calculations for molecules are usually much less computationally demanding, but the errors are less systematic and less reliable [212].

However, many materials of current technological interest are both chemically complex and strongly correlated. Numerous metal oxide materials are relevant to novel energy technologies, such as  $\text{TiO}_2$  for light-harvesting[208] or LiO compounds for batteries[110, 285]. For many cases, DFT calculations find ground-state structures and parameters, but some form of strong correlation method, such as introducing a Hubbard U or applying dynamical mean field theory (DMFT), is needed to correctly align bands and predict gaps[13, 93]. There is thus great interest in developing techniques that use insights from both ends, such as DFT+U and dynamical mean field theory[121, 14, 152, 151, 155, 154].

There are two different approaches to combining DFT with lattice Hamiltonians [43]. In the first, more commonly used, the lattice Hamiltonian is taken as given, and a density function(al) theory is constructed for that Hamiltonian[108]. We say function(al), not functional, as the density is now given by a list of occupation numbers, rather than a continuous function in real space. The parenthetical reminds us that although everything is a function, it is analogous to the functionals of real-space DFT. We will refer to this method as SOFT, i.e., site-occupation function(al) theory[261], although in the literature it is also known as lattice density functional theory [129]. While analogs of the basic theorems of real-space DFT can be proven such as the Hohenberg-Kohn (HK) theorems and the Levy constrained search formulation for SOFT, it is by no means clear [113] how such schemes might converge to the real-space functionals as more and more orbitals (and hence parameters) are added. Alternatively, one may modify efficient solvers of lattice models so that they can be applied to real-space Hamiltonians (as least in 1-D), and use them to explore the nature of the exact functionals and the failures of present approximations [308, 281]. While originally formulated for Hubbard-type lattices, SOFT has been extended and applied to many different models include quantum-spin chains[8], the Anderson impurity model[289, 46], the 1-D random Fermi-Hubbard model[319], and quantum dots[257].

These two approaches are almost orthogonal in philosophy. In the first, one finds approximate function(al)s for lattice Hamiltonians, and can then perform Kohn-Sham (KS) DFT calculations on much larger (and more inhomogeneous) lattice problems[39], but with all the usual caveats of DFT treatments (am I looking at interesting physics or a failure of an uncontrolled approximation?). For smaller systems, one can often also compare approximate DFT calculations with exact results, results which would be prohibitively expensive to calculate on real-space Hamiltonians. The dream of lattice models in DFT is that lessons we learn on the lattice can be applied to real-space calculations and functional developments. To this end, work has been done on understanding self-interaction corrections[302], and on wedding TDDFT and DMFT methods for application to more complex lattices (e.g. 3-D Hubbard)[138]. And while it is beyond the scope of this current review, much work has been done on developing and applying density-matrix functional theory for the lattice as well[178, 179, 180, 181, 253, 254]. While such results can be very interesting, it is often unclear how failures of approximate lattice DFT calculations are related to failures of the standard DFT approximations in the real world.

There is much interest in extracting excited-state information from DFT, and time-dependent (TD) DFT[248] has become a very popular first-principles approach[38, 292, 189]. Because exact solutions and useful exact conditions are more difficult for TD problems, there has been considerable research using lattices. TD-SOFT can be proven for the lattice in much the same way SOFT is proven from ground-state DFT. This generalization is worked out carefully in Refs. [288, 77]. An adiabatic approximation for TDSOFT was introduced in ref. [296]. Applications of TD-SOFT typically involve Hubbard chains both with and without various types of external potentials [16, 139, 290, 187]. However, TD-SOFT has also been applied to the dimer to understand the effects of the adiabatic approximation in TD-DFT[90, 92, 91], strong correlation[290], and TD-LDA results for stretched H<sub>2</sub> in real-space[17]. Unfortunately, we will already fill this article simply discussing the ground-state SOFT problem, and save the TD case for future work.

To get the basic idea, consider Fig. 1.1. It shows the asymmetric Hubbard dimer in two different regimes. In this work we use asymmetric to mean differing on-site potentials. On



Figure 1.1: Many-body view of two distinct regimes of the asymmetric Hubbard dimer. On the left, the charging energy is much greater than the difference in on-site potentials. On the right, the situation is reversed.

the left, the Hubbard U energy is considerably larger than the difference in on-site potentials and the hopping energy t. This is the case most often analyzed, where strong correlations drive the system into the Mott-Hubbard regime if U is also considerably larger than t. The on-site occupations are in this case close to 1. On the right panel, U is in contrast smaller than the on-site potential difference  $\Delta v$ , and here the dimer stays in the charge-transfer regime, where both electrons mostly sit in the same deeper well. This is the many-body view of the physics of an asymmetric Hubbard dimer.

Now we turn to the KS-DFT viewpoint. Here, we replace the interacting Hubbard dimer  $(U \neq 0)$  with a non-interacting (U = 0) tight-binding dimer, called the KS system, that reproduces the Hubbard occupations. In Fig. 1.2, we take the asymmetric dimer with the same on-site potential difference, but we vary U. We plot the occupations, showing how, as U increases, their difference decreases. But we also plot the on-site potentials of the Kohn-Sham model,  $\Delta v_s$ , that are chosen to reproduce the occupations of the interacting system with a given value of U. As U increases, the KS on-site potential difference reduces and the offset from 0 increases. The middle panel corresponds to the charge-transfer conditions of



Figure 1.2: DFT view: occupations n and potentials v of an asymmetric half-filled Hubbard dimer as a function of U. The on-site potential difference  $\Delta v$  is shown in black and the KS on-site potential difference  $\Delta v_s$  is in red. The second and third panels correspond to the situations of Fig. 1.1.

Fig. 1.1, while the last panel corresponds to the Mott-Hubbard conditions of Fig. 1.1. The basic theorems of DFT show that if we know the energy as a function(al) of the density, we can determine the occupations by solving effective tight-binding equations, the KS equations, and then find the *exact* ground-state energy. This is not mean-field theory. It is instead a horribly contorted logical construction, that is wonderfully practical for computations of ground-state quantities. Inside this article, we give explicit formulas for the energy functional of the Hubbard dimer.

We perform a careful study of the Hubbard dimer, to show the differences between SOFT and real-space DFT. We show how it is *necessary* to introduce inhomogeneity into the site occupations in order to find the exact density function(al) explicitly. In Section 1.3.1 we explain the logic of the KS DFT approach in excruciating detail in order to both illustrate the concepts to those unfamiliar with the method and to give explicit formulas for anyone doing SOFT calculations. We elucidate the differences between the KS and the many-body Green's functions in Section 2.1.3. Next, in Sections 2.1 and 2.2 we discuss in detail both concepts and tools for strong correlation, and explain how the gap problem appears in DFT. We construct the adiabatic connection formula for the exact function(al) in Section 2.2.2, showing how it is quantitatively similar to those of real-space DFT. We use the theory to construct a simple parametrization for the exact function(al) for this problem in Section 2.3, where we also demonstrate the accuracy of our formula by finding ground-state energies and densities by solving the KS equations with our parametrization. In Section 2.4.1, we study the broken-symmetry solutions of Hartree-Fock theory, showing that these correctly yield both the strongly-correlated limit and the approach to this limit for strong correlation. In Section 2.4.2 we present BALDA (Bethe-ansatz local density approximation), a popular approximation for lattice DFT, and in Section 2.4.3 we compare the accuracy of BALDA and Hartree-Fock to each other. We discuss fractional particle number and the derivative discontinuity in Section 2.5. Finally, we end with a discussion of our results in Section 2.6. In Table 1.1 we list our notation for the Hubbard dimer, as well as many standard DFT definitions.

Our purpose here is several-fold. Perhaps most importantly, this article is intended to explain the logic of modern DFT to our friends who are more familiar with strongly correlated lattice systems. We believe this should be equally useful to any researcher interested in manyelectron systems such as traditional quantum chemists, or atomic and molecular physicists, since we use and explain the simplest model of strong correlation to illustrate many of the basic techniques of modern DFT. There are many more tricks and constructions, but we save those for future work.

Secondly, the article forms an essential reference for those researchers interested in SOFT, possibly in very different contexts and applied to very different models. It shows precisely how

concepts from first-principles calculations are realized in lattice models. Third, we give many exact results for this simple model, expanding in many different limits, showing that even in this simple case, there are orders-of-limits issues. Fourth, we use DFT techniques to find a simple but extremely accurate parametrization of the exact function(al) for this model. Even though the model can be solved analytically, the function(al) cannot be expressed explicitly. Thus our parametrization provides an ultra-convenient and ultra-accurate expression for the exact function(al) for this model, that can be used in the ever increasing applications of SOFT. Finally, we examine several standard approximations to SOFT, including both restricted and unrestricted mean field theory, and the BALDA, and we find surprising results.

## 1.3 Background

In this section we briefly introduce real-space DFT, and the logical underpinnings for everything that follows. Then we discuss the mean-field approach to the Hubbard model as well as a few well-known results and limits for the Hubbard dimer. Throughout this section we use atomic units for all real-space expressions so all energies are in Hartree and all distances are in Bohr.

#### **1.3.1** Density functional theory

We restrict ourselves to non-relativistic systems within the Born-Oppenheimer approximation with collinear magnetic fields [73]. Density functional theory is concerned with efficient methods for finding the ground-state energy and density of N electrons whose Hamiltonian contains three contributions:

$$\hat{H} = \hat{T} + \hat{V}_{\rm ee} + \hat{V}.\tag{1.1}$$

The first of these is the kinetic energy operator, the second is the electron-electron repulsion, while the last is the one-body potential,

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i).$$
(1.2)

Only N and  $v(\mathbf{r})$  change from one system to another, be they atoms, molecules or solids. In 1964, Hohenberg and Kohn proved that for a given electron-electron interaction, there was at most one  $v(\mathbf{r})$  that could give rise to the ground-state one-particle density  $n_0(\mathbf{r})$  of the system, thereby showing that all ground-state properties of that system were uniquely determined by  $n_0(\mathbf{r})$  [124]. The ground-state energy  $E_0$  could then be found by splitting the variational principle into two steps via the Levy-Lieb constrained search approach[165, 168]. First, the universal functional F is determined,

$$F[n] = \min_{\Psi \to n} \langle \Psi | \, \hat{T} + \hat{V}_{\text{ee}} \, | \Psi \rangle = T[n] + V_{\text{ee}}[n] \tag{1.3}$$

where the minimization is over all normalized, antisymmetric  $\Psi$  with one-particle density  $n(\mathbf{r})$ . This establishes a one-to-one connection between wavefunctions and ground-state densities, and enables us to define the minimizing wavefunction functional  $\Psi[n_0]$ . Then the ground-state energy is determined by a second minimization step of the energy functional E[n],

$$E_0 = \min_n \{E[n]\} = \min_n \left\{ F[n] + \int d^3 r \, n(\mathbf{r}) \, v(\mathbf{r}) \right\}.$$
(1.4)

This shows that  $E_0$  can be found from a search over one-particle densities  $n(\mathbf{r})$  instead of many-body wavefunctions  $\Psi$ , provided that the functional F[n] is known. The Euler equation corresponding to the above minimization for fixed N is simply

$$\frac{\delta F[n]}{\delta n(\mathbf{r})}\Big|_{n_0(\mathbf{r})} = -v(\mathbf{r}).$$
(1.5)

Armed with the exact F[n], the solution of this equation yields the exact ground-state density which, when inserted back into F[n], yields the exact ground-state energy.

To increase accuracy and construct F[n], modern DFT calculations use the Kohn-Sham (KS) scheme that imagines a fictitious set of non-interacting electrons with the same ground-state density as the real Hamiltonian[148]. These electrons satisfy the KS equations:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm s}(\mathbf{r})\right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \qquad (1.6)$$

where  $v_{s}(\mathbf{r})$  is defined as the unique potential that generates single-electron orbitals  $\phi_{i}(\mathbf{r})$ that reproduce the ground-state density of the real system,

$$n_0(\mathbf{r}) = \sum_{occ} |\phi_i(r)|^2.$$
(1.7)

To relate these to the interacting system, we write

$$F[n] = T_{\rm s}[n] + U_{\rm H}[n] + E_{\rm xc}[n].$$
(1.8)

 $T_{\rm s}$  is the non-interacting (or KS) kinetic energy, given by

$$T_{\rm s}[n] = \frac{1}{2} \int d^3 \sum_{i=1}^{N} |\nabla \phi_i(\mathbf{r})|^2 = \min_{\Phi \to n} \langle \Phi | \, \hat{T} | \Phi \rangle, \tag{1.9}$$

where we have assumed the KS wavefunction (as is almost always the case) is a single Slater determinant  $\Phi$  of single-electron orbitals. The second expression follows from Eq. (1.3) applied to the KS system, it emphasizes that  $T_{\rm s}$  is a functional of  $n(\mathbf{r})$ , and the minimizer defines  $\Phi[n_0]$ , the KS wavefunction as a density functional. Then  $U_{\rm H}[n]$  is the classical electrostatic self-repulsion of  $n(\mathbf{r})$ ,

$$U_{\rm H}[n] = \frac{1}{2} \int d^3r \, \int d^3r' \, \frac{n(\mathbf{r}) \, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},\tag{1.10}$$

and  $E_{\rm xc}$  is called the exchange-correlation energy, and is *defined* by Eq. (1.8).

Lastly, we differentiate Eq. (1.8) with respect to the density. Applying Eq. (1.5) to the KS system tells us

$$v_{\rm s}(\mathbf{r}) = -\frac{\delta T_{\rm s}[n]}{\delta n(\mathbf{r})},\tag{1.11}$$

yielding

$$v_{\rm s}(\mathbf{r}) = v(\mathbf{r}) + v_{\rm H}(\mathbf{r}) + v_{\rm xc}(\mathbf{r}) \tag{1.12}$$

where  $v_{\rm H}({f r})$  is the classical electrostatic potential and

$$v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})} \tag{1.13}$$

is the exchange-correlation potential. This is the single most important result in DFT, as it closes the set of KS equations. Given any expression for  $E_{\rm xc}$  in terms of  $n_0(\mathbf{r})$ , either approximate or exact, the KS equations can be solved self-consistently to find  $n_0(\mathbf{r})$  for a given  $v(\mathbf{r})$ . Under standard conditions, and with the exact functional, they always converge[309].

However, we also note that, just as in all such schemes, the energy of the KS electrons *does* not match that of the real system. This 'KS energy' i.e., the energy of the KS electrons, is

$$E_{\rm s}[n] = \sum_{i} \epsilon_i = T_{\rm s} + V_{\rm s},\tag{1.14}$$

but the actual energy is

$$E_0 = F[n_0] + V[n_0] = T_s[n_0] + U_H[n_0] + E_{xc}[n_0] + V[n_0]$$
(1.15)

where  $n_0(\mathbf{r})$  and  $T_s[n_0]$  have been found by solving the KS equations, and inserted into this

expression. Thus, in terms of the KS orbital energies, there are double-counting corrections, which can be deduced from Eqs. (1.14) and (1.15):

$$E_0 = E_{\rm s} - U_{\rm H}[n_0] + E_{\rm xc}[n_0] - \int d^3 r \, n_0(\mathbf{r}) \, v_{\rm xc}[n_0](\mathbf{r}).$$
(1.16)

We emphasize that, with the exact  $E_{\rm xc}[n_0]$ , solution of the KS equations yields the exact ground-state density and energy, and this has been done explicitly in model cases[309], but is computationally exorbitant. The practical use of the KS scheme is that simple, physically motivated approximations to  $E_{\rm xc}[n_0]$  often yield usefully accurate results for  $E_0$ , bypassing direct solution of the many-electron problem.

For the remainder of this article, we drop the subscript 0 for notational convenience, and energies will be assumed to be ground-state energies, unless otherwise noted. For many purposes, it is convenient to split  $E_{\rm xc}$  into a sum of exchange and correlation contributions. The definition of the KS exchange energy is simply

$$E_{\rm x}[n] = \langle \Phi[n] | \hat{V}_{\rm ee} | \Phi[n] \rangle - U_{\rm H}[n].$$
(1.17)

The remainder is the correlation energy functional

$$E_{\rm c}[n] = F[n] - \langle \Phi[n] | \hat{T} + \hat{V}_{\rm ee} | \Phi[n] \rangle, \qquad (1.18)$$

which can be decomposed into kinetic  $T_{\rm c}$  and potential  $U_{\rm c}$  contributions (see Eqs. (2.11) and (2.12) in Sec. 2.2). Additionally, all practical calculations generalize the preceding formulas for arbitrary spin using spin-DFT [304].

For just one particle (N = 1), there is no electron-electron repulsion, i.e.,  $V_{ee} = 0$ . This

means

$$E_{\rm x} = -U_{\rm H}, \quad E_{\rm C} = 0, \qquad (N = 1),$$
(1.19)

i.e., the self-exchange energy exactly cancels the Hartree self-repulsion. Since there is no interaction,  $F^0[n] = T[n] = T_s[n]$ , and for one electron we know the explicit functional:

$$T_{\rm s} = T^{\rm W} = \int d^3r \, |\nabla n|^2 / (8n), \tag{1.20}$$

which is called the von Weisacker functional [312]. For two electrons in a singlet (N = 2),

$$E_{\rm x} = -U_{\rm H}/2, \qquad T_{\rm s} = T^{\rm W}, \qquad (N=2),$$
 (1.21)

but the correlation components are non-zero and non-trivial.

Many popular forms of approximation exist for  $E_{\rm xc}[n]$ , the most common being the local density approximation (LDA)[148, 304, 224], the generalized gradient approximation (GGA)[217, 27, 162, 130, 219], and hybrids of GGA with exact exchange from a Hartree-Fock calculation[28, 220, 5, 120]. The computational ease of DFT calculations relative to more accurate wavefunction methods usually allows much larger systems to be calculated, leading to DFT's immense popularity today[234]. However, all these approximations fail in the paradigm case of stretched  $H_2$ , the simplest example of a strongly correlated system[21, 56, 118].

#### 1.3.2 The Hubbard model

The Hubbard Hamiltonian is possibly the most studied, and simplest, model of a strongly correlated electron system. It was initially introduced to describe the electronic properties of narrow-band metals, whose conduction bands are formed by d and f orbitals, so that electronic correlations become important[127, 85]. The model was used to describe ferromagnetic, antiferromagnetic and spin-spiral instabilities and phases, as well as the metalinsulator transition in metals and oxides, including high-T<sub>c</sub> superconductors[59, 163]. The Hubbard model is both a qualitative version of a physical system depending on what terms are built in[12, 264] and also a testing-ground for new techniques since the simpler forms of the Hubbard model are understood very well[122, 30, 31, 123].

The model assumes that each atom in the lattice has a single orbital. The Hamiltonian is typically written as [191, 109, 76, 283]

$$\hat{H} = \sum_{i,\sigma} v_{i\sigma} \,\hat{n}_{i\sigma} - \sum_{i\,j\,\sigma} \left( t_{ij} \,\hat{c}^{\dagger}_{i\,\sigma} \,\hat{c}_{j\,\sigma} + h.c. \right) + \sum_{i} U_i \,\hat{n}_{i\uparrow} \,\hat{n}_{i\downarrow} \tag{1.22}$$

where at its simplest the on-site energies are all equal  $v_{i\sigma} = 0$  as well as the Coulomb integrals  $U_i = U$ . Further, the hopping integrals  $t_{ij}$  typically couple only nearest neighbor atoms and are equal to a single value t.

We note that here the interaction is of ultra-short range, so that two electrons only interact if they are on the same lattice site. Further, they must have opposite spins to obey the Pauli principle. Simple examples of building in more complicated physics include using next-nearest-neighbor hoppings or nearest neighbors Coulomb integrals for high- $T_c$ cuprate calculations and magnetic properties[174, 71, 61], and varying on-site potentials used to model confining potentials[244]. Also, adding more orbitals per site delivers multiband Hubbard models, where Coulomb correlations may be added to some or all of the orbitals. The Hubbard model has an analytical solution in one dimension, via Bethe ansatz techniques[170, 169].

If the Hubbard U is small enough, a paramagnetic mean-field (MF) solution provides a reasonable description of the model in dimensions equal or higher than two. As an example,

the Hubbard model in a honeycomb lattice can describe correctly a number of features of gated graphene samples [119]. However, for large U or in one dimension, more sophisticated approaches are demanded, which go beyond the scope of this article [170, 85].

We describe briefly the well-known broken-symmetry MF solution, where the populations of up- and down-spin electrons can differ. The standard starting point for the MF solution neglects completely quantum fluctuations:

$$(\hat{n}_{i\uparrow} - n_{i\uparrow}) \ (\hat{n}_{i\downarrow} - n_{i\downarrow}) = 0, \qquad (MF)$$

$$(1.23)$$

where  $n_{i\sigma} = \langle \hat{n}_{i\sigma} \rangle$ , so that

$$\hat{V}_{ee}^{MF} = \sum_{i} U \left( n_{i\uparrow} \,\hat{n}_{i\downarrow} + n_{i\downarrow} \,\hat{n}_{i\uparrow} - n_{i\uparrow} \,n_{i\downarrow} \right). \tag{1.24}$$

The MF hamiltonian is then just an effective single-particle problem

$$\hat{H}^{MF} = \sum_{i\sigma} \hat{h}_{i\sigma}^{\text{eff}}, \qquad (1.25)$$

$$\hat{h}_{i\sigma}^{\text{eff}} = v_{i\sigma}^{MF} \hat{n}_{i\sigma} - t \sum_{j} (\hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + h.c.), \qquad (1.26)$$

where  $v_{i\sigma}^{MF} = v_{i\sigma} + U n_{i\bar{\sigma}}$ . This  $\hat{H}^{MF}$  can be easily diagonalized if one assumes spacehomogeneity of the occupations  $n_{i,\sigma} = n_{\sigma}$ . For large U, the broken symmetry solution (often ferromagnetic) has lower energy than the paramagnetic solution.

#### 1.3.3 The two-site Hubbard model

We now specialize to a simple Hubbard dimer model with open boundaries, but we allow different on-site spin-independent energies by introducing a third term that produces asymmetric occupations,

$$\hat{H} = -t \sum_{\sigma} \left( \hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + h.c \right) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i} v_i \hat{n}_i$$
(1.27)

where we have made the choices  $t_{12} = t_{21}^* = t$  and  $v_1 + v_2 = 0$ . Our notation for this Hamiltonian can be found in Table 1.1. Specifically, the two-site model is useful in comparing approximate methods[185] or investigating highly local properties [40] due to its conceptual simplicity. Recently, the two-site model was realized experimentally using ultracold techniques with the hopes of experimentally building more arbitrary Hubbard models in the future [202]. This model was carefully investigated in a DFT context by Requist and Pankratov[242, 243].



Figure 1.3: Ground-state energy of Hubbard dimer as a function of  $\Delta v$  for several values of U and 2t = 1.

It is straightforward to find an analytic solution of the model for any integer occupation N. However, we specialize to the particle sub-space N = 2,  $S_z = 0$  in what follows unless otherwise stated. We expand the Hamiltonian in the basis set  $[|1 \uparrow 1 \downarrow\}, |1 \uparrow 2 \downarrow\}, |1 \downarrow 2 \uparrow\}, |2 \uparrow 2 \downarrow\}]:$ 

$$\hat{H} = \begin{pmatrix} 2v_1 + U & -t & t & 0 \\ -t & 0 & 0 & -t \\ t & 0 & 0 & t \\ 0 & -t & t & 2v_2 + U \end{pmatrix}$$
(1.28)

The eigenstates are three singlets and a triplet state. The ground-state energy corresponds to the lowest-energy singlet, and can be found analytically. The expressions are given in 2.9. The wavefunction, density difference, and individual energy components are also given there. We plot in Fig. 1.3 the ground-state energy as a function of  $\Delta v$  for several values of U, while in Fig. 1.4, we plot the occupations.



Figure 1.4: Ground-state occupation of Hubbard dimer as a function of  $\Delta v$  for several values of U and 2t = 1.

When U = 0, we have the simple tight-binding result, for which the ground-state energy is

$$E = -\sqrt{(2t)^2 + \Delta v^2} \qquad (U = 0), \qquad (1.29)$$

$$\Delta n = -2\Delta v / \sqrt{(2t)^2 + \Delta v^2} \qquad (U=0).$$
(1.30)

where  $\Delta n$  is defined in Table 1.1. If there is only one electron, these become smaller by a factor of 2. The curves for U = 0.2 are indistinguishable (by eye) from the tight-binding result. We may simplify the expressions by introducing an effective hopping parameter,

$$\tilde{t} = t\sqrt{1 + (\Delta v/(2t))^2}$$
(1.31)

which accounts for the asymmetric potential. Then

$$E = -2\tilde{t}, \qquad (U=0), \qquad (1.32)$$
$$\Delta n = -\Delta v/\tilde{t},$$

i.e., the same equations as when  $\Delta v = 0$ .

In the other extreme, as U grows, we approach the strongly correlated limit. For a given  $\Delta v$ , as U increases,  $\Delta n$  decreases as in Figs. 1.2 and 1.4, see also Fig. 1 in [242], and the magnitude of the energy shrinks. Typically, the  $E(\Delta v)$  curve morphs from the tight-binding result towards two straight lines for U large:

$$E \simeq (U - \Delta v) \Theta(\Delta v - U), \qquad U \gg 2t,$$
(1.33)

$$\Delta n \simeq -2 \Theta(\Delta v - U), \qquad U \gg 2t. \tag{1.34}$$

We also have a simple well-known result for the symmetric limit,  $\Delta v=0$ , where

$$E = -\sqrt{(2t)^2 + (U/2)^2} + U/2, \qquad (\Delta n = \Delta v = 0).$$
(1.35)

This vanishes rapidly with 1/U for large U. Its behavior is different from the case with finite  $\Delta v$ . Results for various limits and energy components are given in 2.9.

#### 1.3.4 Quantum chemistry

Traditional quantum chemical methods (often referred to as *ab initio* by their adherents) usually begin with the solution of the Hartree-Fock equations[282]. For our Hubbard dimer, these are nothing but the mean-field equations of Sec 1.3.2. Expressing the paramagnetic HF Hamiltonian of Eq. (1.26) for two sites yields a simple tight-binding Hamiltonian and eigenvalue equation describing a single-particle in an effective potential:

$$v_i^{\text{eff}}(n_i) = v_i + Un_i/2.$$
 (1.36)

with an eigenvalue:

$$\epsilon^{\text{eff}} = \left(U - \sqrt{(\Delta v^{\text{eff}})^2 + (2t)^2}\right)/2.$$
(1.37)

Writing  $\phi^{\text{eff}} = (c_1, c_2)^T$ , then

$$\Delta n = 2\left(c_2^2 - c_1^2\right) = 2\frac{\xi^2 - 1}{\xi^2 + 1},\tag{1.38}$$

where  $x = \Delta v^{\text{eff}}/2t$ , and  $\xi = \sqrt{x^2 + 1} - x$ . Eq. (1.38) is quartic in  $\Delta n$  and can be solved algebraically to find  $\Delta n$  as a function of  $\Delta v$  explicitly (2.13). Just as in KS, the HF energy
is not simply twice the orbital energy, there is a double-counting correction:

$$E^{MF} = 2\epsilon^{\text{eff}} - U_{\text{H}}$$

$$= \frac{U}{2} \left( 1 - \left(\frac{\Delta n}{2}\right)^2 \right) - 2t\sqrt{1 + x^2}.$$

$$(1.39)$$

These energies are plotted in Fig 1.5. We see that for small U, HF is very accurate, but much



Figure 1.5: Ground-state energy of the Hartree-Fock Hubbard dimer (thick dashed line) and exact ground-state of the Hubbard dimer (thin solid line) as a function of  $\Delta v$  for several values of U and 2t = 1.

less so for  $2t \ll U \ll \Delta v$ . In fact, the HF energy becomes positive in this region, unlike the exact energy, which we prove is never positive in 2.11. The molecular orbitals often used in chemical descriptions have traditionally been those of HF calculations, despite the fact that HF energies are usually far too inaccurate for most chemical energetics[26]. (They have now largely been supplanted by KS orbitals.) In quantum chemical language, the paramagnetic

mean-field solution is called restricted HF (RHF) because the spin symmetry is restricted to that of the exact solution, i.e.,  $S_z = 0$ . For large enough U, the broken-symmetry, or unrestricted, solution is lower, and is labeled UHF, which we discuss in Sec. 2.4.1.



Figure 1.6: Correlation energy  $E_{\rm c}^{\rm trad}$  of Hubbard dimer as a function of  $\Delta v$  for several values of U and 2t = 1.

Accurate ground-state energies, especially as a function of nuclear positions, are central quantities in chemical electronic structure calculations[282]. Most such systems are weakly correlated unless the bonds are stretched. The correlation energy of traditional quantum chemistry is defined as just the error made by the (restricted) HF solution:

$$E_{\rm c}^{\rm trad} = E - E^{\rm HF}.\tag{1.40}$$

This is plotted in Fig 1.6. This is always negative, by the variational principle. Many techniques have been highly developed over the decades to go beyond HF. These are called model chemistries, and for many small molecules, errors in energy differences of less than 1

kcal/mol (0.05 eV) are now routine[204, 24].

Usually  $E_{\rm c}^{\rm trad}$  is a small fraction of E for weakly correlated systems. For example, for the He atom, E = -77.5 eV, but  $E_{\rm c}^{\rm trad} = -1.143$  eV. This is the error made by a HF calculation. In Fig. 1.6 we plot  $E_{\rm c}^{\rm trad}$  just as we plotted E in Fig. 1.5. We see that for strong correlation  $E_{\rm c}^{\rm trad}$  becomes large ( $\sim -U/2$  for  $\Delta v \ll U$ ), much larger than E. However, E is much smaller, and so any strongly correlated method should reproduce E accurately. In fact, one can already see difficulties for weakly correlated approximations in this limit. For weak correlation, a small percent error in  $E_{\rm c}^{\rm trad}$  yields a very small error in E, but produces an enormous error in E in the strong correlation limit. For an infinitely stretched molecular bond,  $t \to 0$  while U remains finite, so only one electron is on each site. Thus  $E \to 0$ , so we can think of E as the ground-state electronic energy relative to the dissociated limit, i.e. the binding energy.

Because HF is accurate for E when correlation is weak, and because quantum chemistry focuses on energy differences, the error is often measured in terms of the accuracy of the exchange-correlation together (if both are approximated as in most DFT calculations). For 2 electrons having  $S_z = 0$ , the exact exchange is trivial, and so we will focus on approximations to the correlation energy.

Notice the slight difference in definition of correlation energy between DFT (Eq. 1.18) and quantum chemistry (Eq. (1.40))[252, 104, 293]. In DFT, all quantities are defined on a given density, usually the exact density of the problem, whereas in quantum chemistry, the HF energy is evaluated on the density that minimizes the HF energy. For weakly correlated systems, this difference is extremely small[97], but is not so small for large U. And, one can prove,  $E_{c}^{trad} \geq E_{c}^{DFT}$ [104], (see 2.11).

We close by emphasizing the crucial difference in philosophy between DFT and traditional approaches. In many-body theory, mean-field theory is an approximation to the manybody problem, yielding an approximate wavefunction and energy which are expected to be reasonably accurate for small U. In DFT, this treatment arises from approximating F for small U, and so should yield an accurate KS wavefunction and expectation values for small U. Thus, only one-body properties that depend only on position are expected to be accurate, and their accuracy can be improved by further improving the approximation to F. For large U, such an approximation fails, but there is still an exact F that yields an exact answer.

### 1.4 Site-occupation function theory (SOFT)

In this section, we introduce the site-occupation function theory for the Hubbard dimer[108, 260, 261, 46, 242, 243, 55]. If we want a physical system where this arises, think of stretched  $H_2[193]$ . We imagine a minimal basis set of one function per atom for the real Hamiltonian. We choose these basis functions to be 1s orbitals centered on each nucleus, but symmetrically orthonormalized. Then each operator in real-space contributes to the parameters in the Hubbard Hamiltonian as seen in 2.14.

It is reasonably straightforward to establish the validity of SOFT for our dimer. So long as each occupation can come from only one value of  $\Delta v$ , for a fixed U, there is a one-to-one correspondence between  $\Delta n$  and  $\Delta v$ , and all the usual logic of DFT follows. But note that  $\hat{T}$ and  $\hat{V}$  in SOFT do *not* correspond to the real-space kinetic energy and potential energy. For example, the hopping energy is negative, whereas the real-space kinetic energy is positive. This means that all theorems of DFT to be used must be reproven for the lattice model. More importantly, the SOFT does not become real-space DFT in some limit of complete basis sets (in any obvious way). We will however apply the same logic as real-space DFT, with the hopping energy in SOFT playing the role of the kinetic energy in DFT, and the on-site energy in SOFT playing the role of the one-body potential. The interaction term obviously plays the role of  $\hat{V}_{ee}$ . Many of the elementary equations and figures in these sections have appeared elsewhere, e.g. [242, 243, 43, 91, 92], some of them as static versions of time-dependent results.

#### 1.4.1 Non-interacting warm-up exercise

To show how SOFT works, begin with the U = 0 case, i.e., tight-binding of two noninteracting electrons. The ground-state is always a spin singlet. From the non-interacting solution, we can solve for  $\Delta v$  in terms of  $\Delta n$ 

$$\Delta v = -\frac{2t\,\Delta n}{\sqrt{4-\Delta n^2}},\tag{1.41}$$

and substitute back into the kinetic energy expectation value to find

$$T(n_1, n_2) = -2t\sqrt{n_1 n_2}.$$
(1.42)

This is the universal density function(al) for this non-interacting problem (see Eq. (1.3)), and can be used to solve every non-interacting dimer.

To solve this N = 2 problem in the DFT way, we note that T is playing the role of  $F(n_1, n_2)$ . So the exact function(al) here is

$$F(n_1) = -2t\sqrt{n_1 n_2}, \qquad (U=0), \qquad (1.43)$$

from which we can calculate all the quantities of interest using a DFT treatment. Note that everything is simply a function(al) of  $n_1$  since  $n_2 = (N - n_1)$ , or alternatively a function(al) of  $\Delta n$ . When N is fixed the formulas look like usual DFT when we use  $\Delta n$ . We then construct the total energy function(al):

$$E(n_1) = F(n_1) + \Delta v \,\Delta n/2, \qquad (U=0) \tag{1.44}$$

and minimize with respect to  $n_1$  for a given  $\Delta v$  to find the ground-state energy and density:

$$E = -\sqrt{(2t)^2 + \Delta v^2}, \tag{1.45}$$

$$\Delta n = -2\Delta v / \sqrt{(2t)^2 + \Delta v^2}. \tag{1.46}$$

Both of these agree with the traditional approach and recover Eqs. (1.29) and (1.30). The N = 1 result is half as great as Eqs. (1.45) and (1.46).

We can deduce several important lessons from this example. First, we need to vary the one-body potential (in this case, the on-site energy difference) to make the density change through all possible values, in order to find the function(al), since it requires knowing the one-to-one correspondence for all possible densities. Second, if we really change the atoms in our 2-electron stretched molecule, of course the minimal basis functions would change, and *both* t and  $\Delta v$  would differ. But here we keep t fixed, and vary  $\Delta v$  simply to explore the function(al), even if we are only interested in solving the symmetric problem. (Real-space DFT does not suffer from this problem, as the kinetic and repulsion operators are universal.) Third, we are reminded that the hopping and on-site operators in no sense represent the actual kinetic and one-body potential terms – they are a mixture of each. Finally, although we 'cheated' and *extracted* the kinetic energy function(al) from knowing the solutions, if someone had given us the formula, it would allow us to solve every possible non-interacting Hubbard dimer by minimizing over densities. And an approximation to that formula would yield approximate solutions to all those problems.

#### 1.4.2 The interacting functional

For the interacting case, we cannot analytically write down the exact function(al)  $F(n_1)$  at N = 2 in closed form. Although we have analytic formulas for both E and  $\Delta n$  as functions of  $\Delta v$ , the latter cannot be explicitly inverted to yield an analytic formula for  $F(\Delta n)$ . However, we can plot the function(al), by simply plotting F = E - V as a function of  $n_1$ , and see how it evolves from the U = 0 case to stronger interaction. The spin state is always a singlet. We



Figure 1.7: F-function(al) of Hubbard dimer as a function of  $n_1$  for several values of U and 2t = 1.

plot in Fig. 1.7 the F-function(al) as a function of  $n_1$  for several values of U. As U increases we can see F appears to tend to  $U|1 - n_1|$ . For any real problem the Euler equation for a given  $\Delta v$  is

$$\frac{dF(n_1)}{dn_1} - \frac{\Delta v}{2} = 0, \tag{1.47}$$

and the unique  $n_1(\Delta v)$  is found that satisfies this. Then

$$E(\Delta v) = F(n_1, \Delta v) + \Delta v \Delta n(\Delta v)/2.$$
(1.48)

The oldest form of DFT (Thomas-Fermi theory[287, 79]) approximates both  $T(n_1)$  and  $V_{ee}(n_1)$  and so leads to a crude treatment of the energetics of the system. A variation on this was used in Ref. [39] to enable extremely large calculations.

#### 1.4.3 Kohn-Sham method

The modern world uses the KS scheme, and not pure DFT[33]. The scheme in principle allows one to find the *exact* ground-state energy and density of an interacting problem by solving a non-interacting one. This scheme is what produces such high accuracy while using simple approximations in DFT calculations today. Next, we see how the usual definitions of KS-DFT should be made for our dimer.

The heart of the KS method is the fictitious system of non-interacting electrons whose density matches with the ground-state density of the interacting system. For our twoelectron system, the KS system is that of non-interacting electrons (U = 0) with an on-site potential difference  $\Delta v_s$ , *defined* to reproduce the exact  $\Delta n$  of the real system. This is just the tight-binding problem with an effective on-site potential difference, and is illustrated in Fig. 1.2.

As stated in Section 1.3.1, in KS-DFT one conventionally extracts the Hartree contribution from the electron-electron repulsion. There are deep reasons for doing so, which center on the remnant, the XC energy, being amenable to local and semilocal-type approximations[35, 233]. To see how the Hartree energy should be defined here, rewrite the electron-electron repulsion as:

$$\hat{V}_{\rm ee} = \frac{U}{2} \sum_{i} (\hat{n}_i^2 - \hat{n}_{i\uparrow}^2 - \hat{n}_{i\downarrow}^2).$$
(1.49)

This form mimics the treatment in DFT. The first term depends only on the total (i.e. spin-summed) density, akin to Hartree in real-space DFT. The remaining terms cancel the self-interaction that arises from using the total density for the electron-electron interaction. For the N = 2 dimer, this decomposition results in

$$U_{\rm H}(\Delta n) = \frac{U}{2} \left( n_1^2 + n_2^2 \right), \tag{1.50}$$

and

$$E_{\rm x}(\Delta n) = -\frac{U}{4} \left( n_1^2 + n_2^2 \right), \tag{1.51}$$

which satisfies  $E_{\rm x} = -U_{\rm H}/2$  for N = 2 as in real-space DFT for a spin singlet, Eq. (1.23). Together, the Hartree-Exchange is

$$E_{\rm HX}(\Delta n) = \frac{U}{4} \left( n_1^2 + n_2^2 \right) = \frac{U}{2} \left( 1 + \left( \frac{\Delta n}{2} \right)^2 \right).$$
(1.52)

In 2.10 we see that the leading order in the U expansion of the F-function(al) yields the same result. A typical mean field treatment of  $\hat{V}_{ee}$  also results in Eq. (1.52). In DFT there is always self-exchange, even for one or two particles. In many-body theory, exchange means only exchange between different electrons. Despite this semantic difference, both approaches yield the same leading-order-in-U expression for the dimer, which we call  $E_{\text{Hx}}$  here (but is often called just Hartree in many-body theory). For the dimer, from Eq. (1.42), the KS kinetic energy is just

$$T_{\rm s}(n_1) = -2t\sqrt{n_1 n_2},\tag{1.53}$$

so that  $F^{\rm HF}(n_1) = T_{\rm s}(n_1) + E_{\rm Hx}(n_1)$  as in Section 1.3.4. We can then define the correlation energy function from Eq. (1.18), so that

$$E_{\rm C}(n_1) = F(n_1) - T_{\rm S}(n_1) - E_{\rm HX}(n_1).$$
(1.54)



In Fig. 1.8, we plot the correlation energy as a function of  $n_1$ . For small U,

Figure 1.8: Plot of exact  $E_{\rm c}$  (blue line) and  $E_{\rm c,par}$  (red dashed line) for different U and 2t = 1.

$$E_{\rm c} \sim -U^2 (1 - (n_1 - 1)^2)^{5/2} / 8 \qquad U \ll 2t$$
 (1.55)

which is much smaller than the Hartree-exchange contribution, and is a relatively small contribution to E. But as U increases,

$$E_{\rm c} \sim -U(1 - |n_1 - 1|)^2/2, \qquad U \gg 2t$$
 (1.56)

with a cusp at half-filling. Combined with  $E_{\rm HX}$ , this creates F for large U as in Fig. 1.7.

Inserting this result into Eq. (1.47), we find that the KS electrons have a non-interacting Hamiltonian:

$$\hat{h}_{\rm s} \left| \phi \right\rangle = \epsilon_{\rm s} \left| \phi \right\rangle,\tag{1.57}$$

where this KS Hamiltonian is

$$\hat{h}_{s}(\Delta n) = -t \left( \hat{c}_{1}^{\dagger} \hat{c}_{2} + h.c. \right) + \sum_{i} v_{s,i}(\Delta n) \hat{n}_{i}.$$
(1.58)

The KS potential difference is

$$\Delta v_{\rm s}(\Delta n) = \Delta v + U \Delta n/2 + \Delta v_{\rm c}(\Delta n), \qquad (1.59)$$

where

$$\Delta v_{\rm C} = -2 \, dE_{\rm C}(n_1)/dn_1,\tag{1.60}$$

the analog of eq. (1.13). For any given form of the (exchange-)correlation energy, differentiation yields the corresponding KS potential. If the exact expression for  $E_{\rm C}(n_1)$  is used, this potential is guaranteed[309] to yield the exact ground-state density when the KS equations are iterated to convergence via a simple algorithm.

In Fig. 1.9, we plot several examples of the dependence of the potentials in the KS system as



Figure 1.9: Plots of  $\Delta v_{\rm s}$  (blue) and its components,  $\Delta v$  (black),  $U\Delta n/2$  (green), and  $\Delta v_{\rm c} + U\Delta n/2$  (red) plotted against  $n_1$  for various U and 2t = 1. The arrows indicate the occupations used in Fig. 1.2. (See also Figs. 5 and 6 of [242].)

a function of  $n_1$ , which range from weakly (U = 0.4) to strongly (U = 10) correlated cases. In each curve, the black line is the actual on-site potential difference as a function of occupation of the first site. The blue line is the KS potential difference, which is the on-site potential needed for two non-interacting (U = 0) particles to produce the given  $n_1$ . This is found by inverting the tight-binding equation for the density, Eq. (1.41). Their difference is the Hartree-exchange-correlation on-site potential, denoted by the red line. Finally, the green line is just Hartree-exchange, which ignores correlation effects. For U = 0.4, we see that the difference between blue and black is quite small, and almost linear. Indeed the Hartreeexchange contribution is always linear (see Eq. (1.59)). Here the red is indistinguishable by eve from the green, showing how small the correlation contribution to the potential is. This means the HF and exact densities will be virtually (but not quite) identical. When we increase U to 2t, we see a similar pattern, but now the red line is noticeably distinct from the green. For any given  $n_1$ , the blue curve is smaller in magnitude than the black. This is because turning on U pushes the two occupation numbers closer, and so their KS on-site potential difference is smaller. Again, the red curve is larger in magnitude than the green, showing that HF does not suppress the density difference quite enough. In our final panel, U = 20t, and the effects of strong correlation are clear. Now there is a huge difference between black and blue curves. Because U is so strong, the density difference is close to zero for most  $n_1$ , making the blue curve almost flat except at the edges. In the KS scheme, this is achieved by the red curve being almost flat, except for a sudden change of sign near  $n_1 = 1$ . These effects give rise to the  $\Delta v_s$  values shown in Fig. 1.2. This effect is completely missed in HF.



Figure 1.10: Plot of  $\Delta v_{\rm C}$  for different U and 2t = 1.

To emphasize the role of correlation, in Fig. 1.10, we plot the correlation potential alone, which is the difference between the red and green curves in Fig. 1.9. Values from the blue curves for  $\Delta v = 2$  were used to make Fig. 1.2.  $\Delta v_{\rm c}$  is an odd function of  $n_1$ . In the weakand strong-coupling limits we can write down simple expressions for  $\Delta v_{\rm c}$  (see 2.10.2):

$$\Delta v_{\rm c} \approx \frac{5 U^2 \Delta n}{32 t} (1 - (\Delta n/2)^2)^{3/2} \qquad (U \ll 2 t)$$
(1.61)

$$\Delta v_{\rm c} \approx U(1 - |\Delta n/2|) \, sgn(\Delta n) \qquad (U \gg 2 \, t). \tag{1.62}$$

These correspond to the 1st and 4th panels in Fig. 1.10. For small U, it is of order  $U^2$  (see 2.10), and has little effect. As U increases, it becomes proportional to U, and becomes

almost linear in U, with a large step near  $n_1 = 1$ . If we now compare this figure with Fig. 1.8, we see that it is simply the derivative of the previous  $E_{\rm C}(n_1)$  curve, as stated in Eq. (1.60).

The self-consistent KS equations, Eqs. (1.57) and (1.58), have, in this case, precisely the same form as those of restricted HF (or mean-field theory), Eqs. (1.26) and (1.36), but with whatever additional dependence on  $n_1$  occurs due to  $\Delta v_{\rm c}(n_1)$ . When converged, the ground-state energy is found simply from:

$$E(n_1) = T_{\rm s}(n_1) + V_{\rm ext}(n_1) + U_{\rm H}(n_1) + E_{\rm xc}(n_1).$$
(1.63)

The energy can alternatively be extracted from the KS orbital energy via Eq. (1.16):

$$E = 2\epsilon_{\rm s} + (E_{\rm c} - \Delta v_{\rm c} \Delta n/2 - E_{\rm HX}), \qquad (1.64)$$

where the second term is the double-counting correction. But note the crucial difference here. We consider HF an approximate solution to the many-body problem whereas DFT, with the exact correlation function(al), yields the exact energy and on-site occupation, but not the exact wavefunction.

Definition	Description
Generic DFT	
$\overline{\Psi[n]}$	Many-body wfn of density $n$
$\Phi[n]$	Kohn-Sham wfn of density $n$
$F = T + V_{\rm ee}$	Hohenberg-Kohn Functional
$E_{\rm xc} = F - T_{\rm s} - U_{\rm H}$	Exchange-correlation energy
$E_{\mathrm{x}} = \langle \Phi   \hat{V}_{\mathrm{ee}}   \Phi \rangle - U_{\mathrm{H}}$	Exchange energy
$E_{\rm x} = -U_{\rm H}/2$	Exchange energy for 2 electrons
$E_{\rm C} = T_{\rm C} + U_{\rm C}$	Total correlation energy
$T_{\rm c} = T - T_{\rm s}$	Kinetic correlation energy
$U_{\rm C} = V_{\rm ee} - U_{\rm H} - E_{\rm X}$	Potential correlation energy
$U_{ m xc}(\lambda) = U_{ m xc}^{\lambda}/\lambda$	Adiabatic connection integrand
$T_{\rm C} = E_{\rm C} - dE_{\rm C}^{\lambda}/d\lambda _{\lambda=1}$	Method to extract $T_{\rm C}$ from $E_{\rm C}$
$U_{ m c} = dE_{ m c}^{\lambda}/d\lambda _{\lambda=1}$	Method to extract $U_{\rm C}$ from $E_{\rm C}$
$\hat{h}_{\mathrm{s}} = -\nabla^2/2 + v_{\mathrm{s}}$	Kohn-Sham hamiltonian
$v_{\mathrm{s}} = v + v_{\mathrm{H}} + v_{\mathrm{xc}}$	Kohn-Sham one-body potential
$E_{\rm c}^{\rm trad} = E - E^{\rm HF}$	Quantum chemical corr. energy
SOFT Hubbard	
$n_1, n_2$	Occupations at sites 1, 2
$N = n_1 + n_2$	Total number of electrons
$\Delta n = n_2 - n_1$	Occupation difference
$\Delta m = m_2 - m_1$	Magnetization difference
$v_1, v_2$	On-site potentials
$\bar{v} = (v_1 + v_2)/2 = 0$	On-site potential average
$\Delta v = v_2 - v_1$	On-site potential difference
$\Delta v_{\rm xc} = v_{\rm xc,2} - v_{\rm xc,1}$	XC potential difference
$U_{\rm H} = U(N^2 + \Delta n^2)/4$	Hartree energy
$E_{\rm HX} = U(N^2 + \Delta n^2)/8$	Hartree-Exchange energy
$T_{\rm s} = -t\sqrt{(2 -  N - 2 )^2 - \Delta n^2}$	Single particle hopping energy
Dimensionless Variables	
$\epsilon = E/2t$	Energy in units of hopping
u = U/2 t	Hubbard $U$ in units of hopping
$\nu = \Delta v/2t$	Pot. diff. in units of hopping
$ ho =  \Delta n /2$	Reduced density difference
$\bar{ ho} = 1 -  ho$	Asymmetry parameter

Table 1.1: Standard DFT definitions and our Hubbard dimer notation.

# Chapter 2

# The Hubbard Dimer: A density functional case study of a many-body problem (part 2)

This chapter is the various results sections of Ref. [47].

## 2.1 The fundamental gap

Now that we have carefully defined what exact KS DFT is for this model, we immediately apply this knowledge to investigate a thorny subject on the border of many-body theory and DFT, namely the fundamental gap of a system.

#### 2.1.1 Background in real space

Begin with the ionization energy of an N-electron system:

$$I = E(N-1) - E(N)$$
(2.1)

is the energy required to remove one electron entirely from a system. We can then define the electron affinity as the energy gained by adding an electron to a system, which is also equal to the ionization energy of the (N + 1)-electron system:

$$A = E(N) - E(N+1). (2.2)$$

In real-space, I and  $A \ge 0$ . For systems which do not bind an additional electron, such as the He atom, A = 0. The charge, or fundamental, gap of the system is then

$$E_g = I - A, (2.3)$$

and for many materials,  $E_g$  can be used to decide if they are metals ( $E_g = 0$ ) or insulators  $(E_g > 0)$ [146]. The spectral function of the single-particle Green's function has a gap equal to  $E_g$ . For Coulombic matter,  $E_g$  has always been found to be non-negative, but no general proof has been given.

Now we turn to the KS system of the *N*-electron system. We denote the highest occupied (molecular) orbital as  $\epsilon^{\text{HOMO}}$  and the lowest unoccupied one as  $\epsilon^{\text{LUMO}}$ . Then the DFT version of Koopmans' theorem[222, 221, 267, 9, 10, 45] shows that

$$\epsilon^{\text{HOMO}} = -I, \tag{2.4}$$

by matching the decay of the density away from any finite system in real space, in the

interacting and KS pictures. However, this condition applies only to the HOMO, not to any other occupied orbitals, or unoccupied ones. The LUMO level is not at -A, in general. Define the KS gap as

$$E_{gs} = \epsilon^{\text{LUMO}} - \epsilon^{\text{HOMO}}.$$
(2.5)

Then  $E_{gs}$  does not match the true gap, even with the exact XC functional[251, 22]. We write

$$E_g = E_{gs} + \Delta_{\rm XC} \tag{2.6}$$

where  $\Delta_{\rm xc} \neq 0$ , and is called the derivative discontinuity contribution to the gap (for reasons that will be more apparent later)[216, 218]. In general,  $\Delta_{\rm xc}$  appears to always be positive, i.e., the KS gap is smaller than the true gap. In semiconductors with especially small gaps, such as germanium, approximate KS gaps are often zero, making the material a band metal, but an insulator in reality. The classic example of a chain of H atoms becoming a Mott-Hubbard insulator when the bonds are stretched is demonstrated unambiguously in Ref. [281].

While this mismatch occurs for all systems, it is especially problematic for DFT calculations of insulating solids. For molecules, one can (and does) calculate the gap (called the chemical hardness in molecular systems[211]) by adding and removing electrons. But with periodic boundary conditions, there is no simple way to do this for solids. Even with the exact functional, the KS gap does not match the true gap, and there's no easy way to calculate  $E_g$  in a periodic code. In fact, popular approximations like LDA and GGA mostly produce good approximations to the KS gap, but yield  $\Delta_{\rm xc} = 0$  for solids. Thus there is no easy way to extract a good approximation to the true gap in such DFT calculations. The standard method for producing accurate gaps for solids has long been to perform a GW calculation[15], an approximate calculation of the Green's function, and read off its gap. This works very well for most weakly correlated materials[295]. Such calculations are now done in a variety of ways, but usually employ KS orbitals from an approximate DFT calculation. Recently, hybrid functionals like HSE06[120] have been shown to yield accurate approximate gaps to many systems, but these gaps are a mixture of the quasiparticle (i.e., fundamental) gap, and the KS gap. Their exchange component produces the fundamental gap at the HF level, which is typically a significant overestimate, which then compensates for the 'too small' KS gap. While this balance is unlikely to be accidental, no general explanation has yet been given.



#### 2.1.2 Hubbard dimer gap

Figure 2.1: Plot of -A, -I,  $\epsilon^{\text{HOMO}}$ , and  $\epsilon^{\text{LUMO}}$  as a function of  $\Delta v$  with U = 1 and 2t = 1.

For our half-filled Hubbard dimer, we can easily calculate both the  $N \pm 1$ -electron energies,



Figure 2.2: Plot of -A, -I,  $\epsilon^{\text{HOMO}}$ , and  $\epsilon^{\text{LUMO}}$  as a function of  $\Delta v$  with U = 5 and 2t = 1.

the former via particle-hole symmetry from the latter[46]. In Fig. 2.1, we plot -I, -A,  $\epsilon^{\text{HOMO}}$ , and  $\epsilon^{\text{LUMO}}$  for U = 1 when 2t = 1, as a function of  $\Delta v$ . We see that A (and even sometimes I) can be negative here. (This cannot happen for real-space calculations, as electrons can always escape to infinity, so a bound system always has  $A \ge 0$ .) The HOMO level is always at -I according to Eq. (2.4) but the LUMO is not at -A. Here it is smaller than -A, and we find this result for all values of U and  $\Delta v$ . The true gap is I - A, but the KS gap is  $\epsilon^{\text{LUMO}} + I$ , which is always smaller. Thus  $\Delta_{\text{xc}} \ge 0$ , just as for real systems.

Fig. 2.1 is typical of weakly correlated systems, where  $\Delta_{\rm xc}$  is small but noticeable. In Fig. 2.2, we repeat the calculation with U = 10 t, where now  $E_g \gg E_{gs}$  at  $\Delta v = 0$ , but we still see the difference become tiny when  $\Delta v > U$ . In both figures,  $\Delta_{\rm xc}$  is the difference between the red line and the green dashed line. In all cases,  $\Delta_{\rm xc} \ge 0$ , and this has always been found to be true in real-space DFT, but has never been proven in general.

#### 2.1.3 Green's functions

To end this section, we emphasize the difference between the KS and many-body approaches to this problem by calculating their spectral functions[207]. We define the many-body retarded single-particle Green's function as

$$G_{ij\sigma\sigma'}(t-t') = -i\,\theta(t-t')\langle\Psi_0|\{\hat{c}_{i\sigma}(t),\hat{c}^{\dagger}_{j\sigma'}(t')\}\,|\Psi_0\rangle$$
(2.7)

where i, j label the site indices,  $\sigma$ ,  $\sigma'$  the electron spins, and  $\{A, B\} = AB + BA$ . For the Hubbard dimer at N = 1 and 3,  $|\Psi_0\rangle$  is a degenerate Kramers doublet and we choose here the spin- $\uparrow$  partner. Fourier transforming into frequency, we find for the diagonal component:

$$G_{\sigma}(\omega) = G_{11\sigma\sigma}(\omega) = \sum_{\alpha} \frac{|M_{1\sigma}^{\alpha}|^{2}}{\omega + E^{N} - E_{\alpha}^{N+1} + i\,\delta} + \sum_{\alpha} \frac{|L_{1\sigma}^{\alpha}|^{2}}{\omega - E^{N} + E_{\alpha}^{N-1} + i\,\delta}$$
(2.8)

where  $M_{1\sigma}^{\alpha} = \langle \psi_{\alpha}^{N+1} | \hat{c}_{1\sigma}^{\dagger} | \psi_{0}^{N} \rangle$ ,  $L_{1\sigma}^{\alpha} = \langle \psi_{\alpha}^{N-1} | \hat{c}_{1\sigma} | \psi_{0}^{N} \rangle$ , and  $\delta > 0$  is infinitesimal. Here,  $\alpha$  runs over all states of the  $N \pm 1$ -particle systems. The other components have analogous expressions. From any component of G, we find the corresponding spectral function

$$A(\omega) = -\Im G(\omega)/\pi \tag{2.9}$$

We represent the spectral function  $\delta$ -function poles with lines whose height is proportional to the weights. Via a simple sum-rule[80], the sum of all weights in the spin-resolved spectral function is 1. There are four quasi-particle peaks for N = 2. These peaks are reflectionsymmetric about  $\omega = U/2$  for the symmetric dimer.

We also need to calculate the KS Green's function,  $G_{\rm s}(\omega)$ . This is done by simply taking

the usual definition, Eq. (2.7), and applying it to the ground-state KS system. This means two non-interacting electrons sitting in the KS potential. The numerators vanish for all but single excitations. Thus the energy differences in the denominators become simply occupied and unoccupied orbital energies. Since there are only two distinct levels (the positive and negative combinations of atomic orbitals), there are only two peaks, positioned at the HOMO and LUMO levels, with weights:

$$M_{1\sigma}^{\alpha} = \frac{1}{2} \left( 1 + \frac{\Delta v_{\rm s}/2}{\sqrt{(\Delta v_{\rm s}/2)^2 + t^2}} \right), \quad (\rm KS)$$
(2.10)

and the sign between the contributions on the right is negative in the L term. Thus the symmetric dimer has KS weights of 1/2.



Figure 2.3: Spectral function of symmetric dimer for U = 1,  $\Delta v = 0$ , and 2t = 1. The physical MB peaks are plotted in blue, the KS in red. Here I = 0.1, A = -1.1, and  $\epsilon^{\text{LUMO}} = 0.9$ , corresponding to  $\Delta v = 0$  in Fig. 2.1.

In Fig. 2.3 we plot the spectral functions for the symmetric case, for U = 1, when 2t = 1. Each pole contributes a delta function at a distinct transition frequency, which is represented by a line whose height represents the weight. The sum of all such weights adds to 1 as it should, and the peaks are reflection-symmetric about U/2 = 0.5. The gap is the distance between the highest negative pole (at -I) and the lowest positive pole (at -A). We see that the MB spectral function also has peaks that correspond to higher and lower quasi-particle excitations. If we now compare this to the *exact* KS Green's function  $G_s$ , we see that, by construction,  $G_s$  always has a peak at -I, whose weight need not match that of the MB function. It has only two peaks, the other being at  $\epsilon^{\text{LUMO}}$ , which does not coincide with the ground-state occupations, nothing else. But clearly, when U is sufficiently small, it is a rough mimic of the MB Green's function. The larger peaks in the MB spectral function each have KS analogs, with roughly the correct weights. One of them is even at exactly the right position. Thus if a system is weakly correlated, the KS spectral function can be a rough guide to the true quasiparticle spectrum.



Figure 2.4: Same as Fig. 2.3, but now U = 5. Here I = -0.3, A = -4.7, and  $\epsilon^{\text{LUMO}} = 1.3$ , corresponding to  $\Delta v = 0$  in Fig. 2.2.

On the other hand, when  $U \gg 2t$ , the KS spectral function is not even close to the true MB spectral function, as illustrated in Fig. 2.4. Now the two lowest-lying MB peaks approach each other, as do the two highest lying peaks, therefore increasing the quasi-particle gap. In addition, the weights tend to equilibrate with each other. In fact, when  $U \to \infty$  and/or  $t \to 0$ , those two lowest-lying peaks gather together at  $\omega = 0$ , having both the same weight of 1/4. And similarly the two highest-lying peaks merge at  $\omega = U$ , also with a weight of 1/4. They are the precursors of the lower and upper Hubbard bands with a quasi-particle gap equal to U. If more sites are added to the symmetric dimer, other quasi-particle peaks appear, that also merge into the lower and upper Hubbard bands as  $U \to \infty$ . Notice that the spectral function has significant weights for transitions between states that differ from the HOMO and LUMO, and are forbidden in the KS spectral function for large U. In Fig. 2.4, we see that not only there is a large difference between the gaps in the two spectral functions, but also the KS weights are not close to the MB weights. The only 'right' thing about the KS spectrum is the position of the HOMO peak.

In Fig. 2.5, we plot the spectral functions for  $\Delta v = 2$  and U = 1 for 2t = 1, to see the effects of asymmetry on the spectral function. Now the system appears entirely uncorrelated, and the KS spectral function is very close to the true one, much more so than in the symmetric case. Here  $\Delta_{\rm xc}$  is negligible. The asymmetry of the potential strongly suppresses correlation effects. In Fig. 2.6, we see that the effects of strong U are largely quenched by a comparable  $\Delta v$ . Here  $\Delta_{\rm xc}$  is small compared to the gap, but not all KS peak heights are close to their MB counterparts.

The situation is interesting even for the 'simple' case, N = 1, in which the ground-state is open-shell[101]. Here the interacting spin- $\uparrow$  and - $\downarrow$  Green's functions differ. To understand why, we choose the N = 1 ground state to have spin  $\uparrow$ . This state has energy  $E(1) = -\sqrt{t^2 + (\Delta v/2)^2}$ . Adding a  $\downarrow$ -spin electron takes the system to the different singlet states at N = 2, and to the triplet state with  $S_z = 0$ . One of them is the ground state at N = 2 whose



Figure 2.5: Same as Fig. 2.3, but now U = 1,  $\Delta v = 2$ . Here I = 0.27, A = -1.27, and  $\epsilon^{\text{LUMO}} = 1.25$ , corresponding to  $\Delta v = 2$  in Fig. 2.1.

energy E(2) < 0 is given in Eq. (2.68) in the appendix. In contrast, adding an  $\uparrow$ -spin electron takes the interacting system to the triplet N = 2 state with  $S_z = 1$ , whose energy is trivially given by  $E(2)_{\text{trip}} = 0$ . Annihilating an  $\uparrow$ -spin electron takes the system to the vacuum, while it is impossible to annihilate a  $\downarrow$ -spin electron. These clearly illustrates that the number and energy of the poles in  $G_{\uparrow}$  and  $G_{\downarrow}$  is different:  $G_{\uparrow}$  has only two quasi-particle peaks, with trivial energies  $E(2)_{\text{trip}} - E(1) = \sqrt{t^2 + (\Delta v/2)^2}$  and  $E(1) - E(0) = -\sqrt{t^2 + (\Delta v/2)^2}$ . This last expression corresponds to the ionization energy  $I = E(0) - E(1) = \sqrt{t^2 + (\Delta v/2)^2}$ .  $G_{\downarrow}$  has four quasiparticle peaks, all corresponding to adding a  $\downarrow$ -spin electron, with nontrivial energies. The lowest of these corresponds to the electron affinity A = E(1) - E(2) = $-\sqrt{t^2 + (\Delta v/2)^2} - E(2)$ . In other words, ionization involves either removing an  $\uparrow$ -spin electron (hence seen as a pole in  $G_{\uparrow}$ ) or adding a  $\downarrow$ -spin electron (hence seen as a pole in  $G_{\downarrow}$ ). The interacting gap is  $E_g = I - A = 2\sqrt{t^2 + (\Delta v/2)^2} + E(2)$ .



Figure 2.6: Same as Fig. 2.5, but now U = 5,  $\Delta v = 5$ . Here I = -1.8, A = -3.2, and  $\epsilon^{\text{LUMO}} = 3$ , corresponding to  $\Delta v = 5$  in Fig. 2.2.

We turn now to the KS Green's function. For N = 1, the KS on-site potentials equal the true on-site potentials,  $\pm \Delta v/2$ . So the ground-state (chosen again to have spin  $\uparrow$ ) has energy  $E_{\rm s}(1) = -\sqrt{t^2 + (\Delta v_{\rm s}/2)^2}$ . Since the other state has energy  $E_{\rm s}(1)$ , and a second  $\uparrow$ -electron occupies that state, the total KS energy is  $E(2)_{\rm S_z=1} = 0$ . On the other hand, annihilating the  $\uparrow$  electron costs an energy E(1). This shows that the  $\uparrow$ -spin KS and interacting Green's functions are identical to one other and trivial for N = 1. Thus  $I = -\epsilon^{\rm HOMO} = \sqrt{t^2 + (\Delta v/2)^2}$ . This result is specific to this model.

Removing a  $\downarrow$ -spin KS electron is impossible, just as in the interacting case. However, adding it means having either two opposite-spin KS electrons with the same energy  $-\sqrt{t^2 + (\Delta v_s/2)^2}$ , or having one with energy  $-\sqrt{t^2 + (\Delta v_s/2)^2}$  and another with energy  $\sqrt{t^2 + (\Delta v_s/2)^2}$ . The first case corresponds to the KS ground-state with energy  $-2\sqrt{t^2 + (\Delta v_s/2)^2}$ , while the second one is an excited state with energy 0. The KS value for the electron affinity is  $A_{\rm s} = E_{\rm s}(1) - E_{\rm s}(2) = \sqrt{t^2 + (\Delta v_{\rm s}/2)^2}$ , which differs from the interacting value. Furthermore, the KS gap  $E_{gs} = 0$  is clearly an incorrect estimate of the true interacting gap, which is given by  $I = \Delta_{xc}$ .



Figure 2.7: Spin- $\downarrow$  resolved spectral function for N = 1 and U = 1,  $\Delta v = 2$ , (2t = 1). Here I = 1.12, A = 0.27, and  $\epsilon^{\text{LUMO}} = \epsilon^{\text{HOMO}} = -1.12$ .

Figs. 2.7 and 2.8 show the spectral function associated with  $G_{\downarrow}$  for the many-body and KS Green's functions for N = 1 and  $\Delta v = 2$ . In the first, U = 1, so it is relatively asymmetric, whereas in the second, U = 5, making it close to symmetric. Thus the HOMO is at the lowest red line, and matches exactly the LUMO, with a KS gap of zero. Thus  $\Delta_{\rm xc}$  is the gap of the interacting system. We see that in the first figure, correlations are weak and the KS spectral function mimics the physical one, but in the second figure (U = 5), they differ substantially, even though N = 1!

The difference in expressions for spin species is illustrated further by work analyzing Koopmans' and Janak's theorems for open-shell systems[100, 102, 106, 101]. Self-energy ap-



Figure 2.8: Spin- $\downarrow$  resolved spectral function for N = 1 and U = 5,  $\Delta v = 2$  (2 t = 1). Here I = 1.12, A = -0.90, and  $\epsilon^{\text{LUMO}} = \epsilon^{\text{HOMO}} = -1.12$ .

proximations beyond GW have been performed on the Hubbard dimer[246, 245], as well as a battery of many-body perturbation theory methods[206] though only for the symmetric case.

The bottom line message of this subsection is that the KS spectral function does not match the quasiparticle spectral function, because it is not supposed to. However, the main features of a weakly correlated system are loosely approximated by those of the KS function, with the gap error shifting the upper part of the spectrum relative to the lower part. This is the motivation behind the infamous scissors operator in solid-state physics. A very accurate DFT approximation can (at best) approximate the KS spectral function, not the many-body one. The exact XC functional does not reproduce the quasiparticle gap of the system. For strongly correlated systems, there are often substantial qualitative differences between the MB and KS spectral functions. These are some of the limitations of KS-DFT. that, e.g., DMFT is designed to overcome [93].

## 2.2 Correlation

# 2.2.1 Classifying correlation: Strong, weak, dynamic, static, kinetic, and potential

There are as many different ways to distinguish weak from strong correlation as there are communities that study electronic structure. Due to the limited degrees of freedom (namely, one), these all overlap in the Hubbard dimer. We will discuss each.

The most important thing to realize is that correlation energy comes in two distinct contributions: kinetic and potential. These are entirely well-defined quantities within KS-DFT. The kinetic correlation energy is:

$$T_{\rm C} = T - T_{\rm S} \tag{2.11}$$

for a given density. Note that we could as easily call this the correlation contribution to the kinetic energy. The potential correlation energy is:

$$U_{\rm C} = V_{\rm ee} - E_{\rm HX},\tag{2.12}$$

and could also be called the correlation contribution to potential energy. For future notational convenience, we also define  $U_{\rm x} = E_{\rm x}$ , i.e., there is no kinetic contribution to exchange. Then, from Eq. (1.18), we see

$$E_{\rm c} = T_{\rm c} + U_{\rm c}.\tag{2.13}$$

We can now use these to discuss the differences between weak and strong correlation. First note that, by construction, and as shown for our dimer in 2.11,

$$E_{\rm c} < 0, \quad T_{\rm c} > 0, \quad U_{\rm c} < 0.$$
 (2.14)

In Figs. 1.8 and 2.9, we plot both  $E_{\rm c}$  and  $T_{\rm c}$ , respectively, for several values of U (with 2t = 1). When U is small,  $T_{\rm c} \approx -E_{\rm c}$ . However, for  $U \gg 2t$ , we see that although  $E_{\rm c}$  becomes very large (in magnitude),  $T_{\rm c}$  remains finite and in fact,  $T_{\rm c}$  never exceeds 2t as proven in 2.11. We can define a measure of the nature of the correlation[34]:

$$\beta_{\rm corr} \equiv \frac{T_{\rm c}}{|E_{\rm c}|}.\tag{2.15}$$

As  $U \to 0$ ,  $\beta_{\text{corr}} \to 1$ , while as  $U \to \infty$ ,  $\beta_{\text{corr}} \to 0$ . Thus  $\beta_{\text{corr}}$  close to 1 indicates weak correlation,  $\beta$  small indicates strong correlation. We plot  $\beta_{\text{corr}}$  as a function of U for several values of  $\Delta v$  in Fig. 2.10. Although  $\beta_{\text{corr}}$  is monotonically decreasing with U for  $\Delta v = 0$ , we see that the issue is much more complicated once we include asymmetry. The curve for each  $\Delta v$  remains monotonically decreasing with U. But consider U = 2 and different values of  $\Delta v$ . Then  $\beta_{\text{corr}}$  at first decreases with  $\Delta v$ , i.e. becoming *more* strongly correlated, but then increases again for  $\Delta v > U$ , ultimately appearing less correlated than  $\Delta v = 0$ .

Quantum chemists often refer to dynamic versus static correlation. Our precise prescription in KS-DFT loosely corresponds to their definition, replacing dynamic by kinetic, and static by potential. Thus, considering an H<sub>2</sub> molecule with a stretched bond, the Hubbard model applies. As the bond stretches, t vanishes, and U/2t grows. Thus  $\beta_{corr} \rightarrow 0$  as  $R \rightarrow \infty$ . The exact wavefunction, the Heitler-London wavefunction[116], has only static correlation in this limit. In many-body language, it is strongly correlated. In DFT language, the fraction of correlation energy that is kinetic is vanishing.



Figure 2.9: Plot of exact  $T_{\rm c}$  (blue line) and  $T_{\rm c,par}$  (red dashed line) for different U and 2t = 1.

#### 2.2.2 Adiabatic connection

With the various contributions to correlation well-defined, we construct the adiabatic connection (AC) formula [160, 107] for the Hubbard dimer. The adiabatic connection has had enormous impact on the field of DFT as it allows both construction [28, 220, 74, 5, 230], and understanding [220, 34, 214], of exact and approximate functionals solely from their potential contributions.

In many-body theory, one often introduces a coupling-constant in front of the interaction. In KS-DFT, a coupling constant  $\lambda$  is introduced in front of the electron-electron repulsion but, contrary to traditional many-body approaches, the density is held fixed as  $\lambda$  is varied (usually from 0 to 1). Via the Hohenberg-Kohn theorem, as long as there is more than 1 electron,



Figure 2.10: Plot of  $\beta_{\text{corr}} = T_{\text{c}}/|E_{\text{c}}|$  as a function of U with 2t = 1.

this implies that the one-body potential must vary with  $\lambda$ , becoming  $v^{\lambda}(\mathbf{r})$ . By virtue of the density being held fixed,  $v^{\lambda=0}(\mathbf{r}) = v_{s}(\mathbf{r})$  while  $v^{\lambda=1}(\mathbf{r}) = v(\mathbf{r})$ . Thus  $\lambda$  interpolates between the KS system and the true many-body system. Additionally,  $\lambda \to \infty$  results in the strictly correlated electron limit[184, 266, 176, 94, 186] which provides useful information about real systems that are strongly correlated.

The adiabatic connection for the Hubbard dimer is very simple. Define the XC energy at coupling constant  $\lambda$  by simply multiplying U by  $\lambda$  while keeping  $\Delta n$  fixed:

$$E_{\rm xc}^{\lambda}(U,\Delta n) = E_{\rm xc}(\lambda U,\Delta n). \tag{2.16}$$

Application of the Hellman-Feynman theorem [81] yields [114, 160, 161, 107]:

$$\frac{dE_{\rm xc}(\lambda U, \Delta n)}{d\lambda} = \frac{U_{\rm xc}(\lambda U, \Delta n)}{\lambda},\tag{2.17}$$

where  $U_{\rm XC}(U, \Delta n)$  is the potential contribution to the XC energy, i.e.,  $U_{\rm X} = E_{\rm X}$  and

$$U_{\rm C}(\lambda U) = V_{\rm ee}(\lambda U) - \lambda E_{\rm HX}(U).$$
(2.18)

Thus, we can extract  $T_{\rm c}$  solely from our knowledge of  $E_{\rm c}(U)$  via

$$T_{\rm c} = E_{\rm c} - U_{\rm c} = E_{\rm c} - \left. \frac{dE_{\rm c}^{\lambda}}{d\lambda} \right|_{\lambda=1}.$$
(2.19)

Thus, any formula for  $E_{\rm c}$ , be it exact or approximate, yields a corresponding result for  $T_{\rm c}$ and  $U_{\rm c}$ , and vice versa[58]. We may then write

$$E_{\rm xc}(U,\Delta n) = \int_0^1 \frac{d\lambda}{\lambda} U_{\rm xc}(\lambda U,\Delta n), \qquad (2.20)$$

and this is the infamous adiabatic connection formula of DFT[160, 107]. We denote the integrand as  $U_{\rm c}(\lambda)$ , defined as

$$U_{\rm c}(\lambda) = \frac{U_{\rm c}(\lambda U)}{\lambda} = \frac{dE_{\rm c}(\lambda U)}{d\lambda}.$$
(2.21)

Plots of  $U_{\rm C}(\lambda)$  from Eq. (2.21) are called adiabatic connection plots, and can be used to better understand both approximate and exact functionals. In Fig. 2.11, we plot a typical case for U = 2t and  $\Delta v = 0$ . They have the nice interpretation that the value at  $\lambda = 1$  is the potential correlation energy,  $U_{\rm C}$ , the area under the curve is  $E_{\rm C}$ , and the area between the curve and the horizontal line at  $U_{\rm C}(1)$  is  $-T_{\rm C}$ . Furthermore, one can also show[166]

$$\frac{dU_{\rm xc}(\lambda)}{d\lambda} < 0, \tag{2.22}$$

from known inequalities for  $T_{\rm C}(\lambda)$  and  $E_{\rm C}(\lambda)$ . This is proven for our problem in 2.11. Interestingly, such curves have always been found to be convex when extracted numerically for various systems[1, 89], but no general proof of this is known. The Hubbard dimer also exhibits this behavior. A proof for the dimer might suggest a proof for real-space DFT.



Figure 2.11: Adiabatic connection integrand divided by U for various values of U. The solid lines are  $\Delta v = 2$  and the dashed lines  $\Delta v = 0$ . Asymmetry reduces the correlation energy but increases the fraction of kinetic correlation.

In Fig. 2.11 we plot  $U_{\rm c}(\lambda)/U$  for  $\Delta v = 0$  and  $\Delta v = 2$ , with various values of U. From the above formulas, one can deduce that the area between the curve and the horizontal line at  $U_{\rm c}(1)$  is  $-T_{\rm c}$ . Thus as U grows, the curve moves from being almost linear to decaying very rapidly, and  $\beta_{\rm corr}$  varies from 1 down to 0.

In Fig. 2.11, we show U up to 10 (for 2t = 1), to show the effect of stronger correlation. Not only has the magnitude of the correlation become larger, but the curve drops more rapidly toward its value at large  $\lambda$ .  $\beta_{corr} \simeq 0.9$  for  $\Delta v = 0$  and U = 1, but  $\beta_{corr} \simeq 0.2$  for  $\Delta v = 0$ and U = 10, reflecting the fact that the increase in correlation is of the static kind.

The weakly correlated limit has been much studied in DFT. Perturbation theory in the

coupling constant is called Goerling-Levy perturbation theory [98]. For small  $\lambda$ ,

$$U_{\rm C}(\lambda U) = \lambda^2 U_{\rm C}^{(2)} + \lambda^3 U_{\rm C}^{(3)} + \dots \quad (\lambda \to 0).$$
(2.23)

In 2.10.2, we show that

$$U_{\rm c}^{(2)}(\Delta n) = -\frac{U^2}{8t} \left(1 - \left(\frac{\Delta n}{2}\right)^2\right)^{5/2},\tag{2.24}$$

and

$$U_{\rm c}^{(3)}(\Delta n) = \frac{3U^3}{32t^2} \left(\frac{\Delta n}{2}\right)^2 \left(1 - \left(\frac{\Delta n}{2}\right)^2\right)^3$$
(2.25)

for the dimer. This yields, for  $T_{\rm C}$ ,

$$T_{\rm C} = -\frac{1}{2}\lambda^2 U_{\rm C}^{(2)} - \frac{2}{3}\lambda^3 U_{\rm C}^{(3)} - \frac{3}{4}\lambda^4 U_{\rm C}^{(4)} - \dots$$
(2.26)

showing that  $\beta \to 1$  as U (or  $\lambda$ ) vanishes. For any system,  $U_{\rm c}^{(2)}$  determines the initial slope of  $U_{\rm c}(\lambda)$ .

On the other hand, in the strongly correlated limit, in real-space[176, 95].

$$E_{\rm c} \to \lambda (B_0 + \lambda^{-1/2} B_1 + \lambda^{-1} B_2 ...), \quad (\lambda \to \infty)$$
 (2.27)

where  $B_k$  (k = 0, 1, 2...) are coupling-invariant functionals of  $n(\mathbf{r})$ [177]. The dominant term is linear in U. Physically, it must exactly cancel the Hartree plus exchange contributions, since there is no electron-electron repulsion to this order when each electron is localized to separate sites. Correctly, such a term cancels out of  $T_c$ , so that its dominant contribution is O(1). From 2.10.2, we see that the Hubbard dimer has a different form, involving only integer powers of  $\lambda$ :

$$E_{\rm c} \to \lambda B_0 + \tilde{B}_1 + \tilde{B}_2/\lambda + \dots \quad (\lambda \to \infty)$$
 (2.28)

where

$$B_0(\Delta n) = -U(1 + \Delta n/2)^2/2, \qquad (2.29)$$

$$\tilde{B}_{1}(\Delta n) = 2 t \sqrt{1 + \Delta n/2} \left( \sqrt{1 - \Delta n/2} - \sqrt{-\Delta n} \right),$$
(2.30)

and

$$\tilde{B}_2(\Delta n) = (1 + \Delta n/2)t^2/U.$$
 (2.31)

But both this term and the next cancel in the total energy (at half filling), so that the ground-state energy is O(1/U), i.e., extremely small as U grows:

$$E \to -\frac{4t^2}{U} \tag{2.32}$$

This illustrates that, although the KS description is exact, it becomes quite contorted in the large U limit (see Fig. 1.2). This has been implicated in convergence difficulties of the KS equations, even with the exact XC functional, because the KS system behaves so differently from the physical system[307].
### 2.3 Accurate parametrization of correlation energy

Although the Hubbard dimer has an exact analytic solution when constructed from manybody theory, the dependence of  $F(\Delta n)$  (or equivalently  $E_{\rm c}(\Delta n)$ ) is only given implicitly. While this is technically straightforward to deal with, in practice it would be much simpler to use if an explicit formula is available. In this section, we show how the standard machinery of DFT can be applied to develop an extremely accurate parametrization of the correlation energy functional.

An arbitrary antisymmetric wavefunction is characterized by 3 real numbers where  $|12\rangle$  means an electron at site 1 and site 2, etc.:

$$|\psi\rangle = \alpha \ (|12\rangle + |21\rangle) + \beta_1 \ |11\rangle + \beta_2 \ |22\rangle. \tag{2.33}$$

Normalization requires  $2\alpha^2 + \beta_1^2 + \beta_2^2 = 1$ . In terms of these parameters, the individual components of the energy are rather simple:

$$T = -4 t \alpha (\beta_1 + \beta_2)$$
  

$$V_{ee} = U(\beta_1^2 + \beta_2^2)$$
  

$$V = -\Delta v (\beta_1^2 - \beta_2^2),$$
(2.34)

so that the variational principle may be written as

$$E = \min_{\substack{\alpha, \beta_1, \beta_2\\1=2\alpha^2+\beta_1^2+\beta_2^2}} E(\alpha, \beta_1, \beta_2).$$
(2.35)

The specific values of these parameters for the ground-state wavefunction are reported in 2.9.

For this simple problem, we are fortunate that we can apply the Levy-Lieb constrained search method explicitly. A variation of this method was used for the derivation of the exact functional of the single- and double-site Anderson model and the symmetric Hubbard dimer[46], and a numerical version of this was used by Fuks et al.[90]. Similar results were obtained by an alternative methods in [242]. The functional F[n] is defined by minimizing the expectation value of  $\hat{T} + \hat{V}_{ee}$  over all possible wavefunctions yielding a given  $n(\mathbf{r})$ . In real-space DFT, there are no easy ways of generating interacting wavefunctions for a given density. But here,

$$\Delta n = 2(\beta_2^2 - \beta_1^2), \tag{2.36}$$

which allows us to simply eliminate a parameter, e.g.,  $\beta_1$  in favor of  $\Delta n$ . Thus

$$F[\Delta n] = \min_{\alpha^2 + \beta_2^2 = \frac{1}{2}(1 + \frac{|\Delta n|}{2})} \left[ T(\alpha, \beta_2, \Delta n) + V_{\text{ee}}(\alpha, \beta_2, \Delta n) \right].$$
(2.37)

With normalization and the density constraint, only one parameter is left free. There exist several possible choices for this. If we choose  $g = 2\alpha (\beta_1 + \beta_2)$  which corresponds to the hopping term, then after some algebra the function(al) can be written nicely as

$$F(\rho) = \min_{g} f(\rho, g) \tag{2.38}$$

with the intermediate quantity

$$f(\rho, g) = -2tg + Uh(g, \rho), \tag{2.39}$$

and

$$h(g,\rho) = \frac{g^2 \left(1 - \sqrt{1 - g^2 - \rho^2}\right) + 2\rho^2}{2(g^2 + \rho^2)}.$$
(2.40)

Note that both t and U appear linearly in  $f(g, \rho)$ . The minimization yields a sextic polynomial, equation (2.81), that g must satisfy. The weak-coupling, strong-coupling, symmetric, and asymmetric limits of g are given in 2.10.

Our construction begins with a simple approximation to  $g(\rho)$ :

$$g_0(\rho) = \sqrt{\frac{(1-\rho)\left(1+\rho\left(1+(1+\rho)^3 u a_1(\rho,u)\right)\right)}{1+(1+\rho)^3 u a_2(\rho,u)}}$$
(2.41)

where

$$a_i(\rho, u) = a_{i1}(\rho) + u \, a_{i2}(\rho), \tag{2.42}$$

and

$$a_{21} = \frac{1}{2}\sqrt{(1-\rho)\rho/2}, \quad a_{11} = a_{21}(1+\rho^{-1}),$$
  

$$a_{12} = \frac{1}{2}(1-\rho), \qquad a_{22} = a_{12}/2.$$
(2.43)

These forms are chosen so  $g_0$  is exact to second- and first- order in the weak- and strongcoupling limits respectively, and to first- and second- order in the symmetric and asymmetric limits respectively. Use of this  $g_0$  to construct an approximation to F,  $f(g_0(\rho), \rho)$ , yields very accurate energetics. The maximum energy error, divided by U, is 0.002.

But for some of the purposes in this paper, such as calculations of  $T_c$ , even this level of error is unacceptable. We now improve on  $g_0(\rho)$  using the adiabatic connection formula of Sec 2.2.2. Like F, we can define functions of two variables for each of the correlation components. Write

$$e_{\rm c}(g,\rho) = f(g,\rho) - T_{\rm s}(\rho) - E_{\rm HX}(\rho).$$
(2.44)

where  $T_{\rm s}$  and  $E_{\rm HX}$  are from Eqs. (1.53) and (1.52), respectively. The kinetic and the potential correlation are given by

$$t_{\rm c}(g,\rho) = T - T_{\rm s} = -2t\left(g - \sqrt{1-\rho^2}\right)$$
 (2.45)

$$u_{\rm c}(g,\rho) = V_{ee} - E_{\rm HX} = U \left[ h(g,\rho) - (1+\rho^2)/2 \right], \qquad (2.46)$$

and their sum yields  $e_{\rm c}(g,\rho)$ . If we insert  $g(\rho)$ , the exact minimizer of  $f(g,\rho)$ , into any of these expressions, we get the exact answers.

But recall also that one can extract  $U_{\rm C}$  from the derivative of  $E_{\rm C}$  with respect to the coupling constant  $\lambda$ , i.e.,

$$U_{\rm C} = dE_{\rm C}(\lambda)/d\lambda|_{\lambda=1}.$$
(2.47)

Now for any g and  $e_{\rm c}(g)$ , we can find the  $\lambda$  dependence by replacing U by  $\lambda U$ . Thus

$$\frac{de_{\rm C}(g,\lambda)}{d\lambda} = \frac{\partial E_{\rm C}(\lambda)}{\partial\lambda} + \frac{\partial E_{\rm C}(\lambda)}{\partial g}\frac{\partial g}{\partial\lambda}$$
(2.48)

Since  $T_{\rm s}$  and  $E_{\rm HX}$  do not depend on g, the minimization of f reduces to  $\partial e_{\rm c}/\partial g = 0$ , so for the exact g the second term on the right of Eq. (2.48) is always zero. But it does not vanish for  $g_0$ .

Equating Eqs. (2.47) and (2.48) and using the definitions, we find the following self-consistent equation for g:

$$g = -\frac{T}{2t} + \frac{1}{2t} \frac{\partial E_{\rm c}}{\partial g} \left. \frac{\partial g(\lambda)}{\partial \lambda} \right|_{\lambda=1}.$$
(2.49)

We may use this to improve our estimate for g. Simply evaluate the right-hand side at  $g_0$ ,

to find:

$$g_1 = g_0 + \left( u \frac{\partial h}{\partial g} - 1 \right) \left. \frac{\partial g(\lambda)}{\partial \lambda} \right|_{\substack{g=g_0\\\lambda=1}}$$
(2.50)

where

$$\frac{\partial g(\lambda)}{\partial \lambda}\Big|_{\substack{g=g_0\\\lambda=1}} = \frac{(1-\rho)(1+\rho)^3 u^2}{2 g_0 (1+(1+\rho)^3 u a_2(u))^2} \times [(3 \rho/2 - 1 + \rho (1+\rho)^3 u a_2(u)) a_{12} - \rho (1+(1+\rho)^3 u a_1(u)) a_{22}]$$
(2.51)



Figure 2.12: Error in  $E_{c,par}(\rho)/U$  for different U and 2t = 1.

The new  $F_{\text{par}}$  and  $E_{\text{C,par}}$  are then obtained by using  $g_1$  in Eqs. (2.39) and (2.44). Using

 $g_1, \ \partial E_{C,par}/\partial g \neq 0$  still, but the error with  $g_1$  is much lower than with  $g_0$ . We plot the the relative error,  $(E_C - E_{C,par})/U$  for several U in Fig. 2.12. The maximum relative error is reduced by almost two orders of magnitude (from  $2 \times 10^{-3}$  to  $5 \times 10^{-5}$ ) in the region  $U \approx 2 - 6, \ |\Delta n| \approx 0.25$ , where  $g_0$  has the largest error. The other regions are also improved. For  $(T_C - T_{C,par})/U$  and  $(U_C - U_{C,par})/U$  the improvement is just of one order of magnitude (from  $2 \times 10^{-2}$  to  $2 \times 10^{-3}$  in both cases relative to the maximum), with different sign, so there is an error cancellation that yields the larger reduction of the  $E_C$  error. We anticipate that g could be improved even further by iteration.



Figure 2.13: Top row: Error in density as a function of  $\Delta v$ . Bottom row: Error in groundstate energy as a function of  $\Delta v$  and 2t = 1.

To test the validity of our parametrization, we use it in the KS scheme to calculate the correlation energy of our Hubbard dimer *self-consistently*. If our parametrization were perfect, we would recover the exact densities and energies from our KS calculation without having to solve the many-body problem. These are plotted in Figs. 2.13, together with the absolute errors committed by the parametric function(al). Notice that in Figs. 1.8 and 2.9 the results obtained from the parametric function(al) are indistinguishable from the exact results. We recommend the use of  $g_0$  for routine use, and  $g_1$  for improved accuracy. We hope the methodology developed here might prove useful to improve accuracy of correlation functionals in other contexts, e.g. using DFT to improve sampling in a Quantum Monte Carlo calculation [273].

We can define the starting point of our parametrization in a multitude of ways. In this section we defined it such that the parameter corresponds to the hopping term. Another possible choice favors the electron-electron term. Define

$$f_2(f,\rho) = -2t\sqrt{1-f} \left(\sqrt{f+\rho} + \sqrt{f-\rho}\right) + Uf.$$
(2.52)

Another choice captures the asymmetric limit. Define,

$$f_3(l,\rho) = -2t\sqrt{2l-l^2-\rho^2} + U\frac{l^2+\rho^2}{2l}.$$
(2.53)

Then,

$$F(\rho) = \min_{f} f_2(f, \rho) = \min_{l} f_3(l, \rho).$$
(2.54)

These also yield high order polynomial equations when minimized. The present parametrization, Eq. (2.41), is quantitatively superior for nearly all values of U, and  $\Delta v$  of interest.

### 2.4 Approximations

The usefulness of KS-DFT derives from the use of approximations for the XC functional, not from the exact XC which is usually as expensive to calculate as direct solution of the manybody problem (or more so). While the field of real-space DFT is deluged by hundreds of different approximations[188] (relatively few of which are used in routine calculations[233]), few approximations exist that apply directly to the Hubbard dimer. The two we explore here are illustrative of many general principles.

#### 2.4.1 Mean-field theory: Broken symmetry

Since time immemorial, or at least the 1930's, folks have realized the limitations of restricted HF solutions for strongly correlated multi-center problems, and performed broken-symmetry calculations[57]. For example, in many-body theory, Anderson solved the Anderson impurity model for a magnetic atom in a metal[11] by allowing symmetry breaking, several years before Kondo's ground-breaking work[149]. In quantum chemistry, Coulson and Fischer identified the Coulson-Fischer point of the stretched H<sub>2</sub> molecule where the broken symmetry solution has lower energy than the restricted solution[57]. Modern quantum chemists like to spin-purify their wavefunctions, but DFT hardliners[223] claim the broken-symmetry solution is the 'correct' one (for an approximate functional). The exact KS functional, as shown in all previous sections, yields the exact energy and spin densities, while remaining in a spin singlet.

If we do not impose spin symmetry, the effective potential in mean-field theory becomes (Sec 1.3.2):

$$v_{i\sigma}^{\text{eff}} = v_i + U \, n_{i\bar{\sigma}},\tag{2.55}$$

with  $\sigma = +1$  for spin up,  $\sigma = -1$  for spin down and  $\bar{\sigma} = -\sigma$ , because the change in the effective field is caused by the other electron. Writing  $n_i = n_{i,\uparrow} + n_{i,\downarrow}$ ,  $m_i = n_{i,\uparrow} - n_{i\downarrow}$  and  $\Delta m = m_2 - m_1$ , and defining

$$\Delta v_{\sigma}^{\text{eff}} = \Delta v + \frac{U}{2} \left( \Delta n - \sigma \,\Delta m \right), \tag{2.56}$$

and

$$t_{\sigma}^{\text{eff}} = t\sqrt{1 + (\Delta v_{\sigma}^{\text{eff}}/2\,t)^2},\tag{2.57}$$

we find the eigenvalues are:

$$e_{\pm,\sigma}^{MF} = \frac{U}{4} \left( N - \sigma M \right) \pm \frac{t_{\bar{\sigma}}^{\text{eff}}}{2}, \qquad (2.58)$$

where N = 2 is the number of particles and M is the total magnetization. We find the ferromagnetic solution (M = 2) to be everywhere above the antiferromagnetic solution (M = 0), and for M = 0:

$$E = \frac{U}{2} \left( 1 - \frac{\Delta n^2 - \Delta m^2}{4} \right) - \frac{1}{2} (t_{\uparrow}^{\text{eff}} + t_{\downarrow}^{\text{eff}}), \qquad (2.59)$$

where  $\Delta m = 0$  is the paramagnetic (spin singlet) solution, and corresponds to our original mean-field or restricted Hartree-Fock solution. We minimize this energy with respect to  $\Delta n$ and  $\Delta m$ , given by

$$\Delta n = -\sum_{\sigma} \frac{\Delta v_{\sigma}^{\text{eff}}}{t_{\sigma}^{\text{eff}}}, \quad \Delta m = -\sum_{\sigma} \sigma \frac{\Delta v_{\sigma}^{\text{eff}}}{t_{\sigma}^{\text{eff}}}, \tag{2.60}$$

These antiferromagnetic (AFM) self-consistency equations always have the trivial solution  $\Delta m = 0$ , which corresponds to the restricted MF solution(RHF). However, there exists a non-trivial solution  $\Delta m \neq 0$  for sufficiently large values of U.

In Fig. 2.14, we plot  $\Delta n$  for both restricted and unrestricted HF solutions for U = 5. The solutions coincide for large  $\Delta v$ , but below a critical value of  $\Delta v$ , they differ. The UHF solution has a significantly lower  $\Delta n$ , which is much closer to the exact  $\Delta n$ .

In Fig. 2.15, we plot the energies, showing that the UHF solution does not rise above zero,



Figure 2.14: Plots of  $\Delta n$  for HF and BALDA as a function of  $\Delta v$  for U = 5 and 2t = 1. The crossover from the charge-transfer to the Mott-Hubbard regime happens at  $U \approx \Delta v$ .

and mimics the exact solution rather closely. For large U, at  $n_1 = 1$ , we can compare results analytically:

$$E \to \frac{U}{2} - 2t$$
 (RHF),  $-\frac{2t^2}{U}$  (UHF),  $-\frac{4t^2}{U}$  (exact) (2.61)

confirming that the UHF energy is far more accurate than the RHF energy, and recovers the dominant term in the strongly correlated limit. Note that the symmetric case is atypical: The constant terms vanish, both exactly and in UHF, so the leading terms is O(1/U), and its coefficient in UHF is underestimated by a factor of 2. The slope of the exact result is two times larger than UHF. Of course, the exact solution is a spin-singlet, so the symmetry of the UHF solution is incorrect, but its energy is far better than that of RHF. This is called the symmetry dilemma in DFT[223]: Should I impose the right symmetry at the cost of a



Figure 2.15: Ground-state energy of the unrestricted Hartree-Fock (thick dashed line), restricted Hartree-Fock (dot dashed line), and exact ground-state (thin solid line) of the Hubbard dimer as a function of  $\Delta v$  for several values of U and 2t = 1. The dot shows the Coulson-Fischer point at which the symmetry breaks spontaneously. For smaller  $\Delta v$  the UHF energy is below RHF while for larger  $\Delta v$  they are the same.

poor energy? Note that the exact KS wavefunction is also a singlet, so a broken-symmetry DFT solution produces the wrong symmetry for the KS wavefunction.

#### 2.4.2 BALDA

In real-space DFT, the local density approximation (LDA) was first suggested by Kohn and Sham[148], in which the XC energy is approximated at each point in a system by that of a uniform gas with the density at that point. Another way to think of this is that one decides to make a local approximation, and then chooses the uniform gas XC energy density to ensure exactness in the uniform limit. On the lattice, we must switch our reference system to incorporate Luttinger-liquid correlations instead of Fermi-liquid correlations[111]. The infinite homogeneous Hubbard chain plays the role of the uniform gas. This can be solved exactly via Bethe ansatz[170], and the corresponding LDA was first constructed and tested in Ref. [261]. Later, Capelle and collaborators[172, 44, 173, 320, 87] used the exact Bethe ansatz solution to create an explicit parametrization for the energy per site, and called this Bethe Ansatz LDA, or BALDA.

Since its inception, BALDA has been applied to many different problems including disorder and critical behavior in optical lattices[313, 41], spin-charge separation[300, 301] and effects of spatial inhomogeneity[270, 171] in strongly correlated systems, confined fermions both with attractive and repulsive interactions[39], current DFT on a lattice[7], electric fields and strong correlation[6], and various critical phenomena in 1-D systems[3, 86]. Extensions to include spin-dependence (BALSDA) have been principally used for studying density oscillations[314, 303], and fermions in confinement[316, 315, 126]. A thermal DFT approximation on the lattice has been constructed using BALDA[317]. BALDA has also been used as an adiabatic approximation in TD-DFT to calculate excitations[296, 167, 157, 291, 298, 140] and also transport properties[159, 299], as well as using BALDA as a gateway to calculate time-dependent effects in 3-D[138]. There has been significant interest in using BALDA to understand the derivative discontinuity in both DFT and TD-DFT[320, 159, 317, 324]. Additionally, the BALDA approach has been developed for other BA-solvable fermionic lattice systems aside from the Hubbard model[318, 4, 256, 198], such as the Anderson model[29, 175, 158], as well as bosonic systems[112, 310, 311].

We use here the semi-analytical approach to BALDA[173, 320] where the expressions are given in 2.12. In Fig. 2.16 we plot the BALDA ground-state energy as a function of  $\Delta v$  for several values of U. At first glance, it seems to do a good job in all regimes. In particular, for either very weak correlation (U = 0.2) or very strong correlation (U = 100), it is indistinguishable from the exact curves. However, for moderate correlation ( $1 \leq U \leq 5$ ) where



Figure 2.16: Ground-state energy versus  $\Delta v$  for several U, with 2t = 1. The BALDA energies are evaluated self-consistently.

 $\Delta v \lesssim U$ , it appears to significantly underestimate the magnitude of E.

Even for the strong correlation regime, its behavior is not quite correct. For the symmetric case:

$$E^{BA} \simeq 2t \left(\frac{4}{\pi} - 1\right) > 0 \qquad (U \gg 2t) \tag{2.62}$$

Thus, for  $\Delta v = 0$  and U = 100 in Fig. 2.16, BALDA is in serious error, but this cannot be seen on the scale of the figure. The origin of this error is easy to understand. BALDA's reference system is an infinite homogeneous chain, and we are applying it to a finite inhomogeneous dimer. The error is in the correlation kinetic energy, which comes from the difference between the exact and KS kinetic energies. The tight-binding energy for an infinite homogeneous chain is different from that of the dimer, and this difference is showing up (incorrectly) in the correlation energy. We could, of course, reparametrize BALDA to use the homogeneous dimer energy, but the analog of real-space DFT is to use the homogeneous extended system (infinite Hubbard chain).



#### 2.4.3 BALDA versus HF

Figure 2.17: Plots of the RMF, UMF, and BALDA  $\Delta E = E^{\text{approx}} - E^{\text{exact}}$  as a function of  $\Delta v$  for U = 0.2, 1, 5, and 10. For small U the RMF and UMF results are indistinguishable. Here 2t = 1.

Lastly we compare BALDA and both the restricted and unrestricted Hartree-Fock approximations. In Fig. 2.17, we plot the errors made in the ground-state energy of all three approximations. For  $U \leq 1$ , HF does not break symmetry, and so UHF=RHF. For very small U, the energy error is comparable to HF. For U = 1, BALDA is better than HF. For larger U, UHF produces a lower energy than HF, and almost everywhere is more accurate than BALDA. The sole exception is at precisely  $U \approx \Delta v$ , where BALDA is much better. In Fig. 2.14, we compare BALDA and UHF densities to the exact density for U = 5 as a function of  $\Delta v$ . Although BALDA does not have a symmetry-breaking point, it unfortunately has a critical value of  $\Delta v$  where  $\Delta n$  vanishes incorrectly. This is the origin of the cusp-like features in the BALDA energies of Figs. 2.16 and 2.17. In fact, the BALDA density appears somewhat worse than UHF for most  $\Delta v$ . But keep in mind that the main purpose of BALDA is to produce accurate energies *without* the artificial spin-symmetry breaking of UHF.

### 2.5 Fractional particle number

We will now show a way that one *can* extract the physical gap from ground-state DFT. This is done simply by changing the number of electrons, but now continuously, rather than just at integers. In fact, we already used this technology implicitly in Sec 2.1, but here we make this much more explicit.

#### 2.5.1 Derivative discontinuity

An extremely important concept in DFT is that of the derivative discontinuity [222, 221, 259, 199, 54, 201, 159, 322, 200]. This is most famous for its implication for the Kohn-Sham gap of a solid, ensuring that the gap (in general) does *not* match the true fundamental (or charge) gap of the solid, as we saw in Sec. 2.1. The expression itself refers to a plot of ground-state energy versus particle number N at zero temperature. In seminal work[222, 221, 216], it was shown that  $E(\mathcal{N})$  consists of straight-line segments between integer values, where  $\mathcal{N}$  is a real variable, where all quantities are now expectation values in a grand-canonical ensemble at zero temperature:

$$E(\mathcal{N}) = (1 - w) E(N) + w E(N + 1), \qquad (2.63)$$

and

$$n_{\mathcal{N}}(\mathbf{r}) = (1 - w) n_N(\mathbf{r}) + w n_{N+1}(\mathbf{r}), \qquad (2.64)$$

where  $\mathcal{N} = N + w$ , i.e., both energy and ground-state density are piecewise linear, with a sudden change at integer values.

Then the chemical potential is

$$\mu = dE/d\mathcal{N} = -I \qquad (\mathcal{N} < N)$$
$$= -A \qquad (\mathcal{N} > N). \tag{2.65}$$

When we evaluated everything at N = 2 in Sec. 2.1, we really meant  $N = 2^{-}$ . Then Janak's theorem[133] shows that, for the KS system,

$$\mu = dE/d\mathcal{N} = \epsilon^{\text{HOMO}} \qquad (\mathcal{N} < N)$$
$$= \epsilon^{\text{LUMO}} \qquad (\mathcal{N} > N) \qquad (2.66)$$

This is the proof of the equivalence of I and  $-\epsilon^{\text{HOMO}}$ .

Because the energy is in straight-line segments, the slope of  $E(\mathcal{N})$ , the chemical potential,  $\mu(\mathcal{N})$ , jumps discontinuously at integer values. Hence the name, derivative discontinuity. The jump in  $\mu$  across an integer N is then  $E_g = I - A$ , the fundamental gap. In the KS system, since the energy is given in terms of orbitals and their occupations, that jump is simply the KS HOMO-LUMO gap,  $E_{gs}$ . Since the KS electrons have the non-interacting kinetic energy, and the external and Hartree potentials are continuous functionals of the density, the difference is an XC effect. Moreover, it implies that  $v_{\rm XC}$  jumps by this amount as one passes through N, an integer.

For solids, addition or removal of a single electron has an infinitesimal effect on the density, but the XC discontinuity shifts the conduction band upward by  $\Delta_{\rm xc}$  when an electron is added, contributing to the true gap. Since local and semilocal approximations to XC are usually smooth functionals of the density, they produce no such shift. They *do* yield accurate approximations to the KS gap of a solid, but *not* to the gap calculated by adding and removing an electron, because of this missing shift. Thus we have no general procedure for extracting accurate gaps using LDA and GGA. An important quality factor in more sophisticated approximations is whether or not they have a discontinuity. Orbital-dependent functionals, such as exact exchange (EXX in OEP)[268, 284, 153, 96, 323, 156] or selfinteraction corrected LDA (SIC)[225, 238, 19, 48, 215], often capture effects due to the discontinuity quite accurately.

#### 2.5.2 Hubbard dimer near integer particle numbers

In Fig. 2.18, we plot  $E(\mathcal{N})$  for our Hubbard dimer. Real-space curves have always been found to be convex, although this has never been proven to be generally true. The vital part for us is that this equivalence of the HOMO level and -I links the overall position of the KS levels to those of the many-body system. For fixed particle number, only the KS on-site energy difference is determined by the need to reproduce the exact site occupancies. But this condition also fixes the mean value of the KS on-site energy,  $\bar{v}_s$ , which in general is non-zero, even though we chose the actual mean on-site energy to be zero always. In Fig. 1.2, this is visible in the mean position of the two KS on-site potentials.

Another way to think about this is that function(al) derivatives at fixed  $\mathcal{N}$  leave an undetermined constant in the potential, whereas that constant is determined if the particle number



Figure 2.18: Plot of  $E(\mathcal{N})$  for U = 1,  $\Delta v = 0$  and 2t = 1.

is allowed to change. We can write many equivalent formulas for the discontinuity:

$$\Delta_{\rm xc} = \frac{\partial E_{\rm xc}}{\partial N} \Big|_{N^+} - \frac{\partial E_{\rm xc}}{\partial N} \Big|_{N^-},$$
  

$$= \bar{v}_{\rm xc}(N^+) - \bar{v}_{\rm xc}(N^-),$$
  

$$= \bar{v}_{\rm s}(N^+) - \bar{v}_{\rm s}(N^-),$$
  

$$= \epsilon_{\rm s}(N^+) - \epsilon_{\rm s}(N^-),$$
(2.67)

all of which are true. Thus another way to find the gap from a KS system is to occupy it with an extra infinitesimal of an electron, and note the jump in potentials or eigenvalues. To illustrate this, in Fig. 2.19 we replot Fig. 2.1, but now for  $N = 2^+$ , showing that now the LUMO matches -A, and the difference between the HOMO and -I is  $\Delta_{\rm xc}$ .

In Fig. 2.20 we plot  $\Delta_{\rm xc}$  for N = 2 for various U, as a function of  $\Delta v$ , scaling each variable



Figure 2.19: Same as Fig. 2.1 except with  $N = 2^+$  instead of  $N = 2^-$ .

by U. We see that the discontinuity always decreases with increasing  $\Delta v$ . In fact, the larger U is, the more abruptly it vanishes (on a scale of U) when  $\Delta v > U$ . In this sense, the greater the asymmetry, the less discontinuous the energy derivative is, and the KS gap will be closer to the true gap.

The situation is reversed when N = 1, as shown in Fig. 2.21. Now the discontinuity grows with increasing  $\Delta v$ . In this case, a large asymmetry puts the electron mostly on one site. When an infinitesimal of an electron is added, it goes to the same site, but paying an energy cost of U. On the other hand, if  $\Delta v$  is small, the first electron is spread over both sites, and so is the added infinitesimal, reducing the energy cost by a factor of 2. So  $\Delta_{\rm xc} \rightarrow U/2$  in the weakly correlated near-symmetric limit.



Figure 2.20: Derivative discontinuity as a function of  $\Delta v$  for U = 1, and U = 5.

### **2.5.3** Discontinuity around $n_1 = 1$ for N = 2

The derivative discontinuity manifests itself in many different aspects of DFT. We have already seen how it affects both energies and potentials as N is continuously moved across an integer. Here we explore how it appears even at fixed particle number, as correlations become strong.

For our Hubbard dimer, with any finite  $\Delta v$ , if  $U \gg \Delta v$ , we know each  $n_i$  is close to 1. The overwhelmingly large U localizes each electron on opposite sites. In the limit as  $U \to \infty$ , all fluctuations are suppressed, and the dimer becomes two separate systems of one electron each. For large but finite U, and finite  $\Delta v$ , one is on the integer deficient side, and the other has slightly more than one electron. All the statements made above about  $\mathcal{N}$  passing through 2 now apply as  $n_1$  passes through 1.



Figure 2.21: Derivative discontinuity for N = 1 as a function of  $\Delta v$  for U = 1, and U = 5.

We can see the effects in many of our earlier figures. In Fig. 1.7, the slope of F for U = 10 appears discontinuous at  $n_1 = 1$ . F contains the discontinuity in both  $T_s$  and  $E_{xc}$  in the limit  $U \to \infty$ . However, in reality, this curve is not really discontinuous. Zooming in on F near  $n_1 = 1$ , one sees that on a scale of O(1/U), F is rounded.

The classic manifestation already appears in Fig. 1.4, the occupation difference as a function of  $\Delta v$ . To emphasize the point, in Fig. 2.22, we plot several curves for U = 100. This is the discontinuous change from having 1 particle on each site to 2 on one site that occurs. This is important because the common approximate density functionals miss this discontinuity effect. Explicit continuous functionals of the density cannot behave this way. For the SOFT case, this is embodied in the HF curves of Fig. 1.9: No matter how strong the value of U, these curves are linear. In RHF,  $\Delta n$  versus  $\Delta v$  never evolves the sudden step discussed above, as shown in Fig. 2.14. On the other hand, the BALDA approximation contains an explicit discontinuity at  $n_1 = 1$  in its formulas, and so captures this effect, at least to leading-order



Figure 2.22: Plots of  $\Delta n$  in HF and BALDA as a function of  $\Delta v$  for U = 100 (2 t = 1). The crossover from the charge-transfer to the Mott-Hubbard regime happens at about  $U \approx \Delta v$ .

in U. In this sense, both BALDA and UHF capture the most important effect of strong correlation. On the other hand, as discussed in Sec 2.4.3, UHF 'cheats', while BALDA retains the correct spin singlet. If BALDA's effects could be (legally) built into real-space approximations, they would be able to accurately dissociate molecules, overcoming perhaps approximate DFT's greatest practical failure.

However, in Fig. 2.23, we simply zoom in on the region of the plot near  $\Delta v = U$ . In fact, the exact curve is S-shaped, with a finite curvature on the scale of t. Now we see that, although both UHF and BALDA reproduce the discontinuous effect, the details are not quite right. UHF is admirably close in shape to the accurate curve, but its slope is too great at  $n_1 = 1$ . BALDA is accurate to leading order in 1/U, and captures beautifully the region  $\Delta v$  a little larger than U, but is quite inaccurate below that. The presence of the gap in the BALDA



Figure 2.23: Same as Fig. 2.22

potentials leads to the incorrect discontinuous behavior near  $\Delta v = 98$ . But once again we emphasize that the important feature is that these approximations do capture the dominant effect, and that BALDA does so without breaking symmetry.

## 2.6 Conclusions and Discussion

So, what can we learn from this exercise in applying DFT methods to the simplest strongly correlated system? Perhaps the most important point is that there is a large cultural difference between many-body approaches and DFT methodology, and a considerable barrier to communication. In Sec. 1.4.3, we saw that even the definition of exchange is different in the two communities. The greatest misunderstandings come not from using different words for

the same thing, but rather from using the same word for two different things.

We can also see that the limitations of DFT calculations are often misunderstood in the broader community. For example, the exact ground-state XC functional has a HOMO-LUMO gap that does not, in general, match the fundamental gap. The KS eigenvalues are not quasiparticle eigenvalues in general, and are in fact, much closer to optical excitations[2]. Even the purpose of a DFT calculation is quite foreign to most solid-state physics. The modern art of DFT is aimed at producing extremely accurate (by physics standards) groundstate energies, and the many properties that can be extracted from those, rather than the response properties that are probed in most solid-state experiments, such as photoemission. (Flipping the coin, most quantum chemists would never describe DFT energies as extremely accurate, as traditional quantum chemical ab initio methods are hyper accurate on this scale.)

We also mention many aspects that we have *not* covered here. For example, time-dependent DFT is based on a distinct theorem (the Runge-Gross theorem[248]), and provides approximate optical excitations for molecular systems[38]. The Mermin theorem[194] generalizes the HK theorem to thermal ensembles[235]. There are many interesting features related to spin polarization and dynamics, but very little is relevant to the system discussed here. There are also many non-DFT approaches, such as GW, which could be tested on the asymmetric dimer.

We also take a moment to discuss how SOFT calculations can be related to real-space DFT. One can easily add more orbitals to each site and create an extended Hubbard model. For the H<sub>2</sub> molecule, adding just  $p_z$  orbitals and allowing them to scale yields a very accurate binding curve. But such an extension (beyond one basis function per site) is extremely problematic for SOFT[113, 258], because it is no longer clear how to represent the 'density'. With 2 basis functions, should one use just the diagonal occupations, or include off-diagonal elements? In fact, neither one is satisfactory, as neither approaches the real-space density functional in the infinite basis limit. An underlying important point of DFT is that it is applied to potentials that are diagonal in  $\mathbf{r}$ , i.e.,  $v(\mathbf{r})$ , and not diagonal in an arbitrary basis. This is a key requirement of the HK theorem, and is the reason why the one-body density  $n(\mathbf{r})$  is the corresponding variable on which to build the theory, and why the local density approximation is the starting point of all DFT approximations.

This inability to go from SOFT calculations to real-space DFT calculations should be regarded as a major caveat for those using SOFT to explore DFT. Here we have shown many similarities in the behavior of SOFT functionals compared to real-space functionals. We have also proven some of the same basic theorems as those used in real-space DFT. But any results (especially unusual ones) that are found in SOFT calculations might not generalize to real-space DFT. The only way to be sure is to find a proof or calculation in real-space. On the other hand, SOFT calculations can be safely used to illustrate the basic physics behind real-space results[281].

Another limitation of SOFT can be seen already in our asymmetric Hubbard dimer. In a real heterogeneous diatomic molecule, say LiH with a pseudopotential for the core Li electrons, the values of U would be different on the two sites. But the real-space DFT is applied to interactions that are the same among all particles. And even if SOFT applies when both U and t become site-dependent, i.e. a one-to-one correspondence can be proven, it is unlikely that such studies would yield behavior that is even qualitatively similar to real-space DFT. Minimal models are usually designed to capture universal features and our Hubbard dimer captures the essential physics of the strongly correlated limit. However the SOFT function(al) is not the same as the DFT one.

Finally, we wish to emphasize once again the importance of testing ideas on the asymmetric Hubbard dimer. Much (but not all) of the SOFT literature tests ideas on homogeneous cases. The essence of DFT is the creation of a universal functional. i.e., F[n] is the same no matter which specific problem you are trying to solve. The symmetric case is very special in several ways, and there are no difficulties in applying any method to the asymmetric case. We hope that some of the results presented here will make that easier.

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# 2.8 Additional Results

The following sections are Ref. [47]'s appendices.

# 2.9 Exact solution, components, and limits

In all appendices, we use dimensionless variables for brevity. Hence  $\epsilon = E/2t$ , u = U/2t, and  $\nu = \Delta v/2t$ . All the results in this appendix are already known, e.g. [242]. Then, the energy of the singlet-ground-state is

$$\epsilon = \frac{2}{3} \left( u - w \sin\left(\theta + \frac{\pi}{6}\right) \right) \tag{2.68}$$

where

$$w = \sqrt{3\left[1 + \nu^2\right] + u^2},\tag{2.69}$$

and

$$\cos(3\theta) = (9(\nu^2 - 1/2) - u^2)u/w^3.$$
(2.70)

The coefficients of the minimizing wavefunction, Eq. (2.33), are

$$\alpha = c \left(1 - \frac{u}{\epsilon}\right), \quad \beta_{1,2} = c \left(u - \epsilon \pm \nu\right), \quad (2.71)$$

$$c^{-2} = 2\left(\nu^2 + (\epsilon - u)^2 \left(1 + \epsilon^{-2}\right)\right).$$
(2.72)

The ground-state expectation values of the density difference and of the different pieces of the Hamiltonian are

$$\Delta n = 4 c^2 \nu (\epsilon - u) \tag{2.73}$$

$$V = \Delta v \,\Delta n/2, \tag{2.74}$$

$$T = 4c^{2}(\epsilon - u)^{2}/\epsilon,$$
 (2.75)

$$V_{\rm ee} = 4 c^2 t u \left( (\epsilon - u)^2 + \nu^2 \right).$$
(2.76)

For fixed asymmetry  $\nu$ , we can expand  $\epsilon$  in the weakly and strongly correlated limits:

$$\epsilon^{w} = -\sqrt{1+\nu^{2}} \left( 1 - (\frac{1}{2}+\nu^{2})\tilde{u} + (\frac{1}{4}+\nu^{2})\frac{\tilde{u}^{2}}{2} + \nu^{4}\frac{\tilde{u}^{3}}{2} \right)$$
(2.77)

where  $\tilde{u} = u/(1 + \nu^2)^{3/2}$ . In the strongly correlated limit:

$$\epsilon^{st} = -u^{-1} + (1 - \nu^2)u^{-3} + O(u^{-5}).$$
(2.78)

We can also expand for fixed u around the symmetric limit:

$$\epsilon^{sym} = \frac{1}{2}(u-r) + \frac{u-r}{r(u+r)}\nu^2, \tag{2.79}$$

where  $r = \sqrt{u^2 + 4}$ . And the asymmetric limit:

$$\epsilon^{asy} = -\nu + u - (2\nu)^{-1} - u/2\nu^{-2} + (1 - 4u^2)(2\nu)^{-3}.$$
(2.80)

# **2.10** Many limits of $F(\Delta n)$

In this appendix we derive the limits that our parametrization in Section 2.3 satisfies. Minimizing  $\tilde{F}$  of Eq. (2.39) with respect to g, we obtain a sextic equation for g:

$$(4+u^2) g^6/4 + (\rho^2 (3+u^2) - 1) g^4 + 2 u \rho^2 g^3 + \rho^2 (\rho^2 (3+u^2) - (2+u^2)) g^2 - 2 u \rho^2 (1-\rho^2) g - \rho^4 (1-\rho^2) = 0$$
(2.81)

where we define  $\rho = |\Delta n|/2$ . The solution defines  $g_m(\rho)$ , and  $F(\rho) = F(g_m(\rho), \rho)$ . Next we expand in several limits. and  $F[U, \rho] = \tilde{F}[U, \rho, g_m]$ . However, equation (2.81) can not be solved analytically in general.

### **2.10.1** Expansions for $g(\rho, u)$

We expand g in 4 different limits, which are built into  $g_0$  of Eq. (2.41) in Section 2.3.

The weakly correlated limit corresponds to  $u \ll 1$ . We thus expand  $g(\rho, u)$  in powers of u for fixed  $\rho$ ,

$$g(\rho, u) = \sum_{n=0}^{\infty} g^{(n)}(\rho) u^n / n!, \qquad (2.82)$$

and insert the expansion into Eq. (2.81). The coefficients  $g^{(n)}$  are found by canceling each term order by order in Eq. (2.81), yielding

$$g^{(0)} = \sqrt{1 - \rho^2}, \quad g^{(1)} = 0, \quad (2.83)$$

$$g^{(2)} = -\frac{(1 - \rho^2)^{5/2}}{4}, \quad g^{(3)} = \frac{3}{4} \rho^2 (1 - \rho^2)^3,$$

$$g^{(4)} = \frac{9}{16} (1 - \rho^2)^{7/2} (1 + 7 \rho^2 - 24 \rho^4).$$

Notice that  $n_{1,2} = 1 \mp sign(\Delta n) \rho$  so that to first order in U, Eq. (2.39) yields the noninteracting kinetic energy functional of Eq. (1.42).

For strongly correlated systems, we expand g in powers of 1/u while holding  $\rho$  fixed

$$g(\rho, u) = \sum_{n=0}^{\infty} \tilde{g}^{(n)}(\rho) \, u^{-n}/n!, \qquad (2.84)$$

and substitute back into Eq. (2.81) to find the coefficients. The result is

$$\tilde{g}^{(0)} = \sqrt{2\rho(1-\rho)}, \quad \tilde{g}^{(1)} = \frac{1-\rho}{2},$$

$$\tilde{g}^{(2)} = \frac{3(1-3\rho)}{8\rho} \tilde{g}^{(0)}.$$
(2.85)

Notice that this expansion breaks down at the symmetric point  $\rho = 0$ .

The other kind of limit keeps u fixed. The symmetric limit is equivalent to  $\rho \to 0$ . We expand g in powers of  $\rho$  while holding u fixed.

$$g(\rho, u) = \sum_{n=0}^{\infty} \bar{g}^{(n)}(u) \,\rho^n / n!, \qquad (2.86)$$

and substitute back into Eq. (2.81) to find the coefficients. The result is

$$\bar{g}^{(0)} = r^{-1}, \quad \bar{g}^{(2)} = \frac{1}{2} \left( u^2 + \frac{u^2/2(u^2/2 + 1) - 1}{r} \right)$$
 (2.87)

where  $r = \sqrt{1 + (u/2)^2}$ .

The asymmetric limit is equivalent to  $\rho \to 1$ . We expand g in powers of  $\bar{\rho} = 1 - \rho$  for fixed u:

$$g(\rho, u) = \sum_{n=0}^{\infty} \tilde{g}^{(n)}(u) \,\bar{\rho}^n / n!, \tag{2.88}$$

and substitute back into Eq. (2.81). The result is

$$\begin{split} \tilde{g}^{(1/2)} &= \sqrt{\pi/2}, \quad \tilde{g}^{(3/2)} = -3\tilde{g}^{(1/2)}/8 \\ \tilde{g}^{(5/2)} &= \left(\frac{1}{16} + u^2\right) 5\tilde{g}^{(3/2)} \\ \tilde{g}^{(3)} &= 12 \, u^3. \end{split}$$

$$(2.89)$$

#### 2.10.2 Limits of the correlation energy functional

Now that we have expressions for g in all four limits we can use our expression for F, eq. (2.39),  $T_{\rm s}$ , and  $U_{\rm H}$  to compute  $E_{\rm c}$  in each regime:

$$e_{\rm c} = -g + uh(g,\rho) - \frac{u}{2}(1+\rho^2) + \sqrt{1-\rho^2}.$$

where  $h(g,\rho)$  is defined in Eq. (2.40). Then, as  $u \to 0, e_{\rm c} \to e_{\rm c}^w$ , where

$$e_{\rm c}^w(\rho) = -\frac{u^2}{8} \left(1 - \rho^2\right)^{5/2} \left(1 - u \,\rho^2 \sqrt{1 - \rho^2}\right). \tag{2.90}$$

Similarly, as  $u \to \infty$ ,  $e_{\rm c} \to e_{\rm c}^{str}$ , where

$$e_{\rm c}^{str}(\rho) = -\frac{u}{2} (1-\rho)^2 + \sqrt{1-\rho} \left(\sqrt{1+\rho} - \sqrt{2\rho}\right) - \frac{1-\rho}{4u}.$$
(2.91)

An alternative expansion is to fix u and expand in  $\rho$ . As  $\rho \to 0$ ,  $e_{\rm c} \to e_{\rm c}^{sym}$ , where

$$e_{\rm C}^{sym}(\rho) = 1 - \sqrt{1 + \left(\frac{u}{2}\right)^2} + \rho^2 \left( \left(\frac{u}{2}\right)^3 - \frac{1}{2} + \sqrt{1 + \left(\frac{u}{2}\right)^2} \left(\frac{1}{2} + \left(\frac{u}{2}\right)^2\right) \right).$$
(2.92)

As  $\rho \to 1$ ,  $e_{\rm C} \to e_{\rm C}^{asym}$ , where

$$e_{\rm c}^{asym}(\rho) = u^2 \,\bar{\rho}^{5/2} \,\left( -\frac{1}{\sqrt{2}} + u \,\sqrt{\bar{\rho}} \right).$$
 (2.93)

where  $\bar{\rho} = 1 - \rho$ .

#### 2.10.3 Order of limits

Finally, we look at how these expressions behave when both parameters are extreme. The weakly correlated limit has no difficulties near the symmetric point:

$$e_{\rm C}^{w}(\rho \to 0) = e_{\rm C}^{sym}(u \to 0)$$
  
=  $-\frac{u^2}{8}\left(1 - \frac{5\rho^2}{2}\right) + \frac{u^3\rho^2}{8}.$  (2.94)

In the asymmetric limit, there are also no problems:

$$e_{\rm C}^{w}(\rho \to 1) = e_{\rm C}^{asym}(u \to 0) = u^{2} \bar{\rho}^{5/2} \left( -\frac{1}{\sqrt{2}} + u \sqrt{\bar{\rho}} \right).$$
(2.95)

Thus, the expansion in powers of u is well-behaved, and there are no difficulties using it for sufficiently small u. In the symmetric case, one sees explicitly that the radius of convergence of the expansion is u = 2.

On the other hand, the strong coupling limit is more problematic. Expanding the strongcouping functional around the symmetric limit, we find

$$e_{\rm c}^{str}(\rho \to 0) = -\frac{u}{2} + 1 - \frac{1}{4u} - \sqrt{2\rho} + \rho \left(u + \frac{1}{4u}\right), \qquad (2.96)$$

while reversing the order of limits yields:

$$e_{\rm C}^{sym}(u \to \infty) = -\frac{u}{2} + 1 - \frac{1}{u} - \frac{\rho^2}{2} \left( 1 - u - \frac{1}{2u} - \frac{u^3}{2} \right).$$
(2.97)

Note the difference beginning in the third terms, i.e., at first-order in 1/u, even for  $\rho = 0$ . Thus for the Hubbard dimer, approximations based on expansions around the strong-coupling limit are likely to fail for some values of the density.

#### 2.11 Proofs of Energy Relations

Using the notation established in Section 2.3, we prove some simple relations about the energy and its components. Start with the general expression for the energy, Eq. (2.39) and (2.40),

$$\epsilon = \min_{\rho,g} \left[ -g + uh(g,\rho) - \nu\rho \right]. \tag{2.98}$$

First take  $\rho \to 0$ . The second term reduces to  $u\left(1-\sqrt{1-g^2}\right)/2$ . Then let  $g \to 0$ , resulting in  $h \to 0$ . This yields  $\epsilon \to 0$  and therefore the exact  $\epsilon \leq 0$ . This process corresponds to choosing a trial wavefunction, and by Rayleigh-Ritz, the ground-state wavefunction will produce a value equal to or below the trial result.

In Hartree-Fock, g reduces to  $g_{\rm HF} = \sqrt{1 - \rho^2}$ . Then,

$$\epsilon^{\rm HF} = \min_{\rho} \epsilon(g_{\rm HF}(\rho), \rho) \ge \epsilon.$$
(2.99)

This shows that  $\epsilon_{c}^{trad} = \epsilon - \epsilon^{HF} \ge 0$ , as in Fig. 1.6. The minimization can be performed analytically though it involves solving the quartic polynomial

$$\frac{\rho}{\sqrt{1-\rho^2}} + u\,\rho - \nu = 0. \tag{2.100}$$

Similarly, a DFT exact exchange (EXX) calculation is defined by

$$\epsilon^{\text{EXX}} = \epsilon(g_{\text{HF}}(\rho_m), \rho_m) \ge \min_{\rho} \epsilon(g_{\text{HF}}(\rho), \rho)$$
(2.101)

where  $\rho_m$  is the minimizing density for the many-body problem. This yields  $\epsilon_{c}^{DFT} = \epsilon - \epsilon^{EXX}$ , and  $\epsilon_{c}^{trad} \ge \epsilon_{c}^{DFT}$ [104].

For the kinetic energy alone,  $t = -g(\rho_m)$ , and

$$t_{\rm s} = \min_{u \to 0,\rho} [-g(\rho)] = -\sqrt{1-\rho^2}.$$
(2.102)

This results in  $t_{\rm C} \ge 0$  since the KS occupation difference is defined to minimize the hopping energy. This combined with the above implies  $u_{\rm C} \le 0$ , as in Eq. (2.14).

For the adiabatic connection integrand, take a derivative of Eq. (2.46):

$$\frac{du_{\rm c}^{\lambda}}{d\lambda} = \frac{u_{\rm c}(\rho,\lambda)}{\lambda} + \lambda u \frac{\partial h}{\partial g} \frac{\partial g}{\partial \lambda}.$$
(2.103)

The first term is less than zero by definition but the second needs more unraveling. To begin, from Eq. (2.39),

$$\frac{\partial f}{\partial g} = -1 + u \frac{\partial h}{\partial g},\tag{2.104}$$

so, at the solution

$$\frac{\partial h}{\partial g} = \frac{1}{u}.\tag{2.105}$$

For  $\lambda$  near 1, Suppose  $g(\lambda) \simeq g(1) + (\lambda - 1)g'(1)$ , and expand  $\partial h / \partial g|_{g(\lambda)}$  in  $g(\lambda)$  around g(1):

$$\frac{\partial h}{\partial g}\Big|_{g(\lambda)} = \frac{\partial h}{\partial g}\Big|_{g(1)} + (\lambda - 1)g'(1)\left.\frac{\partial^2 h}{\partial g^2}\right|_{g(1)}$$
(2.106)

The first term on the left is  $1/(\lambda u) \approx (2-\lambda)/u$ . After some algebra,

$$\left. \frac{\partial g}{\partial \lambda} \right|_{\lambda=1} = -\left( u \left. \frac{\partial^2 h}{\partial g^2} \right|_{g(1)} \right)^{-1} \tag{2.107}$$

Since the hopping term of f is linear in g,  $\partial^2 f/\partial g^2 = \partial^2 h/\partial g^2$ . The energy is a minimum at g so  $\partial^2 f/\partial g^2 > 0$ , thus  $\partial g/\partial \lambda > 0$ . Together, this results in

$$dU_{\rm c}^{\lambda}/d\lambda < 0, \tag{2.108}$$

the adiabatic connection integrand is monotonically decreasing as seen in Fig. 2.11.

# 2.12 BALDA Derivation

For an infinite homogeneous Hubbard chain of density n = 1 + x, the energy per site (in units of 2t) is given approximately by

$$\tilde{\epsilon}^{\text{unif}} = u \, x \, \theta(x) + \alpha(x, \beta(U)) \tag{2.109}$$

where  $\theta(x)$  is the Heaviside function and

$$\alpha(x,\beta) = -\frac{\beta}{\pi} \sin(\pi (1 - |x|)/\beta) / \pi.$$
(2.110)

The function  $\beta(u)$  varies smoothly from 1 at u = 0 to 2 as  $u \to \infty[173]$ , and satisfies

$$\alpha(0,\beta) = -4 \int_0^\infty d\xi \, \frac{J_0(\xi) \, J_1(\xi)}{\xi \, [1 + \exp(u\,\xi))]} \tag{2.111}$$

This simple result is exact as  $u \to 0$ ,  $u \to \infty$  and at n = 1, and a good approximation (accurate to within a few percent) elsewhere[173] to the exact solution via Bethe ansatz[170]. In principle,  $\beta$  depends on n, and this dependence has been fit in later work[87]. Here, we use the simpler original version of a function of u only. In fact, the solution to Eq. (2.111) can be accurately fit (error below 1%) with a simple rational function,

$$\beta^{fit}(u) = \frac{2 + au + bu^2}{1 + cu + bu^2} \tag{2.112}$$

with coefficients  $a = 2c - \pi/4$  and  $b = (a - c)/\log 2$  chosen to recover the small-*u* behavior to first-order, and the large *u* behavior to first order in 1/u, and c = 1.197963 is fit to  $\beta(u)$ . This is useful for quick implementation of BALDA.

At u = 0, the hopping energy per site is just

$$\tilde{t}_{\rm s}^{\rm unif} = -\sin\left(\pi \left(1 - |x|\right)\right)/\pi,$$
(2.113)

while the Hartree-exchange energy per site is a simple local function:

$$\tilde{u}_{\rm HX}^{\rm unif} = u \, n^2 / 4.$$
 (2.114)

Thus the correlation energy per site is just

$$\tilde{\epsilon}_{\rm c}^{\rm unif} = \tilde{\epsilon}^{\rm unif} - \tilde{t}_{\rm s}^{\rm unif} - \tilde{u}_{\rm Hx}^{\rm unif}.$$
(2.115)
The BALDA approximation is then

$$\epsilon_{\rm xc}^{\rm BALDA} = \tilde{\epsilon}_{\rm xc}^{\rm unif}(n_1, U) + \tilde{\epsilon}_{\rm xc}^{\rm unif}(n_2, U).$$
(2.116)

Since the exchange is local, BALDA is exact for that contribution, and only correlation is approximated. Since  $n_{1,2} = 1 \mp \Delta n/2$ ,  $x = \mp \Delta n/2$  for sites 1 and 2 respectively. The BALDA HXC energy is then:

$$\epsilon_{\text{HXC}}^{\text{BALDA}} = 2\left(\alpha(\Delta n/2, U) - \alpha(\Delta n/2, 0)\right) + u|\Delta n|/2, \qquad (2.117)$$

and was inserted into the KS equations (Sec 1.4.3) to find the results of Sec 2.4.2.

#### 2.13 Mean-Field Derivation

The MF hamiltonian for the Hubbard dimer can be written in the number basis  $|1\sigma, 2\sigma\rangle$  as follows

$$\hat{H}_{\sigma}^{MF} = \begin{pmatrix} -\Delta v_{\sigma}^{\text{eff}}/2 & -t \\ -t & \Delta v_{\sigma}^{\text{eff}}/2 \end{pmatrix}$$
(2.118)

with  $\sigma = \pm 1$  for spin up and down respectively. Setting  $M = m_1 + m_2$  and  $N = n_1 + n_2$  as the total magnetization and particle number of the system, the eigenvalues are

$$e_{\pm,\sigma}^{MF} = \frac{U}{4} \left( N - \sigma M \right) \pm \frac{t_{\bar{\sigma}}^{\text{eff}}}{2},$$

$$t_{\sigma}^{\text{eff}} = 2t \sqrt{(\Delta v_{\sigma}^{\text{eff}}/2t)^{2} + 1},$$

$$\Delta v_{\sigma}^{\text{eff}} = \Delta v + \frac{U}{2} \left( \Delta n - \sigma \Delta m \right).$$
(2.119)

The total energy of the system is

$$E^{FM} = e_{-,\uparrow} + e_{+,\uparrow} - U_{\rm H}$$
(2.120)

$$E^{AFM} = e_{-,\uparrow} + e_{-,\downarrow} - U_{\mathrm{H}}, \qquad (2.121)$$

where the Hartree term is written as

$$U_{\rm H} = \frac{U}{4} \left( n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow} \right) = \frac{U}{8} \left( N^2 - M^2 + \Delta n^2 - \Delta m^2 \right).$$
(2.122)

Depending on whether  $E^{AFM}$  is larger or smaller than  $E^{FM}$ , the ground-state of the system may be ferromagnetic (N = 2, |M| = 2) or antiferromagnetic  $(N = 2, M = 0, |\Delta m| \ge 0)$ . The paramagnetic state is a specific case of the AFM state with  $\Delta m = 0$ . Explicitly, for the ferromagnetic state we have the eigenstate energies and self-consistency equations

$$\Delta n = \Delta m = -\Delta v / \sqrt{4t^2 + \Delta v^2} \tag{2.123}$$

$$e_{\mp,\uparrow} = \mp \sqrt{4t^2 + \Delta v^2}/2 \tag{2.124}$$

On the other hand, the M = 0 state ( $|\Delta m| > 0$  is AFM,  $\Delta m = 0$  is PM) corresponds to the eigenvalues,

$$e_{-,\uparrow} = (U - t_{\downarrow}^{\text{eff}})/2, \quad e_{-,\downarrow} = (U - t_{\uparrow}^{\text{eff}})/2,$$
(2.125)

and self-consistency equations

$$\Delta n = -\sum_{\sigma} \frac{\Delta v_{\sigma}^{\text{eff}}}{t_{\sigma}^{\text{eff}}}, \quad \Delta m = -\sum_{\sigma} \sigma \frac{\Delta v_{\sigma}^{\text{eff}}}{t_{\sigma}^{\text{eff}}}, \quad (2.126)$$

and the expressions for  $\Delta v_{\sigma}^{\text{eff}}$  and  $t_{\sigma}^{\text{eff}}$  are given in Eq. (2.119). The self-consistency procedure needs to be carried out numerically in this case.

The total energy can also be written as

$$E^{AFM,PM} = \frac{U}{2} \left( 1 - \frac{\Delta n^2 - \Delta m^2}{4} \right) - \frac{t_{\uparrow}^{\text{eff}} + t_{\downarrow}^{\text{eff}}}{2}.$$
 (2.127)

In the PM case, the expressions can be simplified to give

$$\Delta n = \frac{-2\,\Delta v - U\,\Delta n}{\sqrt{\left(\Delta v + U\Delta n/2\right)^2 + 4\,t^2}}\tag{2.128}$$

for the occupations and

$$E^{PM} = \frac{U}{2} \left( 1 - \left(\frac{\Delta n}{2}\right)^2 \right) - \sqrt{\left(\Delta v + \frac{U}{2}\Delta n\right)^2 + 4t^2}.$$
(2.129)

#### 2.14 Relation between Hubbard model and real-space

To show how SOFT and real-space DFT are connected, begin with the one-electron dimer,  $H_2^+$ , with the protons separated by R. Use a basis of the exact atomic 1s orbitals, one on each site. This is a minimal basis in quantum chemistry. Then

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{1}{r} - \frac{1}{|\mathbf{r} - R\mathbf{z}|}$$
(2.130)

where the bond is along the z-axis. Then the matrix elements of  $\hat{h}$  in the basis set of atomic orbitals are:

$$v_1 = v_2 = \epsilon_A + j(R), \quad t = s(R) \epsilon_A + k(R)$$
(2.131)

where  $\epsilon_A$  is the atomic energy (one Rydberg here) and

$$s(R) = \langle A|B \rangle = e^{-R}(1+R+R^{2}/3)$$
  

$$j(R) = \langle A|\frac{1}{|\mathbf{r}-R\mathbf{z}|}|A \rangle = -(1/R - e^{-2R}(1+1/R))$$
  

$$k(R) = \langle A|\frac{1}{|\mathbf{r}-R\mathbf{z}|}|B \rangle = -e^{-R}(1+R),$$
(2.132)

yielding the textbook eigenvalues (for the generalized eigenvalue problem):

$$\epsilon_{\pm} = \epsilon_A + (j \pm k)/(1 \pm s). \tag{2.133}$$

Of course, the orbitals can always be symmetrically orthogonalized in advance[183], in which case

$$v_{\text{ortho}} = \epsilon_A + (-j + ks)/(s^2 - 1),$$
 (2.134)

$$t_{\rm ortho} = -(sj-k)/(s^2-1).$$
 (2.135)

Although physics textbooks often set the overlap to zero, this is inconsistent, as the size of the overlap is comparable to k(R), say. Setting the on-site potential to zero (but re-adding its value to the energy) and using  $t_{\text{ortho}}$ , makes the solution Eq. (1.29) of the text produce the exact electronic energy in this minimal basis. But quantum chemistry textbooks note that this calculation is horribly inaccurate, yielding a bond-length of 2.5 Bohr and a well depth of 2.75 eV. Inclusion of a  $p_z$  orbital on each site, and allowing the lengthscale of each orbital to vary, produces almost exact results of 2.00 Bohr and 4.76 eV. Thus, even in this simple case, more than one orbital per site is needed to converge to the real-space limit.

Next we consider repeating the minimal-basis calculation with one nuclear charge replaced by value Z. This yields an asymmetric tight-binding problem for which the orbitals can be orthogonalized and values of  $\Delta v$  and t deduced as a function of R. But note that changing Z will change both  $\Delta v$  and t simultaneously, unlike our asymmetric SOFT dimer, where only  $\Delta v$  changes. In real-space DFT, the kinetic energy functional remains the same,  $T_{\rm s}^{\rm W}$  of Eq. (1.20), for all R and every Z.

The situation is even more complicated for  $H_2$  and its asymmetric variants. Clearly U becomes a function of R, but there are also several independent off-diagonal matrix elements that are R dependent. Again, all change as a function of both R and Z, but none of this occurs in SOFT. In real-space DFT,  $T_s$  is still the von Weisacker functional,  $U_H$  is always the Hartree energy, and the exact  $E_{xc}[n]$  is independent of R and Z, but always produces the exact energy when iterated in the KS equations. In Ref. [50], they take a different approach by including a nearest-neighbor Hubbard U.

## Chapter 3

# Exact Thermal Density Functional Theory for a Model System: Correlation components and accuracy of the zero-temperature exchange-correlation approximation

This chapter, in its entirety, is from Ref. [276]. I am the first, and lead, author. I contributed writing, proof reading, ideas, and all figures and formulas. My co-authors were Aurora Pribram-Jones (second) and Kieron Burke (third).

#### 3.1 Abstract

Thermal density functional theory (DFT) calculations often use the Mermin-Kohn-Sham (MKS) scheme, but employ ground-state approximations to the exchange-correlation (XC) free energy. In the simplest solvable non-trivial model, an asymmetric Hubbard dimer, we calculate the exact many-body energies, the exact Mermin-Kohn-Sham functionals for this system, and extract the exact XC free energy. For moderate temperatures and weak correlation, we find this approximation to be excellent. We extract various exact free energy correlation components and the exact adiabatic connection formula.

#### 3.2 Introduction

Recent decades have seen enormous advances in the use of DFT calculations[124] of warm dense matter, a highly energetic phase of matter that shares properties of solids and plasmas[99]. Materials under the extreme temperatures and pressures necessary to generate WDM can be found in astronomical bodies, within inertial confinement fusion capsules, and during explosions and shock physics experiments[205]. These calculations are used in the description of planetary cores[192, 182, 143], for the development of experimental standards[142, 145], for prediction of material properties[125, 141, 247], and in tandem with experiments pushing the boundaries of accessible conditions[277]. Because of this growing interest in WDM and thermal systems in general, we seek to better understand thermal DFT using exactly solvable models.

In almost all thermal DFT calculations, a crucial approximation is made: the exchangecorrelation (XC) free energy in principle depends on the temperature [65, 226], but in practice is approximated by a standard ground-state approximation. Most calculations are for extended systems, and usually use a generalized gradient approximation, such as PBE [219]. These Mermin-Kohn-Sham (MKS)[194, 148] calculations predict several key properties, such as the free energy and density for a given distribution of the nuclei, and any properties that can be extracted from these, such as equations of state of materials and Hugoniot shock curves[18]. If the exact temperature-dependent XC free energy were known, such properties would be exact[235]. In some cases, response properties are extracted from the thermal KS orbitals[125], which involves a further approximation. Although no one has shown that the lack of thermal XC corrections is a fatal flaw in a given calculation, the pervasive use of this uncontrolled approximation is an underlying concern[136] that warrants investigation.

The crucial step that made zero-temperature DFT sufficiently accurate for chemical purposes was the introduction and testing of generalized gradient approximations about 20 years ago[74, 131]. By careful comparison with highly accurate benchmarks produced either by direct solution of the Schrödinger equation or from experiments with well-controlled errors, the general level of accuracy and reliability of such approximations was well documented[209, 325, 250]. With improved binding energies came the ability to determine molecular geometries for complex systems. A similar transformation is occurring in materials science today[132].

But no such database or highly accurate results exist for thermal systems. It is hard to imagine experimental measurements of energies with the required accuracy under the relevant conditions, but calculations should be possible. Various Monte Carlo methods have been developed to study WDM in extended systems[82, 262, 68, 32, 263, 196, 105]. There have been multiple results from combining Monte Carlo and DFT for such cases[195, 305, 69, 70]. But none of these could approach the accuracy needed to invert the Kohn-Sham equations or extract highly accurate correlation energy components. For such purposes, finite molecular systems are often the only ones where sufficient accuracy can be practically achieved.

The prototype case for electronic structure and chemical binding is the simplest molecule,  $H_2$ , and its binding energy curve at zero temperature is simple to calculate, to study the

success of GGA's near equilibrium[213] and their failures as the bond is stretched[21]. But even this system is too difficult to calculate when the electrons are heated: Only the mean number of electrons is fixed, and *all* possible electron numbers must be included in evaluating the grand canonical partition function.

Here we circumvent this difficulty with the simplest representation of a diatomic molecule. In a minimal basis set (one function per atom), the full Hamiltonian is simply a 2-site Hubbard model to which lattice DFT applies[47]. The severe truncation of the Hilbert space makes exact solution possible in thermal DFT. By inverting the MKS equations, we perform the first exact calculations of correlation free energies and their individual components for an inhomogeneous system, an admittedly crude representation of a chemical bond. By performing self-consistent calculations with the exact ground-state exchange-correlation energy functional for this system, we show that the ground-state approximation works well, even becoming relatively exact in the high-temperature limit. We also illustrate several exact conditions on the correlation energy components. While such a simplified model cannot be used to test the accuracy of standard approximations applied in the continuum, such as the local density or generalized gradient approximations, it does provide a first glimpse at the behaviors of correlation energy components as a function of temperature, a subject about which almost nothing is known outside of the uniform electron gas.

This paper is laid out as follows. In section 3.3.1 we review the ground-state of the asymmetric Hubbard model. In section 3.3.2 we briefly outline thermal DFT. Next, in section 3.4 we write out the analytic expressions for the MB and MKS system. Lastly in section 3.6 we discuss some results using the ground-state XC functional.

#### 3.3 Background

#### 3.3.1 Ground-state Hubbard Dimer

Ref. [47] is an exhaustive review of the asymmetric Hubbard dimer for the ground-state case. In this section we briefly review the Hamiltonian and the most salient points. The Hamiltonian is typically written as

$$\hat{H} = -t \sum_{\sigma} \left( \hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + h.c. \right) + \sum_{i} \left( U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + v_i \hat{n}_i \right)$$
(3.1)

where  $\hat{c}_{i\sigma}^{\dagger}(\hat{c}_{i\sigma})$  are electron creation (annihilation) operators and  $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^{\dagger}\hat{c}_{i\sigma}$  are number operators, t is the strength of electron hopping between sites, U the Coulomb repulsion when two electrons are on the same site, and  $v_i$  is the external potential on each site. Without loss of generality, we choose  $v_1 + v_2 = 0$ ,  $\Delta v = v_2 - v_1$ , and denote the occupation difference  $\Delta n = n_2 - n_1$ . All terms in Eq. (3.1) have analogs in an *ab initio* Hamiltonian[47]. The hopping term plays a role logically analogous to the kinetic energy, the Coulomb repulsion is now ultra-short ranged but otherwise the same, and the on-site potential serves as the one-body potential. Most importantly the asymmetry is necessary to perform our analysis. Otherwise the occupation difference would vanish and we could not learn about the function(al) behavior. We choose units where 2t = 1 and we vary U and  $\Delta v$ .

The key observation is that repulsion and asymmetry directly compete. When U dominates over  $\Delta v$  the density,  $\Delta n$ , tends towards 0, while in the opposite limit  $\Delta n$  tends towards 2. Additionally  $U < \Delta v$  is the weakly-correlated regime while  $U > \Delta v$  is strongly-correlated. The difference between weak and strong correlation is very well characterized in the symmetric case, where an expansion in powers of U converges absolutely up to U = 4t and diverges beyond that; similarly, an expansion in 1/U converges absolutely only for U > 4t. Here, we restrict our attention to the weakly correlated regime in order to best mimic typical conditions of thermal DFT calculations.

#### 3.3.2 Thermal Density Functional Theory

In this section we will briefly review the basics of thermal DFT[194]. For a more exhaustive treatment see Ref. [235]. We begin with an ensemble in thermal equilibrium connected to a bath at temperature  $\tau$ . The free energy may be found from:

$$A = \min_{n} \left( F[n] + \int d^3 r \, n(\mathbf{r}) v(\mathbf{r}) \right)$$
(3.2)

where  $v(\mathbf{r})$  is the one-body potential,  $\mu$  is the chemical potential, and the minimization is over all positive densities with finite kinetic energy. The Mermin functional is

$$F[n] = \min_{\Gamma \to n} \operatorname{Tr} \left\{ (\hat{T} + \hat{V}_{ee} - \tau \hat{S}) \Gamma \right\}$$
(3.3)

where  $\hat{T}$  is the kinetic energy operator,  $\hat{V}_{ee}$  the electron-electron repulsion operator,  $\hat{S}$  the entropy operator, and the minimization is over all statistical density matrices with density  $n(\mathbf{r})$ . The average particle number is determined uniquely by  $\mu$ . Then one can construct the MKS equations[235]

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm s}^{\tau}[n](\mathbf{r})\right\}\phi_i^{\tau}(\mathbf{r}) = \epsilon_i^{\tau}\phi_i^{\tau}(\mathbf{r}),\tag{3.4}$$

where

$$v_{\rm s}^{\tau}[n](\mathbf{r}) = v(\mathbf{r}) + v_{\rm H}[n](\mathbf{r}) + v_{\rm xc}^{\tau}[n](\mathbf{r}), \qquad (3.5)$$

and  $v_{\rm H}[n](\mathbf{r})$  is just the usual Hartree potential[236] and

$$v_{\rm xc}^{\tau}[n](\mathbf{r}) = \frac{\delta A_{\rm xc}^{\tau}[n](\mathbf{r})}{\delta n(\mathbf{r})}.$$
(3.6)

The density is the sum over all orbitals,

$$n^{\tau}(\mathbf{r}) = \sum_{i} f_{i}^{\tau} |\phi_{i}^{\tau}(\mathbf{r})|^{2}, \qquad (3.7)$$

where  $f_i^{\tau} = (1 + e^{(\epsilon_i^{\tau} - \mu)/\tau})^{-1}$  are their Fermi occupations. Finally, once self-consistency has been achieved, the free energy of the interacting system is reconstructed as:

$$A^{\tau} = A_{\rm s} - U_{\rm H}[n] + A_{\rm xc}^{\tau}[n] - \int d^3 r \, n(\boldsymbol{r}) v_{\rm xc}^{\tau}[n](\boldsymbol{r}).$$
(3.8)

where  $A_{\rm s}$  is the Kohn-Sham free energy.

If the exact XC free energy density functional (confusingly, often referred to as simply the XC energy) were known and used in the MKS equations, then their solution produces the exact density and free energy (and any other quantity that can be directly extracted from them). However, there are very few cases where we have access to the exact  $v_{\rm xc}(\mathbf{r})$ . All practical MKS calculations use some approximation, and most use a simple ground-state approximation. To distinguish different levels of approximation, we write

$$A_{\rm xc}^{\tau}[n] = E_{\rm xc}[n] + \Delta A_{\rm xc}^{\tau}[n], \qquad (3.9)$$

where  $E_{\rm xc}[n]$  is the *exact* ground-state XC energy, and  $\Delta A_{\rm xc}^{\tau}[n]$  is the difference in XC free energy from its ground-state value. We call this the thermal contribution to  $A_{\rm xc}^{\tau}$ . Then, the *zero-temperature* approximation (ZTA) is where we ignore the thermal contribution to  $A_{\rm xc}^{\tau}$ . i.e.,

$$A_{\rm xc}^{\rm ZTA,\tau}[n] = E_{\rm xc}[n], \qquad (3.10)$$

i.e., we neglect thermal effects, but use the *exact* ground-state XC functional. This allows us to separate thermal from non-thermal XC effects in a completely well-defined manner. Of course, in practice, it is only in simple model systems that one has access to the exact ground-state XC functional.

In this language, most modern QMD calculations can be thought to have made two distinct approximations. The first is to make ZTA and ignore thermal contributions. The second is to use some common approximation for  $E_{\rm xc}[n]$  within ZTA. On the other hand, calculations that use, e.g., thermal LDA, go beyond ZTA, but approximate both the ground-state and thermal contributions to  $A_{\rm xc}^{\tau}[n]$ .

#### 3.4 Analytic results

We apply this technology to the asymmetric Hubbard dimer. The DFT version of a lattice model is called site-occupation functional theory (SOFT)[261] and has the distinct advantage of a truncated Hilbert space. We can compute every energy for every particle number and construct exact thermodynamic and DFT components. The truncation makes the calculation feasible. We expect that, for very high temperatures, the results will not be representative of realistic systems with infinite Hilbert spaces.

#### 3.4.1 Exact many-body solution

To begin, we calculate the finite-temperature many-body energy and density for the Hubbard dimer. Begin with the grand canonical partition function

$$Z_{gc} = \sum_{i,N} e^{(\mu N - E_i(N))/\tau}$$
(3.11)

where  $E_i(N)$  is the *i*-th energy level of the Hamiltonian with N particles. The energies for 0 through 4 particles are calculated explicitly, yielding the exact partition function. From that we construct the grand potential, its derivatives, and the free energy in the usual fashion[25]:

$$\Omega = -\tau \log(Z_{gc}), \qquad S = \frac{\partial \Omega}{\partial \tau} \Big|_{\mu}, \qquad (3.12)$$

$$N = \left. \frac{\partial \Omega}{\partial \mu} \right|_{\tau}, \qquad A = \mu N - \Omega.$$
(3.13)

We choose half-filling,  $\langle N \rangle = 2$ , which means  $\mu = U/2$  (and  $\mu = 0$  for the MKS system)[269]. With the partition function and Boltzmann factors we can calculate ensemble averages:,

$$X = Z_{gc}^{-1} \sum_{i,N} \langle \hat{X} \rangle_{i,N} e^{(\mu N - E_i(N))/\tau},$$
(3.14)

where  $\langle \hat{X} \rangle_{i,N}$  is the expectation value of a general operator  $\hat{X}$  of the *i*-th state for N particles. Using Eq. (3.14) we compute the exact energy components for the dimer. To do this, we calculate the expectation values for each particle number of the quantities of interest such as T,  $V_{ee}$ , and  $\Delta n$ . We list in the appendix all the expectation values for the total energies, energy components, coefficients of the eigenstates, and densities for all the particle numbers.

In Fig. 3.1 and 3.2, we plot the free energy and entropy as a function of temperature for several different values of  $\Delta v$ . For the free energy we include curves for the zero-temperature



Figure 3.1: Free energy for different values of  $\Delta v$ . Solid lines are exact, dashed lines are the zero-temperature XC approximation (ZTA), evaluated on the self-consistent thermal density.

approximation and for the entropy we include the self-consistent Kohn-Sham entropy (both to be discussed later). In both cases we pick a system, i.e. fix  $\Delta v$  and U and see what happens as we heat it up. For the free energy, the values at  $\tau = 0$  recover the groundstate energies reported in Ref. [47]. Increasing temperature results in a decrease in free energy primarily due to the entropic term,  $-\tau S$ , as expected. At small temperatures there is minimal effect as seen in Fig. 3.2 where the entropy is small and further multiplied by a  $\tau \ll 1$  when calculating A. However, once the system is sufficiently warm the entropy plays a much larger role. In contrast, increasing  $\Delta v$  lowers the entropy since the asymmetry restricts the motion of electrons. Lastly, the entropy approaches a maximum value of log(16) for higher temperatures where 16 is the number of states in our grand canonical ensemble.



Figure 3.2: Exact entropy (solid) and self-consistent Kohn-Sham entropy (dashed) for different values of  $\Delta v$ . All curves approach  $4 \log 2$ .

#### 3.4.2 Inversion and correlation components

Next, we construct the exact KS potential as well as various energy components using the MKS approach. To begin we construct the exact occupation difference  $\Delta n$  from Eq. (3.14). We plot the result in Fig. 3.3 for fixed U but against  $\Delta v$  and vary  $\tau$ . In this figure we also plot the ZTA result which will be discussed later. Increasing the temperature pushes the electrons apart, akin to repulsion. As the system heats up,  $\Delta n$  becomes closer to 0 as both electrons sit on separate sites even when  $\Delta v$  is large.

To construct the exact MKS potential, we first give formulas for non-interacting electrons (U = 0, a.k.a. tight-binding).

The grand canonical partition function collapses to the product

$$Z_{gc} = \prod_{i} \left( 1 + e^{\beta(\mu - \epsilon_i)} \right) \tag{3.15}$$



Figure 3.3: Densities as a function of temperature for the system of Fig. 3.1. Solid lines are exact, dashed lines are self-consistent KS using the ZTA.

where  $\epsilon_i$  is the single-particle orbital energy. Eq. (3.12) and (3.13) can then be used. The entropy can also be explicitly given in terms of Fermi factors,

$$S_{\rm s} = -\sum_{i} f_i \log(f_i) + (1 - f_i) \log(1 - f_i).$$
(3.16)

where  $f_i = (1 + e^{\beta(\epsilon_i - \mu)})^{-1}$ . The Kohn-Sham entropy is calculated in Fig. 3.2 where the Fermi factors are calculated from self-consistently solving the MKS equations (see below).

To construct the MKS system for the Hubbard dimer within SOFT, we simply repeat the exact calculation with U = 0, i.e., a tight-binding dimer. We find:

$$\Delta n = -2\sin\phi\tanh\alpha\tag{3.17}$$

where  $\alpha = (4\tau \cos \phi)^{-1}$ ,  $\sin \phi = x/\sqrt{1+x^2}$ ,  $\tau$  is in units of 2 t, and  $x = \Delta v_s/2 t$ . To perform the inversion for a given density from the many-body problem, we perform a binary search at the given temperature on Eq. (3.17) to find  $\Delta v_s(\Delta n)$ , the exact KS site-potential difference that yields the required occupation density. The exact  $\Delta v_{xc}$  for the given  $\Delta n$  is then found by subtracting off the other potential contributions, i.e.,  $\Delta v$  and  $\Delta v_{\rm H}$ . The Hartree energy (in the standard DFT definition[236]) for this model is

$$U_{\rm H}(\Delta n) = U\left(1 + \frac{\Delta n^2}{4}\right),\tag{3.18}$$

and the Hartree potential is simply

$$v_{\rm H}(\Delta n) = U\Delta n/2 \tag{3.19}$$

and both functionals are temperature-independent. For two unpolarized electrons,  $E_{\rm x} = -U_{\rm H}/2$  at all temperatures[235], and so is also independent of  $\tau$ . The thermal MKS hopping energy is just that of this tight-binding problem:

$$T_{\rm s}^{\tau}(\Delta n)/(2t) = \Delta n/x(\Delta n) \tag{3.20}$$

and the tight-binding MKS entropy is

$$S_{\rm s}^{\tau}(\Delta n) = 4\log\left\{2\cosh\alpha\right\} - 4\alpha\tanh\alpha\tag{3.21}$$

With these simple results, we can now extract the correlation free energy for this problem as

$$A_{\rm C}^{\tau} = (T^{\tau} - T_{\rm s}^{\tau}) - \tau (S^{\tau} - S_{\rm s}^{\tau}) + (V_{\rm ee}^{\tau} - U_{\rm HX})$$
(3.22)

where  $T^{\tau}$ ,  $S^{\tau}$ , and  $V_{ee}^{\tau}$  are calculated from the many-body problem via eqs. (3.14), (3.12), and (3.14). Since  $A_{\rm x}^{\tau}$  is trivial and has no thermal contribution for our system,  $A_{\rm c}^{\tau}$  is what we study, and we know of no other exact calculation of this quantity for a finite system.

#### 3.5 Numerical results

Performing the inversion to explicitly analyze the MKS potential shows how the features of interactions are built into the non-interacting potential [286, 53, 203]. The crux of the MKS approach is that we capture the effects of interactions through the modified external potential  $\Delta v_{\rm s}$ . For example, interaction causes the dimer occupations to be more symmetric, thus  $\Delta v_{\rm s} < \Delta v$  for a MB system with U > 0. Similarly, for any given density both potentials,  $\Delta v$  and  $\Delta v_{\rm s}$ , increase with temperature to counteract thermal effects pushing the system towards symmetry. But even in this simple model, there is a vast parameter space to be explored as, choosing 2t = 1, we can vary U,  $\Delta v$ ,  $\tau$ , and  $\langle N \rangle$ . We focus on  $\langle N \rangle = 2$ , and the weakly-correlated and low temperature corner of our parameter space:  $U, \tau < 1$ . In particular, we avoid warming our model so much that properties are strongly influenced by the very limited Hilbert space. Specifically, we check that the system is not too hot by computing the occupations of all the states in the grand canonical ensemble. We test this in the symmetric case because it is most prone to overheating since asymmetry competes against thermal effects. For U = 1, uniform occupation of all states does not occur until  $\tau \gg 8$  and appreciable uniformity does not start to arise until  $\tau \approx 4$ . Thus our results are not limited by the top of our Hilbert space.

We can calculate all the individual contributions to the correlation free energy by subtracting MKS quantities from their physical counterparts. These are the energy differences appearing in Eq. (3.22):

$$T_{\rm c}^{\tau} = T^{\tau} - T_{\rm s}^{\tau}, \quad S_{\rm c}^{\tau} = S^{\tau} - S_{\rm s}^{\tau}, \quad U_{\rm c}^{\tau} = V_{\rm ee}^{\tau} - U_{\rm Hx}.$$
 (3.23)

The kentropic correlation is  $K_{\rm C} = T_{\rm C} - \tau S_{\rm C}$  and plays a key role in thermal DFT[228]. In Fig. 3.4, we plot the exact correlation free energy functional, the sum of kinetic and potential correlation functional, and lastly the entropic correlation functional all for various



Figure 3.4: Panel 1: Correlation free energy functional for various temperatures. Panel 2: Sum of kinetic and potential energy functional for various temperatures. Panel 3: Entropic correlation functional for various temperatures.

temperatures. By fixing U and  $\tau$  and plotting versus  $\Delta n$ , we analyze the correlation as a density functional, i.e. we are no longer looking at a fixed system and instead are looking at the underlying structure of how thermal DFT behaves.

We see that the correlation free energy is always negative, the kentropic contribution is always positive (not shown), and the potential contribution is always negative. These are consistent with conditions on the correlation[228]. This is the first exact investigation of those inequalities. The correlation free energy,  $A_{\rm C}^{\tau}$ , always decreases with temperature at U = 1, even though the components do not behave that way at small temperature.  $T_{\rm C} + U_{\rm C}$  and  $\tau S_{\rm C}$  also decrease for all densities at larger temperature just like  $A_{\rm C}$ . In this regime, thermal effects dominate over interactions, resulting in the interacting system and the non-interacting system having similar energy components and thus relatively smaller correlation. But for small temperature, i.e.  $\tau < 1$  when U = 1, the MKS quantities are furthest from the exact system since neither effect dominates and this results in an even larger difference between the two systems than at  $\tau = 0$ . Overall we see the same behavior as in the ground-state case[47] – correlation decreases as our system becomes more asymmetric. If the electrons are completely pinned on the lower site then there is no motion, the interaction is completely described by the Hartree, and there is only one entropic conformation.



Figure 3.5: Adiabatic connection integrand for the symmetric dimer at several different temperatures.

Next, we consider the adiabatic connection formula [160, 107] that has proven useful in studying and improving density functional approximations. The ground-state version was calculated for the Hubbard dimer in Fig. 21 of Ref. [47]. An alternative version, called the thermal connection formula, was derived in Ref. [232], but that flavor relies on relating the coupling-constant to coordinate scaling. Such a procedure applies to continuum models, but



Figure 3.6: Same as Fig. 3.5, except  $\Delta n = 1$ .

not lattices. So we use the traditional version here, applied to finite temperature [228]:

$$A_{\rm C}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda} U_{\rm C}^{\tau,\lambda}[n] \tag{3.24}$$

where  $\lambda$  is a coupling constant inserted in front of  $\hat{V}_{ee}$  in the Hamiltonian, but (unlike regular many-body theory) the density is held fixed during the variation. Here  $U_{c}^{\tau,\lambda}$  is the potential correlation energy at coupling constant  $\lambda$ , which, for our model, is obtained by replacing Uwith  $\lambda U$ . In Fig. 3.5, for the symmetric case, turning on temperature clearly reduces both the magnitude of the correlation and the degree of static correlation, as judged by the initial slope of the curves. Fig. 3.6 shows this result remains true beyond the symmetric case.

In Fig. 3.7, we repeat the  $A_c^{\tau}$  curves of Fig. 3.4 but now for fixed  $\Delta n = 0$  and increasing U. We start with the U = 1 from earlier and increase into the strongly correlated regime. The curves show a minimum at about  $\tau = 0.25$ , particularly in U = 3 and 4. Thus the derivative with respect to temperature can be negative, and this does not happen even if we look closely at U = 1. Thus the correlation free energy is not generally monotonically



Figure 3.7: Correlation free energy for the symmetric case with increasing values of U ranging from weak to strong correlation.

decreasing in magnitude and the correlation energy is not bounded by the  $\tau = 0$  value.

#### 3.6 Zero-temperature approximation

In this section, we explore the effects of making the zero-temperature approximation (ZTA), in which thermal contributions are ignored (Eq. (3.10)). We use the (essentially) exact parametrization of the ground-state XC energy of the Hubbard dimer of Eq. (108) of Ref. [47]. This substitution is made in the calculation of the total free energy and in the MKS equations via the calculation of the XC potential, Eq. (3.6). We return to Fig. 3.1, where we also plot the free energy in the ZTA by replacing  $A_{\rm c}^{\tau}(\Delta n)$  with  $E_{\rm c}(\Delta n)$ , evaluated on the self-consistent  $\Delta n$ . We see that the error of ZTA is extremely small for  $\tau \leq 0.5$ . Moreover, trends are very well reproduced by the ZTA values, and fractional errors shrink for large  $\tau$ . This suggests that free energies in such calculations may be reliable depending, of course, on the precision needed in a given calculation. The errors grow most rapidly with  $\tau$  when the dimer is asymmetric. Thermal effects push the electrons apart, making the density more symmetric, in direct competition with  $\Delta v$ . For larger  $\Delta n$ , there is a larger error in ignoring thermal effects. Note that since we have only two electrons, our model is a worst case scenario. In many simulations, there are more valence electrons per site, and (exchange-)correlation components are a much smaller fraction of the total energy. In a realistic DFT calculation, the error made by approximating the ground-state functional would likely be much larger than the error due to the lack of temperature-dependence[275].



Figure 3.8: Error in ZTA densities of Fig. 3.3, density from self-consistent MKS subtracted from exact density.

However, this is only part of the story. Real thermal DFT calculations are performed selfconsistently within ZTA. Then both the density and MKS orbitals are often used to calculate response properties (usually on the MKS orbitals)[271, 272, 241, 52, 64, 239, 62, 240, 229]. In Fig. 3.3, we compare the self-consistent density obtained using Eq. (3.4) through Eq. (3.7). In Fig. 3.8, we plot the differences. We see that the maximum errors in the density are small. At first they grow with small temperature but quickly start to lessen as temperature increases which will be further explained below. As  $\Delta v$  gets large the error goes to zero since the asymmetry dominates over thermal effects.

In terms of Fig. 3.4, the ZTA consists of approximating each of the curves by the cor-

responding black one. Because all correlation components tend to vanish with increasing temperature, while the total free energy grows in magnitude, the small error made in the ZTA becomes less relevant with increasing temperature. Specifically, we can analyze the symmetric case where correlation effects are at their strongest. At  $\tau = 0$  correlation is about 20% of the total energy but when the system is at  $\tau = 1$  correlation is roughly 2.5% of the total free energy. More importantly this is due to the total energy magnitude going up by a factor of 5 and the correlation only decreasing by a factor of 2. This explains the small errors in the ZTA free energies of Fig. 3.1 and the behavior of the self-consistent ZTA densities of Fig. 3.8. Note that the temperatures need not be so high as to make the density uniform (i.e., symmetric). Fig. 3.3 shows that, even for the temperature at which density differences can be largest ( $\tau = 1$ ), the density difference can remain substantial as the temperature increases, if the inhomogeneity ( $\Delta v$ ) is large enough.

#### 3.7 Conclusions

In summary, we have solved the simplest possible non-trivial system at finite temperature exactly, both for the many-body case and within MKS density functional theory. We have produced the first exact plots of MKS quantities and the ZTA approximation for a finite system (albeit one with a limited Hilbert space). When the system is weakly correlated system at low to moderate temperatures, the neglect of thermal contributions to the exchangecorrelation functional has relatively little effect on the calculated free energies and even less on the self-consistent densities. Present limitations of ground-state approximations, such as their inability to treat strongly correlated systems, are likely the greatest source of error in these calculations. Future work will explore other quantities of interest within thermal DFT and will analyze the ZTA more deeply.

#### 3.8 Energies and Densities for all States

Here we list all the total energies, energy components, and density components for all particle numbers so that all the relevant ensemble averages of Eq. (3.14) can be reconstructed. We begin with the energies

$$E_{i}(4-N) = (2-N)U + E_{i}(N) \qquad N = 0-4,$$

$$E_{0}(0) = 0,$$

$$E_{0,1}(1) = \pm \sqrt{(2t)^{2} + \Delta v^{2}}/2,$$

$$E_{i}(2) = \frac{2U}{3} - \frac{2r}{3}\cos(\theta + \frac{2\pi}{3}(i+1)) \qquad i = 0, 1, 2,$$

$$E_{i}(2) = 0, \qquad i = 3, 4, 5,$$

where

$$\begin{aligned} r &= \sqrt{3((2\,t)^2 + \Delta v^2) + U^2}, \\ \theta &= \frac{1}{3}\arccos\left[\frac{9U(\Delta v^2 - 2\,t^2) - U^3}{(3((2\,t)^2 + \Delta v^2) + U^2)^{3/2}}\right]. \end{aligned}$$

 $E_1(2)$  and  $E_2(2)$  are both positive and should be ordered 4 and 5 instead. However the three triplets, i.e. the three zero-energy states, give only zero values in the later expectation values, so for notational convenience we order the non-zero 2-particle states 0, 1, and 2 instead of 0, 4, and 5. These energies were used to construct  $Z_{gc}$  in Eq. (3.11) of the main text.

Next are the expectation values needed to construct the three different ensemble averages of

interest, T, V<sub>ee</sub>, and  $\Delta n$  (V<sub>ext</sub> is unnecessary since it is trivially  $\Delta v \Delta n/2$ ):

$$T_{i}(4-N) = T_{i}(n) \qquad N = 0-4$$
  

$$T_{0,1}(1) = \mp \frac{t}{\sqrt{(2t)^{2} + \Delta v^{2}}},$$
  

$$T_{i}(2) = (\beta_{i}^{+} + \beta_{i}^{-})^{2}/E_{i}(2) \qquad i = 0, 1, 2,$$

$$V_{\text{ee,i}}(4-N) = (2-N)U + V_{\text{ee,i}}(N) \qquad N = 0-4,$$
  
$$V_{\text{ee,0,1}}(1) = 0,$$
  
$$V_{\text{ee,i}}(2) = U((\beta_i^+)^2 + (\beta_i^-)^2) \qquad i = 0, 1, 2,$$

$$\Delta n_i(4-N) = \Delta n_i(N) \qquad N = 0-4,$$
  

$$\Delta n_{0,1}(1) = \mp \frac{2\Delta v}{\sqrt{(2t)^2 + \Delta v^2}},$$
  

$$\Delta n_i(2) = 2((\beta_i^-)^2 - (\beta_i^+)^2) \qquad i = 0, 1, 2,$$

and all the 0-particle terms are 0. The  $\beta^{\pm}$ 's are from the N = 2 wavefunction:

$$|\Psi_i(N)\rangle = \alpha_i(N)(|12\rangle + |21\rangle) + \beta_i^+(N)|11\rangle + \beta_i^-(N)|22\rangle$$

with

$$\begin{aligned} \alpha_i &= \frac{2t(E_i(2) - U)}{c_i E_i(2)}, \quad \beta_i^{\pm} = \frac{U - E_i(2) \pm \Delta v}{c_i}, \\ c_i &= \sqrt{2(\Delta v^2 + (E_i(2) - U)^2(1 + (2t/E_i(2))^2))}. \end{aligned}$$

The ket  $|ij\rangle$  signifies an electron at site *i* and site *j*. These expectation values were used with Eq. (3.14) to construct the densities and energy components shown in the figures.

## Chapter 4

## Exact conditions on the temperature dependence of density functionals

This chapter is entirely from Ref. [36]. I am the second author and contributed figures, equation verification, proof reading, and some writing. My co-authors are Kieron Burke (first), Paul Grabowski (third), and Aurora Pribram-Jones (fourth).

#### 4.1 Abstract

Universal exact conditions guided the construction of most ground-state density functional approximations in use today. We derive the relation between the entropy and Mermin free energy density functionals for thermal density functional theory. Both the entropy and sum of kinetic and electron-electron repulsion functionals are shown to be monotonically increasing with temperature, while the Mermin functional is concave downwards. Analogous relations are found for both exchange and correlation. The importance of these conditions is illustrated in two extremes: the Hubbard dimer and the uniform gas.

#### 4.2 Introduction

Warm dense matter (WDM) is a rapidly growing multidisciplinary field that spans many branches of physics, including for example astrophysics, geophysics, attosecond physics, and nuclear physics [142, 51, 63, 197, 249, 277, 279, 143, 49]. In the last decade, quantum molecular dynamics, using DFT with electrons at finite temperatures, has been extremely successful at predicting material properties under extreme conditions, and has become a standard simulation tool in this field [99]. Almost all such simulations use ground-state exchangecorrelation (XC) approximations, even when the electrons are significantly heated. Thermal density functional theory (thDFT) was formalized by Mermin [194], when he showed that the reasoning of Hohenberg and Kohn [124] could be extended to the grand canonical potential of electrons coupled to a thermal bath at temperature  $\tau$ . In recent times, the Mermin-Kohn-Sham (MKS) equations of non-interacting electrons at finite temperature, whose density matches that of the physical system, are being solved to simulate warm dense matter [148, 235]. In most of these calculations, the ground-state approximation (GSA) is made, in which the exchange-correlation (XC) free energy, which typically depends on  $\tau$ , is approximated by its ground-state value. Accurate results for the uniform gas are still being found [32, 135, 83, 263], which provide input to a thermal local density approximation, but LDA is insufficiently accurate for many modern applications, and thermal GGA's are being explored [275].

Many useful exact conditions in ground-state DFT (relation between coupling constant and scaling, correlation scaling inequalities, exchange and kinetic scaling equalities, signs of energy components) were first derived[166] by studying the variational principle in the form of the Levy constrained search[165]. Most of these conditions are satisfied (by construction) by the local density approximation[148] and have been used for decades to constrain and/or improve more advanced approximations[219]. Their finite temperature analogs were derived in Ref. [228] (see also Ref. [72]), and extended in Ref. [232]. Because the kinetic and entropic

contributions always appear in the same combination as the so-called kentropic energy [see Eq. (4.21) and related text], such relations can never be used to extract either component individually.

Many basic thermodynamic relations are proven via quantum statistical mechanics[265]. However, converting these to conditions on density functionals is neither obvious nor trivial. In the present work, we extend these methods to the dependence of the Mermin functional (i.e., the universal part of the free-energy functional) on the *temperature*, rather than on the coupling constant or the scale of the density. We find several new equalities and inequalities which apply to thDFT of all electronic systems. This allows us to separate entropic and kinetic contributions. We show that the entropy density functional is monotonically increasing with temperature, as is the sum of the kinetic and electron-electron repulsion density functionals, and that the temperature derivative of the Mermin functional is the negative of the entropy functional. Thus the Mermin functional is concave downwards as a function of temperature. Applying these conditions to the MKS system yields conditions on the exchange-correlation free energy functionals. Lastly, we illustrate all our findings in the two extreme cases of the uniform gas and the Hubbard dimer. We find a recent parametrization of the XC free energy of the uniform gas violates our conditions, although only for densities that are so low as to be unlikely to significantly affect any property calculated within thLDA.

#### 4.3 Theory

For a given average particle number, define the free energy of a statistical density-matrix  $\Gamma$  as

$$A^{\tau}[\Gamma] = H[\Gamma] - \tau S[\Gamma], \tag{4.1}$$

where  $\hat{H}$  is the Hamiltonian operator, S extracts the entropy, and we use  $\tau$  to denote temperature. Define

$$F_{\rm I}[\Gamma] = T[\Gamma] + V_{\rm ee}[\Gamma], \tag{4.2}$$

where  $\hat{T}$  is the kinetic energy operator and  $\hat{V}_{ee}$  the electron-electron repulsion operator. Then

$$F^{\tau}[\Gamma] = F_{\mathrm{I}}[\Gamma] - \tau S[\Gamma]. \tag{4.3}$$

The Mermin functional, written in terms of a constrained search, is[228]

$$F^{\tau}[n] = \min_{\Gamma \to n} F^{\tau}[\Gamma], \tag{4.4}$$

where the argument distinguishes functionals of the density from those of the density-matrix. The free energy of a given system can be found from

$$A^{\tau} = \min_{n} \left\{ F^{\tau}[n] + \int d^3 r \, v(\mathbf{r}) \, n(\mathbf{r}) \right\}.$$

$$(4.5)$$

We denote by  $\Gamma^{\tau}[n]$  the statistical density matrix that minimizes  $\hat{F}^{\tau}$  and yields density  $n(\mathbf{r})$ . Then:

$$\frac{dF^{\tau}[n]}{d\tau} = \frac{\partial F^{\tau}[\Gamma]}{\partial \tau} + \int d\Gamma \, \frac{\partial F^{\tau}[\Gamma]}{\partial \Gamma} \, \frac{d\Gamma^{\tau}[n]}{d\tau},\tag{4.6}$$

where all are evaluated at  $\Gamma^{\tau}[n]$ . Because  $\Gamma^{\tau}[n]$  is the minimizer, its derivative with respect to temperature (or any variable) vanishes. Thus

$$\frac{dF^{\tau}[n]}{d\tau} = -S^{\tau}[n]. \tag{4.7}$$

This is the DFT analog of the standard thermodynamic relation [265], and implies

$$F^{\tau}[n] = F^{0}[n] - \int_{0}^{\tau} d\tau' S^{\tau'}[n], \qquad (4.8)$$

where  $F^0[n]$  is the ground-state functional[124]. We note that Eq. (4.7) was derived in [49], but only within lattice DFT.

Given a Mermin functional (approximate or exact, interacting or not), Eq. (4.7) defines what the corresponding entropy functional must be. Since coordinate scaling[228] can separate the kentropic and potential contributions in F, Eq. (4.7) allows the entropic and kinetic energy functionals to be separated. Alternatively, given an entropy functional, Eq. (4.7) defines the temperature-dependence of the corresponding Mermin functional. Since the entropy is always positive,

$$dF^{\tau}[n]/d\tau \le 0,\tag{4.9}$$

i.e., the Mermin functional is monotonically decreasing.

Now consider what happens when, for a given density and temperature  $\tau$ , we evaluate the Mermin functional on the density matrix for that density but at a different temperature. By the variational principle, Eq. (4.5),

$$F^{\tau}[\Gamma^{\tau'}[n]] \ge F^{\tau}[n], \tag{4.10}$$

for any value of  $\tau'$ . Thus

$$F_{\rm I}[\Gamma^{\tau'}[n]] - \tau \, S[\Gamma^{\tau'}[n]] \ge F_{\rm I}^{\tau}[n] - \tau \, S^{\tau}[n], \tag{4.11}$$

$$F_{\rm I}^{\tau'}[n] - \tau \, S^{\tau'}[n] \ge F_{\rm I}^{\tau}[n] - \tau \, S^{\tau}[n]. \tag{4.12}$$

Since this result is true for any pair of temperatures, we reverse  $\tau$  and  $\tau'$  to find:

$$F_{\rm I}^{\tau}[n] - \tau' S^{\tau}[n] \ge F_{\rm I}^{\tau'}[n] - \tau' S^{\tau'}[n].$$
(4.13)

Addition of Eqs. (4.12) and (4.13) yields

$$(\tau - \tau') \left( S^{\tau}[n] - S^{\tau'}[n] \right) \ge 0, \tag{4.14}$$

so that the entropy monotonically increases with  $\tau$ :

$$dS^{\tau}[n]/d\tau \ge 0. \tag{4.15}$$

Combining this with Eq. (4.7) implies

$$d^2 F^{\tau}[n] / d\tau^2 \le 0. \tag{4.16}$$

Thus  $F^{\tau}[n]$  is concave downwards.

We can also isolate the behavior of  $F_{I}^{\tau}[n]$ . If we multiply Eq. (4.12) by  $\tau'$ , and Eq. (4.13) by  $\tau$ , and add them together, all entropic contributions cancel, yielding

$$(\tau' - \tau) \left( F_{\rm I}^{\tau'}[n] - F_{\rm I}^{\tau}[n] \right) \ge 0, \quad dF_{\rm I}^{\tau}[n]/d\tau \ge 0.$$
 (4.17)

Both  $F_{I}^{\tau}[n]$  and  $S^{\tau}[n]$  are monotonically increasing, but the net effect is that the Mermin free energy is decreasing.

or

Applying these conditions to the Mermin-Kohn-Sham electrons[235], we find

$$dF_{\rm s}^{\tau}[n]/d\tau = -S_{\rm s}^{\tau}[n],\tag{4.18}$$

and the inequalities

$$\frac{dT_{\rm s}^{\tau}[n]}{d\tau}, \frac{dS_{\rm s}^{\tau}[n]}{d\tau} \ge 0 \ge \frac{dF_{\rm s}^{\tau}[n]}{d\tau}, \frac{d^2F_{\rm s}^{\tau}[n]}{d\tau^2}$$

$$\tag{4.19}$$

where subscript s denotes non-interacting, and  $F_{\rm s}^{\tau}[n] = T_{\rm s}^{\tau}[n] - \tau S_{\rm s}^{\tau}[n]$ . Some of these relations have long been invoked for the uniform and slowly-varying gases and for constructing orbital-free density functionals (see Ref. [137] and references therein), but here they have been proven for every inhomogeneous system.

#### 4.4 Illustration

To illustrate these results, we calculate all energy components for an asymmetric Hubbard dimer, i.e. a two-site Hubbard model with a potential  $v_1 = -v_2$ , as described in Ref. [47] for the groundstate and [276] for the thermal system. Here t is the hopping parameter, U the on-site repulsion, and  $\Delta n$  the difference in site occupations where the difference comes from having an inhomogeneous potential  $\Delta v = v_2 - v_1$ . This is the simplest possible model in which one can perform an exact thermal calculation, including the exact thermal correlation components. Fig. 4.1 shows the energy components, both interacting and non-interacting, as a function of temperature for the homogeneous system with  $\Delta n = 0$ . All our exact conditions are satisfied for many values of  $\Delta n$  and U.

At the other extreme is the uniform electron gas and a modern parametrization of its free energy[135]. In the special case of a uniform density and potential, our formulas become the same as the standard thermodynamic formulas. In Fig. 4.2, we plot the derivative



Figure 4.1: Energy components for the Hubbard dimer in units of 2t, where U = 2t and  $\Delta n = 0$ :  $F^{\tau}, F_{I}^{\tau}, S^{\tau}$ , both interacting (solid) and non-interacting (dashed).

of the free energy per particle for fixed density  $(r_s \text{ value where } r_s = (3/(4\pi n))^{1/3})$  as a function of temperature, on the scale of the Fermi energy and in atomic units. As  $r_s \rightarrow 0$ , these curves converge to their well known[60] non-interacting value, in which the derivative is negative and decreasing everywhere, in accordance with Eq. (4.9). Unfortunately, by decreasing the density so that XC effects become relatively more important, we find that the parametrization violates our conditions for  $r_s > 10$ . Via Eq. (4.7), this implies that the entropy is unphysically negative. While such low densities are irrelevant to most practical calculations using thLDA, parametrizations of the uniform gas should build in simple exact conditions such as ours. Note that our restrictions apply only to continuous parametrizations. The QMC data on which Ref. [135] is based[32] is for the XC energy at discrete values of the density, and so does not directly give the entropy.

For extremely high temperatures, sums over KS eigenstates become impractical, and only pure DFT can be applied. Because the uniform gas satisfies our conditions, and because


Figure 4.2: Temperature dependence of the Mermin functional for spin-unpolarized uniform gas for several values of the Wigner-Seitz radius  $r_{\rm s}$ , using the XC parametrization of Ref. [135], where  $\epsilon_{\rm F}$  is the Fermi energy.

Thomas-Fermi (TF) theory uses local approximations to the kinetic and entropic contributions which satisfy the conditions pointwise, we deduce that TF theory satisfies our conditions. However, recent attempts to go beyond TF theory, such as using generalized gradient approximations for the energy[134, 274, 275], should be tested for satisfaction of these constraints.

### 4.5 Exchange-Correlation

In the final section of this paper, we apply this reasoning to the MKS method. The Mermin functional is written in terms of the MKS quantities and a correction:

$$F^{\tau}[n] = F_{\rm s}^{\tau}[n] + U_{\rm H}[n] + A_{\rm xc}^{\tau}[n], \qquad (4.20)$$

called the exchange-correlation (XC) free energy. (The Hartree energy,  $U_{\rm H}[n]$ , has no explicit temperature dependence). The XC free energy is a sum of three components:

$$A_{\rm xc}^{\tau}[n] = K_{\rm xc}^{\tau}[n] + U_{\rm xc}^{\tau}[n] = T_{\rm xc}^{\tau}[n] - \tau S_{\rm xc}^{\tau}[n] + U_{\rm xc}^{\tau}[n], \qquad (4.21)$$

where  $U_{\rm xc}^{\tau}$  is the potential contribution and  $K_{\rm xc}^{\tau}$  is the kentropic contribution, which in turn consists of  $T_{\rm xc}^{\tau}$ , the kinetic contribution, and  $-\tau S_{\rm xc}^{\tau}$ , where  $S_{\rm xc}^{\tau}$  is the entropic contribution.

Subtract Eq. (4.18) from Eq. (4.7) to find

$$\frac{dA_{\rm xc}^{\tau}[n]}{d\tau} = -S_{\rm xc}^{\tau}[n],\tag{4.22}$$

or

$$A_{\rm xc}^{\tau}[n] = E_{\rm xc}[n] - \int_0^{\tau} d\tau' S_{\rm xc}^{\tau'}[n].$$
(4.23)

All thermal XC effects are contained in the XC contribution to the entropy. This provides an intriguing alternative to the adiabatic connection formula of Ref. [228] or the thermal connection formula of Ref. [232]. Our inequalities do not yield definite signs for XC quantities, just weak constraints that would be difficult to impose universally on an XC approximation:

$$\frac{dT_{\rm xC}^{\tau}}{d\tau} \ge -\frac{dT_{\rm s}^{\tau}}{d\tau}, \quad \frac{dS_{\rm xC}^{\tau}}{d\tau} \ge -\frac{dS_{\rm s}^{\tau}}{d\tau}.$$
(4.24)

We can also combine these with the coupling-constant derivatives of Ref. [232] to find Maxwell-style relations:

$$\left(\frac{\partial U_{\rm xc}}{\partial \tau}\right)_{\lambda} = -\lambda \left(\frac{\partial S_{\rm xc}}{\partial \lambda}\right)_{\tau} \tag{4.25}$$

where  $\lambda$  denotes evaluation at coupling-constant  $\lambda$ , holding the density fixed [228].

Exchange can be isolated by considering the limit of either weak interaction or scaling to the high-density limit [228]. The exchange free energy is

$$A_{\rm x}^{\tau}[n] = V_{\rm ee}[\Gamma_{\rm s}^{\tau}[n]] - U_{\rm H}[n]$$
(4.26)

in a case of no degeneracies (the only case we consider here). Because  $\Gamma_s^{\tau}$  minimizes the kentropy alone, to first order in  $\lambda$ , kentropic corrections must be zero. Thus

$$K_{\rm x}^{\tau}[n] = 0, \quad T_{\rm x}^{\tau}[n] = \tau \, S_{\rm x}^{\tau}[n] = -\tau dA_{\rm xc}^{\tau}[n]/d\tau. \tag{4.27}$$

It may seem odd to consider a kinetic contribution to exchange (impossible in the ground state), but  $T_{\rm x}^{\tau}$  vanishes as  $\tau \to 0$  in Eq. (4.27). For a uniform gas, the thermal exchange energy is well-known[60]. But for our Hubbard dimer[276], when  $\langle N \rangle = 2$ , we find  $E_{\rm x}[n] = -U_{\rm H}[n]/2$ , so that  $T_{\rm x}^{\tau} = S_{\rm x}^{\tau} = 0$ .



Figure 4.3: Correlation entropy in the Hubbard dimer for several values of  $\Delta n$  as a function of temperature, in units of 2t, where U = 2t.

The results of Eq. (4.23) apply to correlation alone and can be used in either direction, just as the relation for the full functional. They are well-known for the uniform gas from statistical mechanics[128, 226, 227]. But for an inhomogeneous system, they are non-trivial, and so we illustrate them on the asymmetric Hubbard dimer. In Fig. 4.3, we plot the entropic correlation as a function of temperature for several values of  $\Delta n$ , the occupation difference that arises from the asymmetric potential. Eq. (4.23) is satisfied within numerical precision. The derivative of  $S_{\rm C}^{\tau}$  can change sign, even though both  $S^{\tau}(\Delta n)$  and  $S_{\rm S}^{\tau}(\Delta n)$  are monotonically increasing (This explains the small dip seen in Fig. 7 of Ref. [276]).

### 4.6 Discussion and Conclusions

Finally, we explain the apparent success of the ground-state approximation (GSA) for  $A_{\rm xc}^{\tau}[n]$ in MKS equilibrium calculations. Almost all present-day calculations of WDM use this approximation, and a recent calculation on the Hubbard dimer[276] found that GSA worked well when neither the temperature nor the strength of the correlations were large (the conditions corresponding to most WDM calculations). Now we explain why. Write

$$F^{\tau,\text{GSA}}[n] = F_{\text{s}}^{\tau}[n] + U_{\text{H}}[n] + E_{\text{xc}}[n].$$
(4.28)

Clearly, all temperature dependence is contained only in the KS part (usually a very dominant piece). Since the KS piece satisfies all the different inequalities and equalities, then so does any GSA calculation. But attempt to add corrections to a GSA calculation by writing

$$A_{\rm xc}^{\tau,\rm GSA}[n] = E_{\rm xc}^{\rm GSA}[n] + \Delta A_{\rm xc}^{\tau}[n].$$

$$(4.29)$$

Only the thermal correction appears in the exact conditions we have derived, since they all contain temperature derivatives. But there is no simple way to know if the corrections will satisfy the exact conditions for all possible systems. The only case would be using local approximations for all temperature-dependent quantities, and then using energy densities from the uniform gas. Thus a TF calculation, with thermal LDA corrections, would satisfy these conditions, since they would be satisfied pointwise, as the uniform gas satisfies these conditions for every density. But in any MKS calculation using approximate thermal XC corrections, this is not guaranteed. Unless special care is taken to guarantee satisfaction of our conditions, only GSA automatically does this. This is analogous to the situation in TDDFT (at zero temperature): The adiabatic LDA, which ignores the history dependence that is known to exist in the TDDFT functionals, satisfies most exact conditions, while the time-dependent LDA (the Gross-Kohn approximation[103]) violates several important constraints[66]. All this explains why the GSA has been working well in many situations[142, 144]. The GSA appears to be correct in both the low- and high-temperature limits and, at least for model systems, reproduces the exact KS orbitals accurately [276]. Of course, this depends on the specific property being calculated and the acceptable level of error, and does not preclude moderate deviations, especially between these extremes, i.e., warm dense matter. But any calculation that includes, e.g., semilocal thermal XC corrections, risks violating the exact conditions listed here that GSA automatically satisfies, and should be checked for such violations. On the other hand, the Hartree-Fock approximation (or rather, the DFT equivalent, called EXX[156]), must satisfy the conditions since any expansion in powers of the coupling constant up to some order must satisfy all our conditions.

To conclude, the formulas presented here are exact conditions applying to every thermal electronic system when treated with DFT, and should guide the future construction of approximate functionals.

### Chapter 5

## Conclusion

In this dissertation I have focused on understanding and developing ground-state and thermal density functional theory using the asymmetric two-site Hubbard model since it is a system that can be solved exactly. This proves useful as one can compute exact densities, energies, etc. even in the thermal case where exact results are not computationally feasible even for simple atomic systems.

Chapter 1 lays the foundation for ground-state DFT, site-occupation functional theory, and the Hubbard dimer. It illustrates these with exact calculations of fundamental quantities such as the energy, density, and various potentials. Chapter 2 is a continuation of Chapter 1. This chapter provides further background and demonstrates the breadth of concepts where the Hubbard dimer can be applied. These aspects include working to clarify the so-called gap problem in DFT and demonstrations of Green's functions. We delve into understanding correlation and also create a parametrization of the universal functional so the Hubbard dimer can be easily used as a density functional. We also looked at approximations but are hampered by the lack of clear parallels to real-space approximations, e.g. BALDA vs. LDA.

With the foundation laid, chapter 3 introduces thermal density functional theory and shows

the first ever exact thDFT calculation. In doing so we analyze the successes of the zerotemperature approximation and gain increased understanding of why ZTA in conjunction with LDA and GGA has seen so much success in the warm dense matter community. Additionally, we showed that there is non-monotonic behavior in the free energy with respect to temperature and importantly that the free energy is not bounded by its  $\tau = 0$  value as commonly thought.

Next, in chapter 4 we delve into new exact conditions. We show the importance of understanding known quantities from a density functional mindset and that the current thLDA at that time did not satisfy our new conditions. The Hubbard dimer is used to illustrate the new conditions and shows the extreme behavior of the correlation entropy as a function of temperature.

The asymmetric two-site Hubbard model has limitations. It captures the qualitative nature of many physical phenomena but it can not capture all of them nor can it get quantitatively useful results. But it has all the above mentioned results despite, and in many ways because, of these limitations.

There are many possible paths for future work. In chapters 3 and 4 I demonstrates new thermal results with the Hubbard dimer, but there are still many results from chapter 2 that can be generalized to the thermal case. There is also a likely rich parameter space that can still be explored with thermal DFT as well as testing rough analogs of thermally dependent  $A_{\rm xc}$  approximations to see what effects they may have. Additionally, there have been advances in thermal reduced-density-matrix-functional theory[23] that can be benchmarked and illustrated using the Hubbard dimer. Lastly as time progresses and new theories are developed, the applications of the Hubbard dimer will increase. I have used it for thermal DFT and others have used it for ensemble DFT and time-dependent DFT. It is likely that more flavors of DFT as well as new many-body theories are to come and the Hubbard dimer will prove useful once again.

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