THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Nonlocal Correlations in Density Functional Theory

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ABSTRACT

In Density Functional Theory, the widely used local and semilocal approximations to the exchange-correlation energy, the local density approximation (LDA) and the generalized gradient approximations (GGAs), lack a physical description of truly nonlocal correlation effects, which are absolutely essential for a proper description of soft matter. A scheme is proposed that provides a basis for systematic improvements beyond LDA and GGA, including correlations at intermediate and long range, giving rise to bonds of pure van der Waals type as well as more intricate, intermediate-range correlation bonds. The scheme is developed with regard to computational efficiency as well as physical soundness, and incorporated into the standard DFT formalism. The method is applied to a generic set of systems, illuminating different aspects of nonlocal correlations. Studies of van der Waals interactions in molecules, of nonlocal correlations between surfaces, and of bonds in graphite and between graphene layers are included. Successful account of energetics, bond lengths and compressibilities of graphitic systems clearly illustrates the significance of using approximate exchange-correlation energy functionals that are based on the true physics of the system. Finally an explicit formula is given for a general nonlocal correlation density functional, suitable for incorporation into standard DFT schemes.

Keywords: density-functional theory, functional, nonlocal, DFT, LDA, GGA, vdW, van der Waals, exchange, correlation, determinants, polarization, graphene, graphite, first principles, surface states, physisorption, adsorption, adhesion, bonding.

LIST OF PUBLICATIONS

This thesis consists of an introductory part and the following papers, referred to by Roman numerals in the text:

I. **Van der Waals Interactions in Density Functional Theory**
D.C. Langreth, Y. Andersson, E. Hult, H. Rydberg, P. Apell, and B.I. Lundqvist
in Electronic density functional theory: Recent progress and new directions, Eds. J.F. Dobson, G. Vignale, and M.P. Das, Plenum Press, New York, page 243. (1997)

II. **Dispersion Coefficients for van der Waals Complexes, Including C_{60} - C_{60}**
Y. Andersson and H. Rydberg
Physica Scripta **60**, 211-216 (1999)

III. **Unified Treatment of Asymptotic van der Waals Forces**
E. Hult, H. Rydberg, B.I. Lundqvist, and D.C. Langreth
Physical Review B **59**, 4708-4713 (1998)

IV. **Tractable Nonlocal Correlation Density Functionals for Flat Surfaces and Slabs**
H. Rydberg, B.I. Lundqvist, D.C. Langreth, and M. Dion
Physical Review B **62**, 6997-7006 (2000)

V. **Hard Numbers on Soft Matter**
H. Rydberg, N. Jacobsson, P. Hyldgaard, S.I. Simak, B.I. Lundqvist, and D.C. Langreth
Submitted to Nature (2001)

VI. **Long- and Medium-Ranged Nonlocal Correlations in Density Functional Theory**
H. Rydberg
Applied Physics Report **2001-49**, *In cooperation with D.C. Langreth, M. Dion, and B.I. Lundqvist. To be published* (2001)

Scientific publications not included in this thesis:

Density Functionals and van der Waals Interactions at Surfaces
B.I. Lundqvist, E. Hult, H. Rydberg, A. Bogicevic, J. Strömqvist, and D.C. Langreth
Progress in Surface Science **59**, 149-165 (1999)

Self-consistent Description of the Nanotube-Nanotube van der Waals Interaction
E. Schröder, H. Rydberg, and P. Hyldgaard
Applied Physics Report **2000-99** (1999)

Density-functional Bridge Between Surfaces and Interfaces
B.I Lundqvist, A. Bogicevic, K. Carling, S.V. Dudiy, S. Gao, J. Hartford, P. Hyldgaard, N. Jacobson, D.C. Langreth, N. Lorente, S. Ovesson, B. Razaznejad, C. Ruberto, H. Rydberg, E. Schröder, S.I. Simak, G. Wahnström and Y. Yourdshahyan
Surface Science **493**, 253 (2001)

My contributions to the publications are the following:

I. I contributed with the calculations for molecules and van der Waals complexes, using the local cutoff response model.

II. I contributed to the further development of the cutoff formalism, and performed the calculations of van der Waals coefficients from molecular densities.

III. I applied the full-field theory to the molecules using an in-house finite element program, developed by me, and contributed to the writing of the manuscript.

IV. In a dialogue with the other authors, I came up with the tractable renormalization procedure for the Adiabatic Connection Formula, expressed in terms of polarizabilities. The article was written jointly.

V. I performed the application of Paper IV to graphitic systems, by calculating the nonlocal correction from graphene and graphite electron densities, calculated by other authors. The article was written jointly.

VI. In a dialog with the other authors, I showed how to make a valid expansion, and how it might be symmetrized. The polarization model and parameterization were done in dialog with the other authors. The report was written by me.

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CHAPTER 1

INTRODUCTION

The subject of this thesis is nonlocal correlations in electron systems, and how to incorporate the effect of such correlations into the *ab initio* theory of materials, the Density Functional Theory (DFT) [1, 2]. Already in its simplest form, the Local Density Approximation (LDA) [2, 3], and the Local-Spin Density Approximation (LSDA) [2, 4, 5, 6], has been remarkably successful. It predicts properties of *hard* materials such as close-packed metals, semiconductors and insulators [7, 8, 9, 10, 11] well. The extension to account also for *soft* matter, which comprise numerous physical, chemical, and biological systems, such as physisorption, adhesion and liquids, van der Waals (vdW) complexes and polymers, has proven to be much more difficult. The basic reason for this predicament is to be found in the energy and length scales involved.

Hard materials are tightly bound, requiring large amounts of energy to distort or dissociate. The typical binding energy per atom is on the eV scale, and typical bond lengths are 2 - 3 Å. Since the largest contributions to the binding energies are well understood, a good account for them may be achieved.

Soft materials, on the other hand, are much more weakly bound. The typical binding energy per atom is in the meV range, or hundreds of times smaller compared to hard materials, and the corresponding bondlengths are about 4 - 7 Å. The interactions giving rise to these tiny bonds are not so well described; in fact, they are completely absent from the for hard materials so successful LDA. It is not surprising then that it fails to account for them.

A systematic improvement over the LDA has been developed successively during the last 20 years, and goes under the collective name of Generalized Gradient Approximations (GGA) [12, 13, 14, 15, 16]. For a large class of systems it brings accuracy close to the level of requirements from chemists and materials scientists. The energy scale that can be accounted for is closing in on tenths of an eV, still far from the energy scale applicable in the soft regime.

In this thesis, a systematic extension to DFT is proposed that also takes into account the very weak nonlocal correlations. In the chapters that follow the concepts behind how to account for these correlations so that systematic improvement is guaranteed, will be outlined. The theory is the result of an organic development, and the story will be told in a consistent framework and language, reformulating some of the early results for clarity.

As the remaining story will not strictly follow the evolution of time, a brief historic account for the work on nonlocal correlations will be given here. For a more thorough discussion, the reader is referred to the review, paper I.

1.1 BRIEF HISTORY OF NONLOCALITIES

Back in the 70's, after the introduction of the DFT [1], the *exchange-correlation energy* functional E_{xc}, and the first successful approximation to E_{xc}, LDA [2], attempts were made to increase the accuracy of LDA. Being based on the energy of the uniform electron gas, it seemed an appropriate cause of action to expand that energy in powers of gradients (GA) [2]. However, it turned out that a straightforward such expansion makes the situation much worse [6, 17].

The source of the problem can be understood in terms of the *exchange-correlation hole*, $n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}')$, which contains all the many-body effects of the total-energy density functional. A Fourier analysis [18] of $n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}')$ showed that the major contribution to the exchange-correlation energy comes from a region of small q-values, where $q \to 0$ corresponds to the total integral $\int d^3r' n(\mathbf{r}, \mathbf{r}')$ of the hole, which is fixed to -1 by a simple charge-conserving sum rule [6]. However, GA severely violates this sum rule, and hence makes a large error in E_{xc}. A stringent criterion for when the GA actually does work was developed [18].

To overcome these problems, several attempts were made to take advantage of the gradient corrections, while making sure that the basic sum rules are still obeyed [19, 12, 20, 21, 22], schemes collectively called GGAs. Although implemented differently, they all in one way or another lean on the rigorous limits of GA, introducing cutoffs to throw away those parts that can be proven to be small but badly represented. Due to its simplicity and ease of implementation into general schemes, the GGAs have been used and tested extensively for atoms, molecules and solids [23], and are still being improved upon [16, 24, 25].

The GGAs have a *semilocal* dependence on the density $n(\mathbf{r})$, which can account for *short-ranged* fluctuations in the density, meaning, fluctuations smaller than the average screening length. They cannot, however, by construction, account for the *nonlocal* correlations occurring between distant points, such as the long-ranged van der Waals interactions, or even correlations at more intermediate ranges but outside the average screening length.

In parallel to the development of GGA, descriptions aiming at the nonlocal effects were suggested in the form of the Average-Density (ADA) and Weighted-Density Approximations (WDA) [26]. These schemes have later been applied with quite some success but they are hampered by computational complexity, since the interactions need to be considered not only spatially but also self-consistently.

To capture the nonlocal correlations as a whole, focus in the 80's turned to the general expression for E_{xc} [6, 18, 23], the Adiabatic Connection Formula, which provides a systematic way for studying local and nonlocal correlations.

In the early 90's, the question of long-ranged nonlocal correlations was approached in terms of long-wavelength, or plasma oscillations [27, 28], using a sharp but general and physical cutoff to arrive at an asymptotic electron-electron interaction identical to the London expression between separated objects. In the mid 90's, the approach was used to construct a general density functional for the asymptotic van der Waals interactions between atoms [29, 30, 31] and shortly after also for molecules [32], atoms at surfaces [33], and surfaces [34].

Although the proposed method was quite sensitively dependent on the cutoff, the dynamical properties of the long-wavelength polarizability were well accounted for, and so the sensitivity could be drastically reduced [33, 35] by fitting to known static polarizabilities, which are much easier to obtain from local theories.

Successful as they were in predicting the asymptotic behaviors, the problem of seamlessly merging these new findings with the existing DFT schemes remained. Several formulations of general theories were developed, some utilizing the polarizability formulation [31], and some starting from time-dependent DFT [36], but they all suffered badly from computational complexity. In the late 90's a tractable method for non-local density functionals restricted to planar systems was developed, and the first results reported [37] and compared to benchmark data [38]. The method was later used to resolve a long-lasting dilemma about the nonapplicability of LDA and GGA in a system of particular interest, graphite [39].

The problem of finding a general nonlocal correlation functional suitable for incorporation into existing DFT schemes is addressed in this thesis, and a systematic theory is proposed for how this problem could be solved in general. An explicit functional is given as a first instance of this manifold of possibilities, and is shown to perform well when tested on already reported systems.

1.2 OUTLINE OF THESIS

In a series of articles, my collaborators and I have explored the problem of nonlocal correlation density functionals, and the bulk of this thesis is devoted to provide the background and explain the theory behind these articles. The exception is Chap. 4, which is about soft matter, and where I give most of the results we have achieved so far (Papers II-V). In Chap. 2, I go through the basic definitions and major results of DFT, and in Chap. 3, I present a more detailed view of the concepts behind nonlocal correlations. I give the now-standard definition of RPA, and report how we have applied, in this approximation, a nonlocal density functional for surfaces (Paper IV). In Appendix A, I give an extension to multi-dimensions of the proof found in Paper IV. Chapter 3 also includes a crash-course in operator algebra.

In the remaining two chapters, I develop further our theory for nonlocal correlations, and give some results, referring to Paper VI. In the last chapter, Chap. 6, I give the current status of a general exchange-correlation density functional, and the applications and future development of the functional is discussed.

CHAPTER 2

DENSITY FUNCTIONAL THEORY

The appeal of Density Functional Theory (DFT) is that it is simple in theory and powerful in practice. The theory dates back to the early sixties, and groundbreaking work done mainly by a handful of actors [1, 2, 6, 18, 15, 11, 16], of whom the most prominent, Walter Kohn, received the Nobel prize in 1998. The theory is well documented [7, 8, 9, 40], and will not be repeated in its entirety here. An account for the prior application of DFT to the problem of long-ranged interactions may be found in Paper I in this thesis. Here, only the necessary definitions and results needed will be given.

The exact ground-state energy of a fermionic many-electron system is a combinatorial problem, and therefore impossible to find for arbitrarily large systems – with less computer power than Nature itself provides. The energy E of a system of N electrons in an external potential $v(\mathbf{r})$ is a functional of $v(\mathbf{r})$ and the many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, required to have nodes (vanish) whenever two particles coincide, causing Ψ to consequently switch sign along $N(N-1)$ lines in a $3N$-dimensional space; a mind-boggingly complex topology. But the problem can, at least conceptually, be immensely simplified.

The probability $p(\mathbf{r})$ to find an electron at a certain position in space, times the number of electrons N, form the electron density of the system, $n(\mathbf{r}) = Np(\mathbf{r})$. With this at hand, the energy E_{ext} due to an external potential $v(\mathbf{r})$ can be immediately written down,

$$E_{\text{ext}}[n, v] = \int d^3r\, n(\mathbf{r})v(\mathbf{r}), \tag{2.1}$$

measured in the natural atomic units,[*] which are used through out the thesis.

The probability $p(\mathbf{r}, \mathbf{r}')$ to find a pair of electrons at positions $\mathbf{r}$ and $\mathbf{r}'$ respectively, times the number of pairs $N(N-1)$, form the pair-probability density $n_2(\mathbf{r}, \mathbf{r}') = N(N-1)p(\mathbf{r}, \mathbf{r}')$. With this measure, the energy of the Coulomb

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[*] In the atomic units, $\hbar = 1$. Distances are measured in bohr, 1 bohr being the size a_0 of a hydrogen atom, 1 bohr $= a_0 = \hbar^2/me^2$. Energies are measured in hartrees, 1 hartree $= e^2/a_0$. As a consequence, $\hbar = a_0 = e = m = 1$.

interaction E_{coul} between all the electrons is given by

$$E_{\mathrm{coul}}[n_2] = \frac{1}{2}\int d^3r d^3r' \, \frac{n_2(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{2.2}$$

dividing by two to avoid double-counting.

The third quantity is somewhat less intuitive; the *density matrix* $\gamma(\mathbf{r},\mathbf{r}')$ of the wave function Ψ measures the correlation (scalar product) of the wavefunction Ψ, when an electron is fixed at position $\mathbf{r}$, and of Ψ, when the same electron is fixed at position $\mathbf{r}'$, times the number of electrons, and will be defined later. With this quantity, the kinetic energy T is conveniently expressed as

$$T[\gamma] = -\frac{1}{2}\int d^3r \, [\nabla^2\gamma(\mathbf{r},\mathbf{r}')]_{\mathbf{r}=\mathbf{r}'}, \tag{2.3}$$

where the 1/2 is due to the unit system. In spite of the sign, Eq. (2.3) is always positive.

The total energy of the N-fermion system is simply the sum of the external, kinetic and potential energies,

$$E = T[\gamma] + E_{\mathrm{coul}}[n_2] + E_{\mathrm{ext}}[n,v]. \tag{2.4}$$

Conceptually, Eq. (2.4) is not so difficult to grasp, but the problem has of course not been simplified. The electron density $n(\mathbf{r})$ is easily expressed in terms of the pair-density $n(\mathbf{r},\mathbf{r}')$, but the real complexity is hidden in the relation between $n(\mathbf{r},\mathbf{r}')$ and the density matrix $\gamma(\mathbf{r},\mathbf{r}')$, which is very, very, complex.

It is not so surprising, then, that there was quite a stir in the physics community, when it was shown that the total energy E can in fact be expressed as a functional of the simplest of the quantities, $n(\mathbf{r})$,

$$E[n,v] = F[n] + E_{\mathrm{ext}}[n,v], \tag{2.5}$$

where $F[n] = T[\gamma] + E_{\mathrm{coul}}[n_2]$ *together* is provably a functional of the density only, but not by themselves [1]. Of course neither does this treatment simplify matters *per se*, but the practical benefit of a functional of the density $n(\mathbf{r})$ only, is that it can be *approximated* in a sense that could not be done before [2].

2.1 EXCHANGE-CORRELATION ENERGY

Hohenberg and Kohn [1] proved that $F[n]$ of Eq. (2.5) is a functional of the density only. Kohn and Sham [2] took advantage of that by noting that although the density matrix $\gamma(\mathbf{r},\mathbf{r}')$ is a very complex quantity,

$$\gamma(\mathbf{r},\mathbf{r}') = N\int d\mathbf{R}\, \Psi(\mathbf{r},\mathbf{R})\Psi^*(\mathbf{r}',\mathbf{R}), \tag{2.6}$$

where $\mathbf{R}$ denotes all the other particles, there is a simpler version of Eq. (2.6), valid for a set of non-interacting fermions ($E_{\text{coul}} = 0$). It can be written explicitly in terms of orthogonal one-particle functions $\psi_k(\mathbf{r})$, as

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^{N} \psi_k(\mathbf{r}) \psi_k^*(\mathbf{r}'). \tag{2.7}$$

The equivalent of Eq. (2.3), T_s, should, they argued, be close to T. In the same manner, E_{coul} should be close to yet another quantity, the Hartree energy,

$$E_H[n] = \frac{1}{2} \int d^3r d^3r' \, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{2.8}$$

which only involves the electron density $n(\mathbf{r})$. Scrapping up whatever is left into the *exchange-correlation* (XC) energy E_{xc}, they proposed the decomposition

$$F[n] = T_s[n] + E_H[n] + E_{\text{xc}}[n], \tag{2.9}$$

which has the virtue that both $T_s[n]$ and $E_H[n]$ are practically simple to calculate, and that $E_{\text{xc}}[n]$ should be a small number compared to the first two energies. They proposed a simple approximation of $E_{\text{xc}}[n]$, based on the energy of the uniform electron gas, the LDA, which has proven very useful in practical calculations [7, 8].

2.2 ADIABATIC CONNECTION FORMULA (ACF)

Although practical and well-defined in the limit of almost uniform density, the theory of Hohenberg, Kohn and Sham was further boosted by the emergence of an explicit formula for $E_{\text{xc}}[n]$, the *adiabatic connection formula* (ACF), which was derived independently by Langreth and Perdew [41], and by Gunnarsson and Lundqvist [6]. They noted that although the full problem Eq. (2.9) may be difficult, there is a related problem which is exactly solvable, the one where $E_H = E_{\text{xc}} = 0$, and that both these terms are due to the Coulomb interaction Eq. (2.2). In order to keep the density fixed, the non-interacting system must be due to a different external potential $v_0(\mathbf{r})$. Starting from there, one could then imagine slowly turning on the Coulomb interaction, at the same time adjusting the external potential and keeping track of how the energy changes, until the fully interacting state is reached.

The derivation makes use of the *Pauli-Hellmann-Feynman* theorem, stating the simple but profound fact that for any Hamiltonian system on the form $E(\lambda) = x_\lambda^\dagger H(\lambda) x_\lambda$, with x_λ normalized ($x_\lambda^\dagger x_\lambda = 1$) and sitting in its *ground state*, the first-order change with respect to λ becomes $\delta E/\delta\lambda = x_\lambda^\dagger (\delta H(\lambda)/\delta\lambda) x_\lambda$. In this case, $H(\lambda) = v_\lambda + \lambda V$, yielding

$$\frac{\delta E(\lambda)}{\delta\lambda} = E_{\text{coul}}^{\lambda} + \int d^3r \, \frac{\delta v_\lambda(\mathbf{r})}{\delta\lambda} n(\mathbf{r}), \tag{2.10}$$

where $E^{\lambda}_{\text{coul}}$ should be evaluated at coupling strength λ. Now integrating up to full coupling strength gives

$$E = E(0) + \int_0^1 d\lambda \, \frac{\delta E(\lambda)}{\delta \lambda} = E(0) + \int_0^1 d\lambda \, E^{\lambda}_{\text{coul}} + \int d^3r \, (v_1(\mathbf{r}) - v_0(\mathbf{r}))n(\mathbf{r}). \quad (2.11)$$

But $E(0) = T_s + E^{\lambda=0}_{\text{ext}}$, so after insertion into Eq. (2.11) one obtains

$$E = T_s + E_{\text{ext}} + \int_0^1 d\lambda \, E^{\lambda}_{\text{coul}}. \quad (2.12)$$

Comparing to Eq. (2.5), all the terms are the same except $E_{\text{xc}} = \int_0^1 d\lambda \, (E^{\lambda}_{\text{coul}} - E_H)$, which is customarily written as [6]

$$E_{\text{xc}} = \frac{1}{2} \int d^3r \, \frac{n(\mathbf{r}) n_{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.13)$$

where

$$n_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda \, (g(\lambda, \mathbf{r}, \mathbf{r}') - 1) n(\mathbf{r}') \quad (2.14)$$

is known as the *exchange-correlation hole*, and $g(\lambda; \mathbf{r}, \mathbf{r}')$ is the pair-distribution function of density $n(\mathbf{r})$, taken at coupling strength λ.

Equation (2.13) constitutes a real simplification of the many-fermion problem. Although finding the pair-distribution function $g(\lambda, \mathbf{r}, \mathbf{r}')$ is equivalent to finding the pair-density $n_2(\mathbf{r}, \mathbf{r}')$, the reference to $\gamma(\mathbf{r}, \mathbf{r}')$ has dropped out of the equations. Moreover, Eq. (2.13) has a physical appeal to it, since it can be viewed as the interaction of the electron with its XC hole, which is a depletion in the density due to its own presence. For this hole, it has been shown that

$$\int d^3r' \, n_{\text{xc}}(\mathbf{r}, \mathbf{r}') = -1. \quad (2.15)$$

In other words, the XC hole has precisely the size of the absence of the electron [41].

CHAPTER 3

NONLOCAL CORRELATIONS

The concept of correlation is a very subtle part of quantum mechanics, and in fact often misunderstood. To begin with, a correlation force, like the van der Waals [42] interaction, is *not* the result of any explicit fundamental force, but is the effect of the Coulomb interaction in a purely dynamical system, in which only the detailed behavior has quantum nature. Although an electron behaves quite differently from a classical particle, many of the correlation effects arising in a many-particle system *do* have a classical counterpart, and so the quantum nature of the effects in a material should not be overrated.

The van der Waals interaction is a striking example. It is a long-ranged interaction, due to interaction between instantaneous dipoles.* But a similar kind of interaction also occurs for classical systems, like the one between molecules with a permanent dipole moment at high temperature. The thing that matters is how the material polarizes; applying a time-dependent electric field, the charges of the material moves in response to the field, and the material becomes polarized. If this effect is large enough or happens quickly enough, spontaneous fluctuations in two separated objects begin to align themselves under the influence of the Coulomb interaction, giving rise to a net attraction between them.

To predict the van der Waals attraction requires a quantum-mechanical treatment, simply because the details of how the electrons polarize are subject to real quantum effects.

Historically, the treatment of van der Waals forces has been carried by chemists [43, 44, 45], because of its fundamental impact on weakly bonded atomic and molecular species. In recent years, weak nonlocal correlations have attracted the attention also of physicists, in particular with the aim to incorporate such effects into DFT [27, 28, 29, 31, 36, 38, 37], and the prediction of the asymptotic van der Waals attraction has been quite successful [33, 34, 36, 35].

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*The valence electrons surrounding the cores in a material are very polarizable, and under the influence of an time-dependent external field, they easily align themselves in a concerted motion, known as plasma oscillations.

3.1 FLUCTUATION AND DISSIPATION

The nonlocal correlation effects are all present in the adiabatic connection formula, Eq. (2.13). To be useful, a more detailed description of the XC hole $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ or the pair-density function $n_2(\mathbf{r},\mathbf{r}')$ is needed. This is provided in terms of the *many-body response function*.

The time-dependent density response $\delta n(\mathbf{r},t)$ to an applied potential $\delta v(\mathbf{r},t)$ is formally given by the first-order Taylor expansion[†]

$$\delta n(\mathbf{r},t) = \int d^3r' \, \chi(\mathbf{r},\mathbf{r}';t-t')\delta v(\mathbf{r}',t'), \tag{3.1}$$

where $\chi(\mathbf{r},\mathbf{r}',t-t') = \delta n(\mathbf{r},t)/\delta v(\mathbf{r}',t')$ is the many-body linear response kernel of the system. In terms of its Fourier components,

$$\chi(\mathbf{r},\mathbf{r}';t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \chi(\mathbf{r},\mathbf{r}';\omega) e^{i\omega(t-t')}. \tag{3.2}$$

As the system adjusts itself to the presence of the external field, it reveals information about the correlations present in the system. A very powerful relation, that relates $\chi(\mathbf{r},\mathbf{r}';\omega)$ to the pair-density $n_2(\mathbf{r},\mathbf{r}')$, is the *fluctuation-dissipation theorem*,

$$\oint_C \frac{d\omega}{2\pi i} \, \chi(\mathbf{r},\mathbf{r}';\omega) = n_2(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') + \delta^3(\mathbf{r}-\mathbf{r}')n(\mathbf{r}), \tag{3.3}$$

first derived in Ref. [48], and here restated in terms of response and pair-density [6, 41]. The virtue of Eq. (3.3) is that conceptually the response function χ is easy to understand and allows a direct comparison to experiments, since the response $\delta n(\mathbf{r},t)$ is a measurable quantity.

As a technical comment, the contour integration picks up the poles along the positive real axis, and can equivalently be viewed as the integral from $i\infty$ to $-i\infty$ along the imaginary axis,

$$-\int_{-\infty}^{\infty} \frac{du}{2\pi} \, \chi(\mathbf{r},\mathbf{r}';iu) = n_2(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') + \delta^3(\mathbf{r}-\mathbf{r}')n(\mathbf{r}). \tag{3.4}$$

This formulation has the benefit of a more direct coupling to dissipation; after infinitely long time, the system has adjusted itself to the new ground state with the external potential present, via an infinitesimal dissipation of energy to the environment. From the Schrödinger equation, this is equivalent to an infinitesimal step down-hill in imaginary time, which can be expressed as an integral over all imaginary frequencies, yielding Eq. (3.4). The imaginary-time formulation also has the advantage of being easier to implement numerically, $\chi(\mathbf{r},\mathbf{r}',iu)$ being a smooth, real function.

[†] The translational invariance in time, $t-t'$, only holds for time-independent hamiltonians. In time-dependent DFT [46, 47], that restriction is relaxed.

An important property of $\chi(\mathbf{r}, \mathbf{r}'; iu)$ is that it must be *charge-conserving*; one thing an applied electric field cannot do is change the number of electrons, so the total density change at each moment in time must integrate to zero,

$$\int d^3r \, \delta n(\mathbf{r}, t) = 0. \tag{3.5}$$

Consequently, this must apply also to $\chi(\mathbf{r}, \mathbf{r}, iu)$, and with the additional knowledge that χ is hermitean [31], one obtains

$$\int d^3r \, \chi(\mathbf{r}, \mathbf{r}'; iu) = \int d^3r' \, \chi(\mathbf{r}, \mathbf{r}'; iu) = 0. \tag{3.6}$$

3.2 CRASH-COURSE IN OPERATOR ALGEBRA

There is a beautiful formalism that really simplifies the mathematical treatment of many problems in physics, and in particular the treatment of the exchange-correlation energy. Operators have been used in quantum field theories since the beginning of Quantum Mechanics, and present precisely that sharpness and simplicity needed to avoid errors, and enables an easy-minded approach to calculations. In a simple language, one treats functions as vectors and operators as matrices, and applies all the advances of linear algebra, which most physicists learned already in high-school.[‡]

The operator unity is denoted by 1 and defined as a delta-function in the appropriate number of dimensions. It is thus infinite along the diagonal. By the the trace of an operator A is meant the integral

$$\mathrm{Tr}\,[A] = \int d^3r \, A(\mathbf{r}, \mathbf{r}), \tag{3.7}$$

and a product $C = AB$ means an integral

$$C(\mathbf{r}, \mathbf{r}') = \int d^3r'' \, A(\mathbf{r}, \mathbf{r}'')B(\mathbf{r}'', \mathbf{r}'), \tag{3.8}$$

which works just like an ordinary matrix product. By the conjugate-transposed operator $A^\dagger$ is meant

$$A^\dagger(\mathbf{r}, \mathbf{r}') = A^*(\mathbf{r}', \mathbf{r}), \tag{3.9}$$

just as for matrices. An hermitean operator has $A^\dagger = A$. By the inverse $\phi = A^{-1}$ is meant the solution ϕ to the equation $A\phi = \phi A = 1$. As an example, the Coulomb Green's function $\mathrm{G}(\mathbf{r}, \mathbf{r}') = -1/4\pi\,|\mathbf{r} - \mathbf{r}'|$ is the solution to $\nabla^2\mathrm{G} = 1$ that vanishes at infinity, explicitly

$$\nabla^2\mathrm{G}(\mathbf{r}, \mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}'), \tag{3.10}$$

[‡] A more stringent approach is based on functional analysis, and the analysis of functional spaces like the Hilbert spaces, projected onto finite basis sets, resulting in matrix representations.

and to $\mathrm{G}\nabla^2 = 1$, so $\mathrm{G}^{-1} = \nabla^2$, the inverse of the laplacian. Note that the boundary conditions are built into the Greens function, and can thus not be specified explicitly.

A diagonal representation of an operator A is its decomposition into orthonormal eigenfunctions,

$$A(\mathbf{r}, \mathbf{r}') = \sum_i \lambda_i \psi_i(\mathbf{r}) \phi_i^\dagger(\mathbf{r}'). \tag{3.11}$$

For hermitean matrices, $\phi_i = \psi_i$, and λ_i are all real. An operator function is a mapping $B = f(A)$ from one operator A to another operator B. It is defined in terms of the eigenvalues,

$$B(\mathbf{r}, \mathbf{r}') = f[A](\mathbf{r}, \mathbf{r}') = \sum_i f(\lambda_i) \psi_i(\mathbf{r}) \phi_i^\dagger(\mathbf{r}'). \tag{3.12}$$

Operators may also be expanded just like Taylor series. For example, the operator $B = (1 - A)^{-1}$ has the familiar expansion

$$B = (1 - A)^{-1} = \sum_{n=0}^{\infty} A^n. \tag{3.13}$$

Normally, the ordering of operators is crucial, since it is the only property that differs from ordinary numbers. By the commutator $[A, B]$ is meant the operation

$$[A, B] = AB - BA. \tag{3.14}$$

Operators which commute, $[A, B] = 0$, can be treated together just as if they were numbers. Specifically, $[A, A] = 0$, so one can always write for instance

$$(1 - A)^{-1} = \frac{1}{1 - A}. \tag{3.15}$$

This crash-course ends with a warning: in general,

$$e^{A+B} \neq e^A e^B, \tag{3.16}$$

which will become apparent in the application in the next section.

3.3 RANDOM PHASE APPROXIMATION (RPA)

With the aid of the fluctuation-dissipation theorem, Eq. (3.3), the ACF, Eq. (2.13), may be reformulated as [29, 37]

$$E_{\mathrm{xc}} = -\int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \operatorname{Tr}\left[\chi_\lambda(iu) V\right] - E_{\mathrm{self}}, \tag{3.17}$$

where $V(\mathbf{r}, \mathbf{r}') = 1/\left|\mathbf{r} - \mathbf{r}'\right|$ and where $\chi_\lambda(\mathbf{r}, \mathbf{r}; iu)$ is the many-body response function at coupling strength λ. E_{self} is an infinite Coulomb self-energy of all electrons, emerging from the term $\delta^3(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$ in Eq. (3.4). It is exactly cancelled by a corresponding term in $\chi_\lambda(iu)V$. The trace is defined in Eq. (3.7).

The response function χ_λ gives the first-order density change $\delta n = \chi_\lambda \Phi_{\mathrm{ext}}$ of the system at coupling strength λ, in response to an external potential Φ_{ext}. It satisfies the Dyson equation

$$\chi_\lambda(iu) = \tilde{\chi}_\lambda(iu) + \lambda \tilde{\chi}_\lambda(iu) V \chi_\lambda(iu), \tag{3.18}$$

where $\tilde{\chi}_\lambda$ is the density response to the screened potential Φ_λ,

$$\delta n = \tilde{\chi}_\lambda \Phi_\lambda, \tag{3.19}$$

for a system at coupling strength λ. Using Eq. (3.18), $\chi_\lambda V$ may be expressed in terms of $\tilde{\chi}_\lambda$ as

$$\chi_\lambda(iu)V = \frac{\tilde{\chi}_\lambda(iu)V}{1-\lambda\tilde{\chi}_\lambda(iu)V}. \tag{3.20}$$

The *random-phase approximation* (RPA) assumes that the λ-dependence of $\tilde{\chi}$ and Φ can be neglected. Physically, it corresponds to the assumption that the polarization properties of the material changes negligibly due to the polarization itself. With no λ-dependence in $\tilde{\chi}$, the λ-integral of Eq. (3.17) can be performed to yield[§]

$$E_{\mathrm{xc}} = \int_0^\infty \frac{du}{2\pi} \operatorname{Tr}\left[\ln(1-\tilde{\chi}(iu)V)\right] - E_{\mathrm{self}}. \tag{3.21}$$

The RPA is exact in the high-density limit, and its application to the uniform electron gas is wellknown [49]. Approximate expressions exist [50, 51, 52]. It has also been used to calculate the nonlocal contribution to the surface energy [41, 53, 54], and the correlation interaction between two parallel slab surfaces [38], and an application to small diatomic molecules is under development [55].

3.4 COMPUTATIONAL COMPLEXITY OF THE RPA

Although manageable in some special cases, the RPA is still computationally too demanding to be worthwhile, considering that it still is an approximative treatment of the many-body problem. If one wants to go about and calculate it anyways, to the author's knowledge, the best way would be to make use of the fact that $\operatorname{Tr}[\ln(A)] = \ln(\det(A))$, and write

$$E_{\mathrm{xc}} = \int_0^\infty \frac{du}{2\pi} \ln(\det(1-\tilde{\chi}(iu)V)) - E_{\mathrm{self}}, \tag{3.22}$$

where det() means the functional determinant [37]. The determinant of an $N \times N$ discrete matrix can be solved using standard LU-factorization, for which efficient

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[§] In Paper IV, there is a misprint showing $\log_{10}$ instead of ln. Moreover, the argument of the logarithm is positive, so Re [] may be omitted.

$\mathcal{O}(N^3)$ algorithms exist [56], whereas the logarithm requires a complete solution of the eigenvalue problem, which also scales like $\mathcal{O}(N^3)$ but is more complex and time-consuming [56]. In both Eq. (3.21) and Eq. (3.22), an additional benefit is not having to calculate the intermediate χ_λ's, needed if the λ integration is done explicitly.

A complexity-reducing approximation to the RPA, which in the three-dimensional case reduces the operation count to $\mathcal{O}(N^2)$ (Appendix A), and for the one-dimensional case to $\mathcal{O}(N)$ (Paper IV), can be made if $\tilde{\chi}(iu)$ is known in its diagonal form,

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}'; iu) = \sum_i \lambda_i(iu)\psi_i(\mathbf{r}, iu)\psi_i^*(\mathbf{r}', iu), \tag{3.23}$$

with the additional assumption that the topology of a special overlap matrix S,

$$S_{i,j} = \int d^3r \, \psi_i^*(\mathbf{r}, iu)(-\nabla^2)\psi_j(\mathbf{r}, iu), \tag{3.24}$$

is such that $|S_{i,j}|$ is appreciable on a nearest-neighbor lattice only. S is then a block-tridiagonal matrix, for which efficient computational algorithms exist [57], and Eq. (3.22) may be evaluated as

$$E_{\mathrm{xc}} = \int_0^\infty \frac{du}{2\pi} \ln\left(\frac{\det(S(iu) - \Lambda(iu))}{\det(S(iu))}\right) - E_{\mathrm{self}}, \tag{3.25}$$

with $\Lambda_{i,j} = 4\pi\lambda_i\delta_{i,j}$. In one dimension, Eq. (3.25) coincides with the method described in Paper IV. In higher dimensions, it has not been applied yet; it is given here for future reference. Details of a possible algorithm are found in Appendix A.

Although the general approach is reminiscent of the tight-binding method [58], Eq. (3.25) is quite different in that Eq. (3.23) describes the electrons only, and for the purpose of calculating the full RPA. Besides, the ϕ_i's do not necessarily need to be localized in order for the overlaps $S_{i,j}$ to vanish.

The ultra-fast method of Paper IV is based on the observation that the determinant, as a function of system size, can be made to satisfy the homogeneous differential equation of which operator it is the determinant, subject to particular boundary conditions. In higher dimensions, the single homogeneous differential equation is replaced by a manifold, satisfying a complete set of boundary conditions. However, since the boundary is of lower dimension than the enclosed space, the complexity is reduced.

In summary, Paper IV contains an explicit form for the vdW functional that applies to flat surfaces. Compared to the DW98 functional [38], the virtues are the computational simplifications gained from choosing a particular sub-class of response functions and utilizing a differential formulation and sparse matrices.

3.5 POLARIZATION OPERATOR

The polarization operator $\alpha_{\mu,\nu}$ is defined as the polarization along direction $\hat{\mathbf{r}}_\mu$ due to the total field E_ν along direction $\hat{\mathbf{r}}_\nu$. In matrix notation, $\mathbf{P} = \boldsymbol{\alpha} \cdot \mathbf{E}$. The polarization is related to the induced charge, $\delta n = -\boldsymbol{\nabla} \cdot \mathbf{P}$, and the total field to the screened potential, $\mathbf{E} = -\boldsymbol{\nabla}\Phi$, so

$$\delta n(\mathbf{r}) = \boldsymbol{\nabla} \cdot \boldsymbol{\alpha} \cdot \boldsymbol{\nabla}\Phi. \tag{3.26}$$

But the response δn to the screened potential Φ is just $\tilde{\chi}$, so

$$\tilde{\chi} = \boldsymbol{\nabla} \cdot \boldsymbol{\alpha} \cdot \boldsymbol{\nabla}. \tag{3.27}$$

The dielectric operator $\epsilon_{\mu,\nu}$ is defined in terms of $\alpha_{\mu,\nu}$ as

$$\boldsymbol{\epsilon} = \mathbf{1} + 4\pi\boldsymbol{\alpha}. \tag{3.28}$$

In terms of $\boldsymbol{\epsilon}$, Eq. (3.21) takes the form [37]

$$E_{\mathrm{xc}} = \int_0^\infty \frac{du}{2\pi}\,\mathrm{Tr}\left[\ln(\boldsymbol{\nabla} \cdot \boldsymbol{\epsilon} \cdot \boldsymbol{\nabla}\mathrm{G})\right] - E_{\mathrm{self}}, \tag{3.29}$$

where $\mathrm{G} = -V/4\pi$ is the Coulomb Green's function, which was mentioned in Sec. 3.2. What makes Eq. (3.29) interesting is that for a uniform translationally invariant system, $\epsilon_{\mu,\nu} = \delta_{\mu,\nu}\epsilon$, and $[\boldsymbol{\nabla}, \epsilon] = 0$, so

$$\boldsymbol{\nabla} \cdot \boldsymbol{\epsilon} \cdot \boldsymbol{\nabla}\mathrm{G} = \epsilon\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\mathrm{G} = \epsilon. \qquad \text{(uniform)} \tag{3.30}$$

As noted in Paper IV, a large portion of E_{xc} should therefore be given by

$$E_{\mathrm{xc}}^0 = \int_0^\infty \frac{du}{2\pi}\,\mathrm{Tr}\left[\ln(\epsilon)\right] - E_{\mathrm{self}}, \tag{3.31}$$

where ϵ is the isotropic scalar operator $\epsilon = \frac{1}{3}\sum_\mu \epsilon_{\mu,\mu}$, which becomes exact in the uniform limit, due to Eq. (3.30). With the additional assumption that ϵ in Eq. (3.29) is also isotropic, the remaining XC energy is a pure correlation energy, $E_c^{\mathrm{nl}} = E_{\mathrm{xc}} - E_{\mathrm{xc}}^0$, and is in Paper IV found to be

$$E_c^{\mathrm{nl}} = \int_0^\infty \frac{du}{2\pi}\,\mathrm{Tr}\left[\ln(1 + \epsilon^{-1}\left[\boldsymbol{\nabla}, \epsilon\right] \cdot \boldsymbol{\nabla}\mathrm{G})\right]. \tag{3.32}$$

In Paper VI, Eq. (3.32) is shown not to depend on the isotropic assumption, nor on RPA, but is an exact formulation of the deviation from Eq. (3.31).

3.6 ASYMPTOTIC VAN DER WAALS ENERGY

The asymptotic van der Waals energy between two bounded species, separated by a distance R, is given by

$$E_{\mathrm{vdW}} = -\frac{C_6}{R^6}, \tag{3.33}$$

where the strength of the interaction is determined by the coefficient C_6. In second-order perturbation theory, it can be expressed in terms of the total polarization properties, or the polarizabilities, $\alpha(iu)$, of the two species as [43]

$$C_6 = \frac{3}{\pi}\int_0^\infty du\, \alpha_A(iu)\alpha_B(iu). \tag{3.34}$$

The polarizability is obtained from the isotropic polarization operator to the external field,

$$\alpha(iu) = \int d^3r d^3r' \alpha_{\mathrm{ext}}(\mathbf{r}, \mathbf{r}'). \tag{3.35}$$

In analogy with Eq. (3.20), the polarization operator $\boldsymbol{\alpha}_{\mathrm{ext}}$ to the external field is¶

$$\boldsymbol{\alpha}_{\mathrm{ext}} = (\mathbf{1} - \boldsymbol{\alpha} \cdot \boldsymbol{\nabla} V \boldsymbol{\nabla})^{-1} \cdot \boldsymbol{\alpha}, \tag{3.36}$$

so that $\boldsymbol{\nabla} \cdot \boldsymbol{\alpha}_{\mathrm{ext}} \cdot \boldsymbol{\nabla} = \chi$, in conjunction with Eq. (3.27).

Estimates of the asymptotic form Eq. (3.34) may be obtained in a number of ways. By expanding Eq. (3.21) to second order in $\tilde{\chi}$, or by expanding the same equation to second order in the interaction V between separated objects, one obtains formulas precisely on the form Eqs. (3.33), (3.34) and (3.35). The expansions result in different estimates of Eq. (3.36), in terms of the simpler $\boldsymbol{\alpha}$, which may be physically approximated. The first alternative is considered too crude. The second alternative is evaluated approximately in Paper II, and fully in Paper III. In Paper IV, the whole RPA expansion Eq. (3.21) is performed.

A third alternative is to expand Eq. (3.32) to second order in the argument $\epsilon^{-1}\left[\boldsymbol{\nabla}, \epsilon\right] \cdot \boldsymbol{\nabla} \mathrm{G}$, leading to a third estimate of Eq. (3.36), in terms of a related, generalized polarization operator. The benefit is that the expansion is more robust, and may be applied not only in the asymptotic limit, but also at intermediate range, as worked out and performed in Paper VI.

¶The field $\mathbf{E}$ that satisfies $\boldsymbol{\nabla} \cdot \boldsymbol{\epsilon} \cdot \mathbf{E} = \boldsymbol{\nabla} \cdot \mathbf{E}_{\mathrm{ext}}$, and tends to $\mathbf{E}_{\mathrm{ext}}$ at infinity may be written $\mathbf{E} = (\mathbf{1} - \boldsymbol{\nabla} V \boldsymbol{\nabla} \cdot \boldsymbol{\alpha})^{-1} \cdot \mathbf{E}_{\mathrm{ext}}$. Expanding the inverse, it is readily seen that $\boldsymbol{\nabla} \times \mathbf{E} = 0$, so $\mathbf{E} = -\boldsymbol{\nabla}\Phi$. Multiplying by $\boldsymbol{\nabla} \cdot (\mathbf{1} - \boldsymbol{\nabla} V \boldsymbol{\nabla} \cdot \boldsymbol{\alpha})$ from the right yields $\boldsymbol{\nabla} \cdot \mathbf{E} + 4\pi \boldsymbol{\nabla} \cdot \boldsymbol{\alpha} \cdot \mathbf{E} = \boldsymbol{\nabla} \cdot \mathbf{E}_{\mathrm{ext}}$, which becomes $\boldsymbol{\nabla} \cdot \boldsymbol{\epsilon} \cdot \mathbf{E} = \boldsymbol{\nabla} \cdot \mathbf{E}_{\mathrm{ext}}$. Finally evaluating $\mathbf{P} = \boldsymbol{\alpha} \cdot \mathbf{E}$ one obtains Eq. (3.36).

CHAPTER 4

SOFT MATTER

Soft matter is a collective name for a broad class of systems, including both soft materials like polymers, liquid crystals, biosurfaces and membranes and soft molecules such as biomacromolecules and van der Waals complexes [59]. These systems play an important role in such phenomena as lubrication, physisorption and adhesion, and the interactions are to a large extent characterized by the weak ubiquitous van der Waals interaction.

To describe soft matter, a DFT approach that also accounts for those important nonlocal correlations is essential. At the same time as being generally applicable, the method should be efficient and accurate. A development of successively more versatile such functionals is reflected in Papers I-VI, and the major results presented here.

4.1 VAN DER WAALS COMPLEXES

A van der Waals complex consists of two or more stable molecules held together by van der Waals forces [59]. The bond energies are typically in the meV range. This is extremely small compared to covalently bonded molecules, with bond energies in the eV range.

In Paper II, a previously proposed [30, 33] van der Waals density functional is applied to van der Waals complexes. Dynamic polarizabilities and dispersion coefficients, C_6, are obtained with a useful accuracy and at a low computational cost, using ground-state electron densities as input.

As the basic approximation, a very simple model of the polarization response is used,

$$\alpha(\mathbf{r},\mathbf{r}';iu) = \frac{\kappa(\mathbf{r})n(\mathbf{r})}{u^2}\delta^3(\mathbf{r}-\mathbf{r}'), \tag{4.1}$$

where $n(\mathbf{r})$ is the electron density. With $\kappa = 1$, Eq. (4.1) was essentially proposed already by Drude in the end of the nineteenth century. The addition, $\kappa(\mathbf{r})$, is an essential cutoff, which from the gradients of the density locally detects when the polarization properties cannot be approximated as simply as in Eq. (4.1).

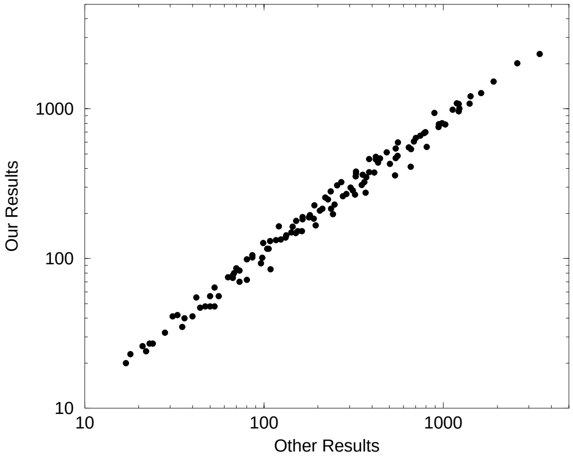

Figure 4.1: Paper II: Values for C_6 of the about 100 van der Waals complexes studied, compared with other results.

In the outer regions of a molecule, the length scale l_d for density variations is shorter than the screening length l_s of the electron gas, which renders Eq. (4.1) to overestimate the response. This essentially only happens at the boundaries of a body, however, where the density is rapidly decaying. The true response in those regions is small, and so better approximated with zero than anything else.

Expressing l_d and l_s in terms of the density and its gradients, the cutoff takes the form

$$\kappa(\mathbf{r}) = \theta(n(\mathbf{r}) - C\,|\boldsymbol{\nabla}\ln(n(\mathbf{r}))|^6), \tag{4.2}$$

where C is a semi-empirical constant, estimated from an analysis of the homogeneous electron gas [60, 28, 12, 20].

As a complexity-reducing step, the electrodynamics is approximated by the solution in the uniform limit, which leads to

$$\alpha_{\text{ext}}(\mathbf{r}, \mathbf{r}') = \frac{\kappa(\mathbf{r})n(\mathbf{r})}{u^2 + 4\pi n(\mathbf{r})}\delta^3(\mathbf{r} - \mathbf{r}'), \tag{4.3}$$

where the κ in the denominator may and has been omitted.

Using Eq. (4.3), the results for C_6 for small and medium-sized molecules are compared with existing results obtained using more cumbersome methods (Fig. 4.1). The simplicity of the functional is such that although the deviations at some points are quite large, the overall statistical agreement is overwhelming.

4.2 FULL-FIELD CALCULATIONS

One of the two major approximations in Paper II is to omit the dependence of the electrodynamics on the density variations (Eq. (4.3)). This omission also

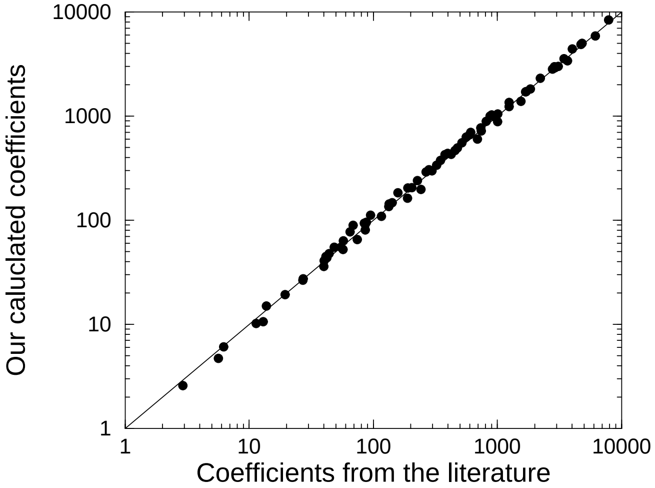

Figure 4.2: Paper III: Values for C_6, for atoms and molecules, obtained by the modified cutoff scheme and the full electrodynamics, compared with other results.

leads to a fully isotropic response to an external field, which is not the case for asymmetric systems, like the interaction between diatomic molecules. In Paper III, the full electrodynamics is performed.

When doing the full electrodynamics a technical complication is that for general geometries, the Poisson equation in a nonuniform dielectric needs to be done. Moreover, due to the cutoff function $\kappa(\mathbf{r})$, this nonuniformity is *stiff*, leading to quite tough calculations. Those are done using a finite element method with an adaptive net-mesher [61].

For atoms and molecules, the major effect of κ is to reduce the response from the outer tails of the species. However, Eq. (4.2) also introduces spurious regions *within* the species, the intra-shell region, leading to severe problems with the numerical solutions. To overcome this problem, and also to unify the treatment of atoms and molecules with the treatment at surfaces [62, 34], the function κ is slightly modified. In the outer tails of a molecule, the density is decaying exponentially, so that $|\boldsymbol{\nabla} \ln(n)|$ is almost constant. Henceforth, an equivalent description, avoiding the intra-shell cutoffs, is to take

$$\kappa(\mathbf{r}) = \theta(n(\mathbf{r}) - c[n]), \tag{4.4}$$

where c is a constant, but dependent on the particular system under study.

This system-dependence reflects a physical property that could not be appropriately assessed in Paper II; the static polarizability, α_0, which can be obtained quite accurately from standard DFT calculations. Fixing the constant $c[n]$ so as to reproduce α_0 has several benefits: (i) The polarizability $\alpha(iu)$ becomes comparable to values from more advanced calculations; (ii) The computational issues becomes manageable; (iii) The statistical error in the calculations of C_6 coefficients goes down; (iv) The procedure is equivalent to the one previously

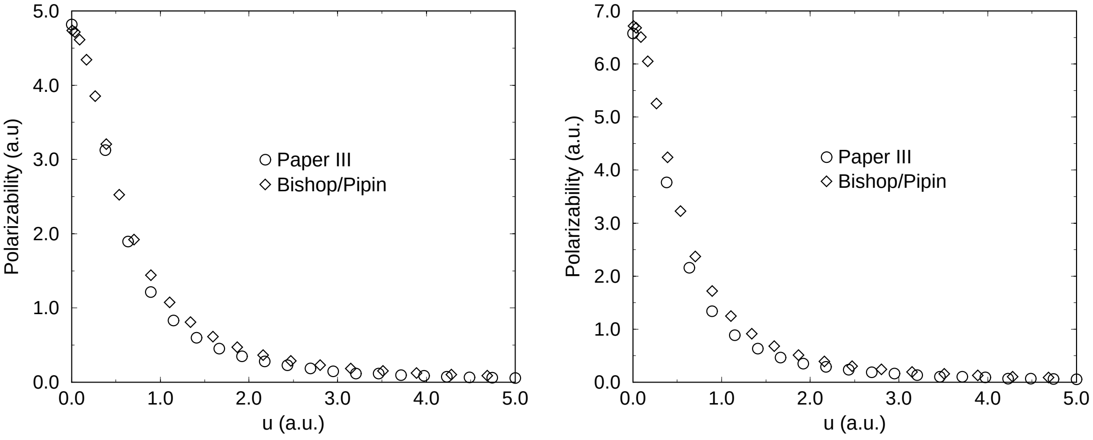

Figure 4.3: Anisotropic polarizability of H_2, as calculated in Paper III, compared to a more accurate calculation [64]. Hartree atomic units. *Left:* $\alpha_{xx}(iu)$. *Right:* $\alpha_{zz}(iu)$.

introduced for surfaces [33]. Equation (4.4) thus gives a consistent treatment of all systems [30, 32, 33, 63, 34] studied.

In Paper III, the full electrodynamics is performed to obtain α_{ext}, using the simple model Eqs. (4.1) and (4.4). Figure 4.2 shows the results obtained by applying the method to atoms and small molecules. The close agreement with more elaborate calculations is reassuring as well as intriguing.

A virtue of doing the full dynamics is that the anisotropic effects can be calculated. Those effects depend on the model for κ. In Fig. 4.3 the results obtained for the hydrogen molecule are shown, compared to a more accurate calculation.

In summary, the prediction of van der Waals coefficients from a knowledge of the density only has been achieved with a reasonable accuracy, and to a low computational cost.

4.3 JELLIUM SURFACES

As exemplified in Papers II and III, the asymptotic properties of the exchange-correlation energy, E_{xc}, are quite successfully described, and the next step is to investigate how a simple model like Eq. (4.1) performs for intermediate-range interactions. In Paper IV this is done within the full RPA. Due to the increased computational complexity, a suitable starting point is the case of two parallel surfaces or slabs, where the equations simplify due to symmetry.

Equation (4.1) gives the correct behavior of the polarizability for slowly varying fields (small wave-vectors q), as in the asymptotic interaction between two pieces of matter. For more rapidly varying fields (larger wave-vectors q), it is not appropriate to consider the polarizability at a certain point to depend on the field in that point only, so the basic polarization model needs to be generalized

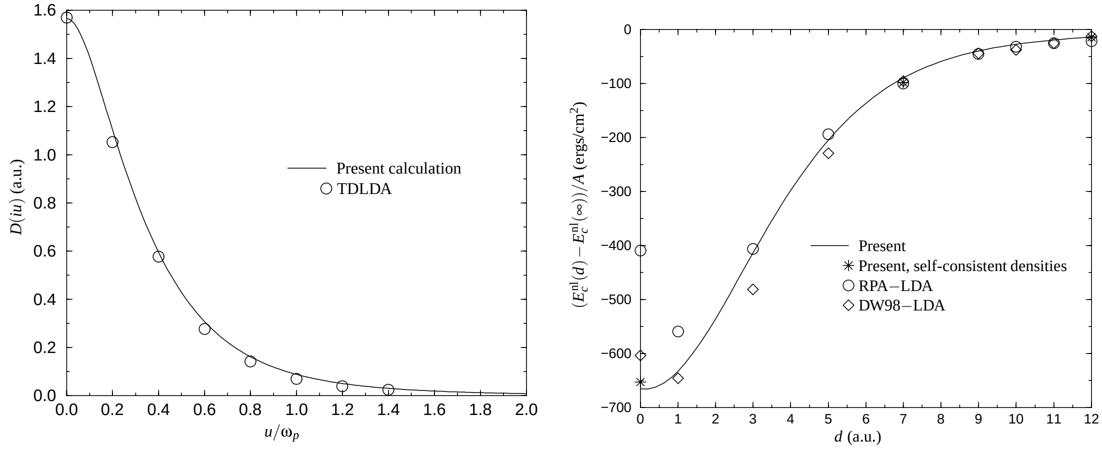

Figure 4.4: *Left:* The D-function $D(iu)$ for a jellium profile of $r_s = 2$, compared to a more accurate calculation [65]. *Right:* Small-separation (d) variation of the non-local correlation energy (ergs/cm^2) between two parallel aluminium jellium slabs, compared to benchmark data [38].

to arbitrary fields. The sharp cutoff function κ is also inappropriate for large wave-vectors q, and it would be desirable to incorporate the *effect* of κ directly into the model of the polarization operator.

A suitable generalization of Eq. (4.1) is to decompose it into Fourier components,

$$\alpha(\mathbf{r}, \mathbf{r}'; iu) = \int \frac{d^3q}{(2\pi)^3} \alpha(\mathbf{r}, \mathbf{q}; iu) e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}, \tag{4.5}$$

and introduce a model for $\alpha(\mathbf{r}, \mathbf{q}; iu)$. In the small-wavevector ($q \to 0$) limit, it should reduce to Eq. (4.1). A simple model obeying this constraint is the plasmon-pole approximation [66],

$$\alpha(\mathbf{r}, \mathbf{q}; iu) = \frac{n(\mathbf{r})}{u^2 + \omega_q^2(\mathbf{r})}, \tag{4.6}$$

where ω_q is a dispersion relation introduced in Paper IV, obtained from experimental experience and studies of the uniform electron gas.

There are several benefits of Eq. (4.6). One is to remedy a deficiency of Eq. (4.1), known as the F-sum rule: $\alpha \to n/u^2$ should hold for large u, and should not be cutoff by κ. Another benefit is that Eq. (4.6) implements the cutoff in a smooth fashion: For example, consider $\alpha_{\rm ext}$ in the uniform limit, the analog of Eq. (4.3). As $q \to 0$ and $u \to 0$, the polarization due to the external field tends to $\alpha_{\rm ext} \to n/(\omega_0^2 + 4\pi n)$, using Eq. (4.6), as opposed to $\alpha_{\rm ext} \to \kappa n/4\pi n = \kappa/4\pi$, obtained from Eq. (4.1). Provided ω_0^2 varies slowly with the density and tends to zero slower than n, Eq. (4.6) cuts off in the same manner as Eq. (4.4).

A deficiency of Eq. (4.6) is that it is not necessarily symmetric (hermitean) for a particular dispersion model ω_q. This is remedied in Paper VI.

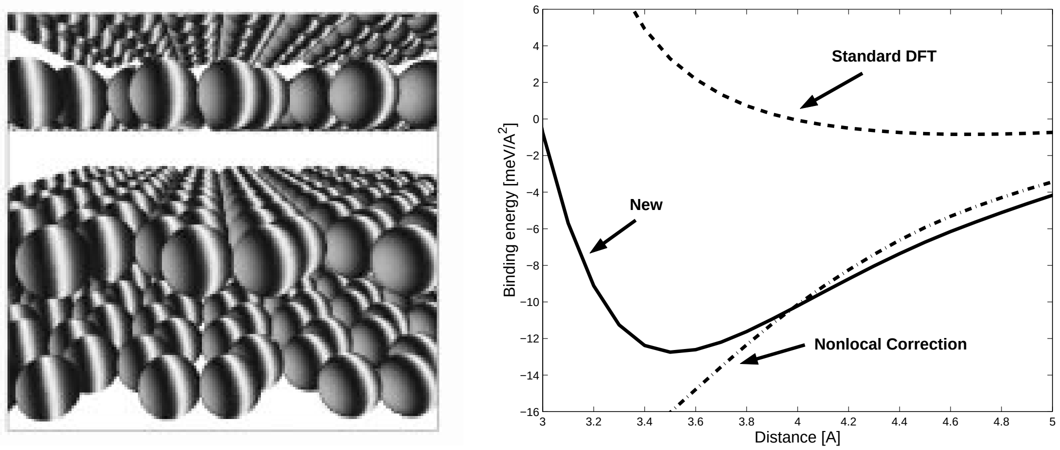

Figure 4.5: *Left:* The hexagonal graphite structure. *Right:* The graphene-graphene binding-energy curve of Paper V, calculated with the method of Paper IV, and compared with a standard DFT calculation.

In Paper IV, the full RPA is performed on the case of two parallel jellium slabs, a distance d apart. Due to the translational symmetry, a reasonable polarization operator can be introduced, which retains the property of being symmetric, readily invertible and yet sufficiently similar to the uniform gas to be useful.

Just as in Paper III, the smoothed cutoff of Paper IV is adjusted so as to reproduce the static polarization properties of the jellium surface. The appropriate quantity here is the induced surface charge and a related function $D(iu)$, which is fixed to results of accurate calculations of $D(0)$. The dynamic behavior of $D(iu)$ is then well reproduced, as shown in Fig. 4.4.

A benchmark test is made, comparing the results for the nonlocal correlation at intermediate range to a complete RPA calculation (DW98), without the simplifying polarization model. The agreement with DW98 reflects the inherent similarities.

The computational speedup enabled by the simple polarization model and the method derived in Paper IV is about a thousand times compared to DW98, due to the overall lower complexity.

4.4 GRAPHITE

As a full-fledged application of the functional developed in Paper IV, the functional is in Paper V applied to the familiar material graphite, and the interaction of graphene layers. Graphite has a layered structure, consisting of planes of tightly bound carbon atoms, arranged in a hexagonal honeycomb lattice (Fig. 4.5). The bond between the planes is very weak, with a tiny electronic overlap. Standard DFT estimates the exchange-correlation effects from this small overlap only, but the physical interaction is *between* the layers, which explains the inability of the

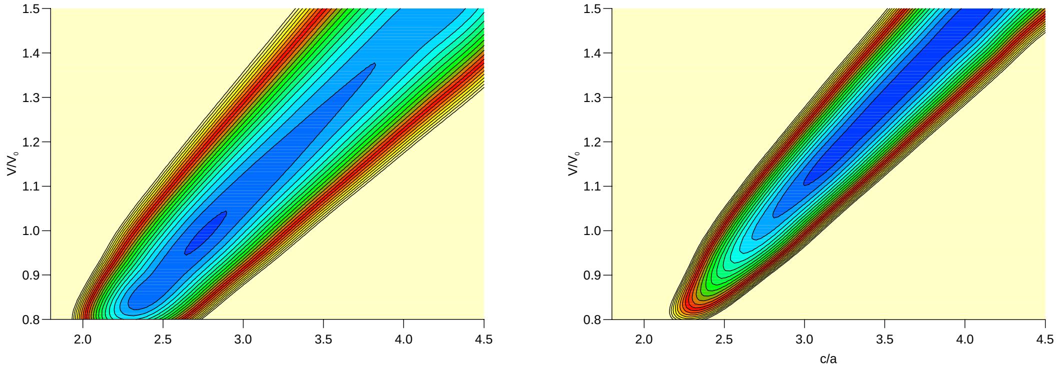

Figure 4.6: Paper V: Total-energy contour plot, in the $V/V_0 - c/a$ plane calculated with standard DFT. The direction of the trough corresponds to a changing distance between the planes. *Left:* LDA, which exhibits a coincidal minimum. *Right:* GGA, which is a refined functional, shows no minimum.

standard DFT to account for the van der Waals interactions.

The result of the application to two graphene layers (Paper V) is shown in Fig. 4.5 (right). The results for graphite are almost indistinguishable from this simpler system, as shown in Paper V. The bond length, binding energy and bulk modulus obtained for graphite are all in good agreement with experiment [67, 68, 69], whereas the standard DFT clearly does not apply in this extreme case (Fig. 4.6).

During the last two decades, ample results for Graphite have been calculated, using LDA [70, 71, 72, 73, 74, 75, 76], and reporting results in reasonable agreement with experiment. This can be nothing but a coincidence, since the LDA cannot, by construction, account for van der Waals bonds.

An interesting fact, which should add significant research-sociological questions, is that no-one so far has reported that standard DFT gives results for graphite in strong disagreement with experiment (Fig. 4.6). The use of the methods derived in Papers IV and VI seems to be one way to remedy this restriction in applicability of the standard DFT, and extend it to also include soft matter.

CHAPTER 5

TOWARDS A UNIVERSAL FUNCTIONAL

A general XC functional should be robust; it should work for all systems, in particular yielding physical behavior for all inhomogeneous systems. As shown in Papers II and III, the asymptotic form of the XC functional is well accounted for [30, 32, 35], and a first step towards more medium-ranged interactions is given in Papers IV and V. To date, these long- and medium-range investigations have been completely separated from close-ranged studies of the exchange-correlation [52, 22] and kinetic [77, 78, 79] energies. This reflects the fact that close-range energetics and asymptotic forms are quite unrelated properties of the XC functional, but in the intermediate-range regime that is no longer the case. As the regimes are merged, the information from both ends becomes equally important.

In Paper VI, the method developed in Paper IV and explored in Paper V is generalized to arbitrary geometries. One way to do this, in general, is to calculate the full RPA on an approximate dielectric function, as described in Chap. 3. Another way is to do an approximate evaluation of the RPA, with a different approximation as input, as is explored and pursued in Paper VI.

5.1 AN EXPANSION THAT WORKS

In order to find a suitable approximate evaluation of the RPA, the problem needs to be reformulated. It turns out that in doing so, it becomes possible, in principle, to push the approximation *beyond* RPA, in a systematic way.

In Paper IV, the exchange-correlation energy was decomposed into two parts; one regular part representing the present knowledge of the functional, and one containing the nonlocal properties. The word ”regular” is here used in the sense ”major”, and emphasizes that the regular portion of the XC energy is large and well known within the framework of the LDA and GGA [2, 6, 18, 15, 16].

The present approach to E_c^{nl} has the following guiding principles: (i) Express E_{xc}^0 and E_c^{nl} in the *same* quantity, the generalized polarization operator s_{xc}; (ii) Make a simple parameterization of s_{xc}, based on previous studies of nonlocal functionals [30, 32, 35, 37]; (iii) Adjust the parameterization to both regular and nonlocal key properties, utilizing previous studies of the XC hole [6, 18, 51, 52, 22].

The generalized polarization operator, s_{xc}, is in Paper VI defined as the logarithmic expression

$$s_{\mathrm{xc}}[n] = \ln(\epsilon[n]). \tag{5.1}$$

It has a number of useful properties: (i) In the uniform limit, it is exactly related to the exact coupling-constant averaged many-body response function; (ii) Its frequency integral is exactly related to the exchange-correlation hole [6, 18]; (iii) The regular (major) part of the XC energy hole is a linear functional of s_{xc}; (iv) The nonlocal part of the XC energy hole is to a good approximation a quadratic functional of s_{xc}.

The key point behind the last statement is the observation that the nonlocal energy Eq. (3.32) is expressed quite conveniently in terms of s_{xc}, via the series

$$\epsilon^{-1}\left[\boldsymbol{\nabla}, \epsilon\right] \cdot \boldsymbol{\nabla} \mathrm{G} = \sum_{n=1}^{\infty} \frac{1}{n!} \mathbf{d}_n \cdot \mathbf{d}_0 \mathrm{G}, \tag{5.2}$$

where

$$\mathbf{d}_{n+1} = \left[s_{\mathrm{xc}}, \mathbf{d}_n\right], \tag{5.3}$$

together with the starting criterion $\mathbf{d}_0 = \boldsymbol{\nabla}$. As shown in Paper VI, the convergence of the series Eq. (5.2) is extremely rapid in the limit of small variations, and also for slightly more general conditions.

5.2 EVALUATION OF E_C^{NL}

In terms of the generalized polarization operator s_{xc}, the regular XC energy is expressed as

$$E_{\mathrm{xc}}^{0} = \int_0^\infty \frac{du}{2\pi} \operatorname{Tr}\left[s_{\mathrm{xc}}\right] - E_{\mathrm{self}}, \tag{5.4}$$

and the nonlocal correlation energy as

$$E_c^{\mathrm{nl}} = \int_0^\infty \frac{du}{4\pi} \operatorname{Tr}\left[s_{\mathrm{xc}}^2 - (s_{\mathrm{xc}}\mathbf{T})^2\right] + \mathcal{O}(\delta^3), \tag{5.5}$$

where δ is a small measure discussed in Paper VI, and $\mathbf{T} \equiv \boldsymbol{\nabla}\mathrm{G}\boldsymbol{\nabla}$ is the 3×3 dyadic operator, such that $\mathbf{T}^2 = \mathbf{T}$, and the trace over the 3x3 matrix yields 1.

Several points can be made about Eq. (5.5). (i) It is positive for all s_{xc}, and hence the nonlocal contributions (to second order) are always positive. (ii) For a uniform system, it vanishes identically, since s_{xc} then commutes with $\mathbf{T}$. (iii) It is equivalent to the second-order expansion of the expression used in Paper IV, for which $\delta = 0$ holds rigorously. Hence, Eq. (5.5) is a three-dimensional generalization of that functional, with the addition of allowing more realistic polarizability models.

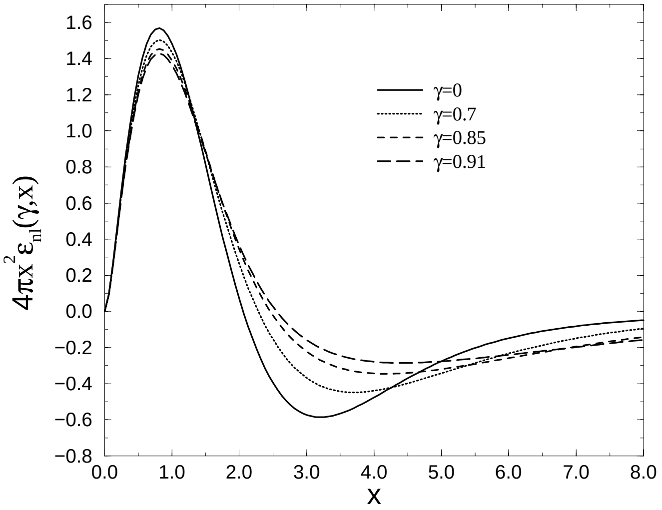

Figure 5.1: The universal nonlocal correlation-interaction $\varepsilon_{\rm nl}(\gamma, x)$ of Paper VI. The figure shows the interaction as a function of scaled distance $x = q_{\rm eff}\,|\mathbf{r} - \mathbf{r}'|$, for varying differences between the end points $\mathbf{r}$ and $\mathbf{r}'$, expressed in the parameter $\gamma \in [0, 1[$. The density-dependent parameters $q_{\rm eff}$ and γ are defined in the text.

5.3 EXPLICIT NONLOCAL CORRELATION DENSITY FUNCTIONAL

The major part of Paper VI is devoted to an investigation of a particular parameterization of $s_{\rm xc}$, based on the simple polarization operator Eq. (4.5). With this particular parameterization, $E_c^{\rm nl}$ becomes a two-point integral over a correlation-interaction $\varepsilon_{\rm nl}(\gamma, x)$, explicitly expressed as

$$E_c^{\rm nl} = \frac{1}{2}\int d^3r d^3r'\, n(\mathbf{r})n(\mathbf{r}')\varepsilon_{\rm nl}\left(\frac{q_0^2(\mathbf{r}) - q_0^2(\mathbf{r}')}{q_0^2(\mathbf{r}) + q_0^2(\mathbf{r}')}, \sqrt{\frac{q_0^2(\mathbf{r}) + q_0^2(\mathbf{r}')}{2}}\,|\mathbf{r} - \mathbf{r}'|\right). \quad (5.6)$$

Here, $\varepsilon_{\rm nl}(\gamma, x)$ is a (within the model) universal interaction function, shown in Fig. 5.1. The interaction is governed by two properties: (i) the effective scale, $q_{\rm eff}$, on which the interaction occurs; and (ii) a measure of the difference in electronic density at the interacting points, γ. Notably, $\varepsilon_{\rm nl}(\gamma, x)$ is almost independent of γ at short range, whereas the effect becomes large at intermediate and long range. This explains why long-ranged interactions are so much harder to predict than short- and intermediate-ranged interactions.

The effective scale of the interaction, $q_{\rm eff}$, is a function of the local scale function, q_0, at the interacting points. It is defined as

$$q_0(\mathbf{r}) = k_F(\mathbf{r}) f(n(\mathbf{r}), s(\mathbf{r})), \quad (5.7)$$

where $f(n, s)$ is a function of the density n and the reduced density gradient s [15, 16], and behaves very similarly to the enhancement factor, $F_{\rm xc}$ [22]. In

Paper VI, it is given by

$$f(n,s) = F_{\mathrm{xc}}^{\mathrm{RPA}}(n) + \mu s^2, \tag{5.8}$$

where $F_{\mathrm{xc}}^{\mathrm{RPA}}$ is the enhancement factor obtained by doing the local density approximation in the RPA, and μ is the effective gradient coefficient of GGA [16].

For low densities, Eq. (5.6) is precisely the deviation from the LDA. For higher densities, a semilocal correction, E_c^{sl}, needs to be added, as discussed in Paper VI. Explicitly, the total correlation energy is given by

$$E_c = E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}} + E_c^{\mathrm{sl}}. \tag{5.9}$$

Eq. (5.9) is the first correlation functional that explicitly contains the van der Waals interaction.

The parameterization of s_{xc} performed in Paper VI is the first of a manifold of possible parameterizations, of which a large class eventually would lead to a function of the kind shown in Fig. 5.1. One should expect that the details of $\varepsilon_{\mathrm{nl}}(\gamma, x)$ are subject to minor changes, as more refined analyses are performed.

At this point there might be objections referring to computational tractability. Undoubtly, a two-point integral, like Eq. (5.6), might seem computationally more demanding than a simple local functional, like the LDA. However, that is not necessarily so, mainly for two reasons: (i) In the general context of diagonalizing a set of N electrons, an $\mathcal{O}(N^3)$ process, the $\mathcal{O}(N^2)$ work needed to evaluate a two-point integral over the basis functions is not a hindrance, and (ii) in the unlikely event of being the bottleneck, a nonlocal functional may, rigorously and unambiguously, be approximated by a power series in gradients, which might be used in future XC functionals that would set their foot on much the same path, where already the GGA has walked.

CHAPTER 6

CONCLUSIONS AND OUTLOOK

In this thesis, the many-faceted nature of nonlocal correlations has been explored. The examples presented illuminate the importance of physical models for the interactions, all in order to gain stability, robustness, and transferability between systems. A scheme has been outlined, with which a systematic improvement beyond LDA and GGA, including long- and medium-ranged correlations, may be achieved. Studies of van der Waals interactions in molecules, and of nonlocal correlations between surfaces illustrate the physical effects of such a scheme. Finally an explicit formula for a general nonlocal correlation density functional has been given. In conclusion, it has been clearly shown that a future general functional for practical work with DFT should include the nonlocal correlations, and the methods developed in Papers IV and VI are candidates for such a general functional.

6.1 REASONS FOR A NONLOCAL PERSPECTIVE

An important reason for using nonlocal functionals is the physical insights that can be gained from doing so. For instance, consider the attractive tail of the universal function $\varepsilon_{\mathrm{nl}}(\gamma, x)$ in Fig. 5.1: it is not hard to imagine that once applied, it will make well-separated species approach each other. That is not so easily seen from a local function.

Another desirable property of a nonlocal functional is the robustness gained, and the potential unnecessity to take the self-consistency scheme into extremes; it is my belief that the local character of the existing functionals is responsible for the requirement of such detailed self-consistency, simply because the sensitivity to the density is so much higher when all dependency is concentrated to a single point.

As an example of the benefits of a nonlocal picture, I would like to briefly discuss a current topic, concerning the applicability of GGA to van der Waals complexes. In a recent study [80], the authors conclude:

> Despite its occasional difficulties with dispersion the PW91 functional may be a viable alternative to the *ab initio* methods, certainly in

> situations where large complexes are being studied.

The study concerns, among other species, the molecules Ne_2 and Ar_2. I think the above quote can only be true to the extent that the species are *not* van der Waals or correlation bonded, and can thus not be considered a viable alternative. First, another study [81] shows that the major binding in these systems is due to an overlap of atomic densities, which in my opinion explains why the GGA gives a binding at all. Secondly, there is a natural reason for this restriction.

In GGA, the exchange is a function of the reduced density gradient s. The exchange energy shows a simple trend in the interaction between two separate species, whether it be atoms or surfaces. It increases with distance, up to some critical point, where it starts to decrease. At large separations, it continues to decrease. Generally, there is a (chemical) binding at short separations, whereas at large separations, there is only repulsion. For a correlation bonded species, this repulsion must be balanced by an attractive correlation. But the correlation is based on the same measure, s, as the exchange, so *effectively* there is only one energy, the exchange-correlation energy, which by necessity should show the same trend, although possibly more intricately. Trying to grasp additional features only obscures the physics by more complex behavior, and is likely to destroy transferability.

Given this simple argument, a GGA cannot in principle, and *should not* in practice, distinguish between a chemical bond and a correlation bond. The solution is of course to add on a truly nonlocal correlation energy.

6.2 ACTIVE AREA OF RESEARCH

The theory of nonlocal density functionals is only in its cradle. As the desire to treat more of soft matter increases, the desire to investigate those functionals will also increase. However, beginning to investigate nonlocal functionals immediately opens up a new can of worms, with consequences that can only be imagined. In departing from the LDA, and attacking systems outside the limit of applicability of gradient expansions, a whole new set of questions arise. One or two of those questions might have been answered in this thesis, but the overwhelming majority still remains.

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APPENDIX A

DETERMINANTS

The block determinants that emerge from differential equations in any dimension may be simplified. Here we start out by finding the appropriate recursion formula, which is similar in structure to the simple tridiagonal formula.

Definition 1 Let A_k,B_k,C_k denote a set of quadratic matrices of rank m. Let the assembly of a larger, tridiagonal block matrix M, consisting of those matrices, be called a *tridiagonal m-block matrix of order n*,

$$\mathrm{M} = \begin{pmatrix} A_1 & B_1 & 0 & \dots & \dots & 0 \\ C_1 & A_2 & B_2 & \ddots & \ddots & \vdots \\ 0 & C_2 & A_3 & B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & C_{n-2} & A_{n-1} & B_{n-1} \\ 0 & \dots & \dots & 0 & C_{n-1} & A_n \end{pmatrix}. \tag{A.1}$$

Let $N = mn$ denote the rank of M.

Theorem 1 *Let* $|\mathrm{M}|$ *be the determinant of the m-block matrix* M *of order n. Then,*

$$|\mathrm{M}| = |\tilde{A}_n|, \tag{A.2}$$
$$\tilde{A}_k = C_{k-1}\tilde{A}_{k-1}C_{k-1}^{-1}A_k - C_{k-1}C_{k-2}\tilde{A}_{k-2}C_{k-2}^{-1}B_{k-1},$$

With the initial conditions $\tilde{A}_{-1} = 0$ *and* $\tilde{A}_0 = 1$. *Any undefined* A_k, B_k *or* C_k *may be chosen arbitrarily.*

Proof of Theorem 1 Extract the lower diagonal of M of Eq. (A.1), yielding

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & C_1 & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} A_1 & B_1 & 0 & \dots & \dots & 0 \\ 1 & C_1^{-1}A_2 & C_1^{-1}B_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.3}$$

Divide the left and multiply the right part of the second row by A_1,

$$\left|\begin{array}{cccccc} 1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & C_1A_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \cdots & \cdots & 0 & 0 & C_{n-1} \end{array}\right\| \left.\begin{array}{cccccc} A_1 & B_1 & 0 & \cdots & \cdots & 0 \\ A_1 & A_1C_1^{-1}A_2 & A_1C_1^{-1}B_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \cdots & \cdots & 0 & 1 & C_{n-1}^{-1}A_n \end{array}\right|. \tag{A.4}$$

Subtract the right part of the first block from the second,

$$\left|\begin{array}{cccccc} 1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & C_1A_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \cdots & \cdots & 0 & 0 & C_{n-1} \end{array}\right\| \left.\begin{array}{cccccc} A_1 & B_1 & 0 & \cdots & \cdots & 0 \\ 0 & A_1C_1^{-1}A_2 - B_1 & A_1C_1^{-1}B_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \cdots & \cdots & 0 & 1 & C_{n-1}^{-1}A_n \end{array}\right|. \tag{A.5}$$

Put back another factor of C_1 on the second row,

$$\left|\begin{array}{cccccc} 1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & C_1A_1^{-1}C_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \cdots & \cdots & 0 & 0 & C_{n-1} \end{array}\right\| \left.\begin{array}{cccccc} A_1 & B_1 & 0 & \cdots & \cdots & 0 \\ 0 & C_1A_1C_1^{-1}A_2 - C_1B_1 & C_1A_1C_1^{-1}B_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \cdots & \cdots & 0 & 1 & C_{n-1}^{-1}A_n \end{array}\right|. \tag{A.6}$$

The left part of the second row simplifies to A_1^{-1}.

$$\left|\begin{array}{cccccc} 1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & A_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \cdots & \cdots & 0 & 0 & C_{n-1} \end{array}\right\| \left.\begin{array}{cccccc} A_1 & B_1 & 0 & \cdots & \cdots & 0 \\ 0 & C_1A_1C_1^{-1}A_2 - C_1B_1 & C_1A_1C_1^{-1}B_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \cdots & \cdots & 0 & 1 & C_{n-1}^{-1}A_n \end{array}\right|. \tag{A.7}$$

Define

$$\begin{aligned} \tilde{A}_{k+1} &= C_k\tilde{A}_kC_k^{-1}A_{k+1} - C_k\tilde{B}_k, \\ \tilde{B}_{k+1} &= C_k\tilde{A}_kC_k^{-1}B_{k+1}, \\ \tilde{A}_0 &= 1, \\ \tilde{A}_{-1} &= 0. \end{aligned} \tag{A.8}$$

Applying Eq. (A.8) to Eq. (A.7) we get

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & 1 & C_2^{-1}A_3 & C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.9}$$

Now, multiply the third row by the approriate factor,

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2\tilde{A}_2^{-1} & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & \tilde{A}_2 & \tilde{A}_2C_2^{-1}A_3 & \tilde{A}_2C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.10}$$

Subtract the second row,

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2\tilde{A}_2^{-1} & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & 0 & \tilde{A}_2C_2^{-1}A_3 - \tilde{B}_2 & \tilde{A}_2C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.11}$$

Put back the extra factor of C,

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2\tilde{A}_2^{-1}C_2^{-1} & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & 0 & C_2\tilde{A}_2C_2^{-1}A_3 - C_2\tilde{B}_2 & C_2\tilde{A}_2C_2^{-1}B_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.12}$$

Again, the left part simplifies, and putting in the definitions (A.8) yields

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & \tilde{A}_2^{-1} & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & C_{n-2} & 0 \\ 0 & \dots & \dots & 0 & 0 & C_{n-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & 0 & \tilde{A}_3 & \tilde{B}_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 1 & C_{n-2}^{-1}A_{n-1} & C_{n-2}^{-1}B_{n-1} \\ 0 & \dots & \dots & 0 & 1 & C_{n-1}^{-1}A_n \end{vmatrix}. \tag{A.13}$$

Repeating the steps above, we end up with the matrix

$$\begin{vmatrix} 1 & 0 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_1^{-1} & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & \tilde{A}_2^{-1} & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & \tilde{A}_{n-2}^{-1} & 0 \\ 0 & \dots & \dots & 0 & 0 & \tilde{A}_{n-1}^{-1} \end{vmatrix} \begin{vmatrix} \tilde{A}_1 & \tilde{B}_1 & 0 & \dots & \dots & 0 \\ 0 & \tilde{A}_2 & \tilde{B}_2 & \ddots & \ddots & \vdots \\ 0 & 0 & \tilde{A}_3 & \tilde{B}_3 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & \tilde{A}_{n-1} & \tilde{B}_{n-1} \\ 0 & \dots & \dots & 0 & 0 & \tilde{A}_n \end{vmatrix}. \tag{A.14}$$

The left determinant if just the product of the determinants of the diagonal blocks. The right determinant is upper triangular, which again means the product of diagonal blocks. The terms $\tilde{A}_1$ to $\tilde{A}_{n-1}$ hence cancel, yielding

$$|M| = |\tilde{A}_n|, \tag{A.15}$$

which completes the proof.

Discussion 1.1 Clearly, if the blocks are of rank m and A_k is d-sparse, *i.e.,* have at most d off-diagonal elements, and B_k and C_k are diagonal, which is the common case for differential operators, then the work to complete the determinant is $\mathcal{O}(dnm^2 + m^3)$. With N denoting the rank of the total matrix, and assuming that N is equally distributed in all dimensions, $N = n^d$, $m = n^{d-1}$, the total work scales as $\mathcal{O}(dN^{2-1/d} + N^{3(1-1/d)})$. Note that this is considerably better the general case, $\mathcal{O}(N^3)$, when d is small. In three dimensions for instance, it is $\mathcal{O}(N^2)$.

Definition 2 Let S be the symmetric tridiagonal m-block matrix of order n,

$$\mathrm{S} = \begin{pmatrix} P_1 & Q_1^\dagger & 0 & \dots & \dots & 0 \\ Q_1 & P_2 & Q_2^\dagger & \ddots & \ddots & \vdots \\ 0 & Q_2 & P_3 & Q_3^\dagger & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & Q_{n-2} & P_{n-1} & Q_{n-1}^\dagger \\ 0 & \dots & \dots & 0 & Q_{n-1} & P_n \end{pmatrix}, \tag{A.16}$$

constructed from the symmetric blocks P_k and Q_k. Let Q denote the matrix constructed from the blocks Q_k,

$$\mathrm{Q} = \begin{pmatrix} Q_1 & 0 & 0 & \dots & \dots & 0 \\ 0 & Q_2 & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & Q_3 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & Q_{n-1} & 0 \\ 0 & \dots & \dots & 0 & 0 & Q_n \end{pmatrix}, \tag{A.17}$$

where Q_n is arbitrary. Let x be a m-block vector of order n,

$$\mathrm{x} = \begin{vmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_{n-1} \\ x_n \end{vmatrix}. \tag{A.18}$$

Theorem 2 *Let* S *be a symmetric tridiagonal m-block matrix of order n. Then*

$$|\mathrm{S}| = (-1)^{mn}|\mathrm{Q}||x_{n+1}|, \tag{A.19}$$

with x *satisfying the homogeneous equation* $\mathrm{Sx} = 0$,

$$\begin{aligned} Q_{k-1}x_{k-1} + P_k x_k + Q_k^\dagger x_{k+1} &= 0, \\ x_1 &= 1, \\ x_0 &= 0. \end{aligned} \tag{A.20}$$

Proof of Theorem 2 Extract $-Q$ from Eq. (A.16),

$$\begin{vmatrix} -Q_1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & -Q_2 & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & -Q_3 & 0 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 & -Q_{n-1} & 0 \\ 0 & \cdots & \cdots & 0 & 0 & -Q_n \end{vmatrix} \begin{vmatrix} -Q_1^{-1}P_1 & -Q_1^{-1}Q_1^\dagger & 0 & \cdots & \cdots & 0 \\ -Q_2^{-1}Q_1 & -Q_2^{-1}P_2 & -Q_2^{-1}Q_2^\dagger & \ddots & \ddots & \vdots \\ 0 & -Q_3^{-1}Q_2 & -Q_3^{-1}P_3 & -Q_3^{-1}Q_3^\dagger & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & -Q_{n-1}^{-1}Q_{n-2} & -Q_{n-1}^{-1}P_{n-1} & -Q_{n-1}^{-1}Q_{n-1}^\dagger \\ 0 & \cdots & \cdots & 0 & -Q_n^{-1}Q_{n-1} & -Q_n^{-1}P_n \end{vmatrix}. \tag{A.21}$$

Note that Q_n is arbitrary. The left determinant may be written as $(-1)^{mn}|\mathrm{Q}|$,

$$(-1)^{mn}|\mathrm{Q}| \begin{vmatrix} -Q_1^{-1}P_1 & -Q_1^{-1}Q_1^\dagger & 0 & \cdots & \cdots & 0 \\ -Q_2^{-1}Q_1 & -Q_2^{-1}P_2 & -Q_2^{-1}Q_2^\dagger & \ddots & \ddots & \vdots \\ 0 & -Q_3^{-1}Q_2 & -Q_3^{-1}P_3 & -Q_3^{-1}Q_3^\dagger & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & -Q_{n-1}^{-1}Q_{n-2} & -Q_{n-1}^{-1}P_{n-1} & -Q_{n-1}^{-1}Q_{n-1}^\dagger \\ 0 & \cdots & \cdots & 0 & -Q_n^{-1}Q_{n-1} & -Q_n^{-1}P_n \end{vmatrix}. \tag{A.22}$$

Let

$$\begin{aligned} A_k &= -Q_k^{-1}P_k, \\ B_k &= -Q_k^{-1}Q_k^\dagger, \\ C_k &= -Q_{k+1}^{-1}Q_k. \end{aligned} \tag{A.23}$$

Inserting into the recursion formula derived in Theorem1 yields

$$\begin{aligned} \tilde{A}_k = C_{k-1}\tilde{A}_{k-1}C_{k-1}^{-1}A_k - C_{k-1}C_{k-2}\tilde{A}_{k-2}C_{k-2}^{-1}B_{k-1} &= \\ (-Q_k^{-1}Q_{k-1})\tilde{A}_{k-1}(-Q_k^{-1}Q_{k-1})^{-1}(-Q_k^{-1}P_k) - (-Q_k^{-1}Q_{k-1})(-Q_{k-1}^{-1}Q_{k-2})\tilde{A}_{k-2}(-Q_{k-1}^{-1}Q_{k-2})^{-1}(-Q_{k-1}^{-1}Q_{k-1}^\dagger) &= \\ (-Q_k^{-1}Q_{k-1})\tilde{A}_{k-1}(-Q_{k-1}^{-1}Q_k)(-Q_k^{-1}P_k) - (-Q_k^{-1}Q_{k-1})(-Q_{k-1}^{-1}Q_{k-2})\tilde{A}_{k-2}(-Q_{k-2}^{-1}Q_{k-1})(-Q_{k-1}^{-1}Q_{k-1}^\dagger) &= \\ (-Q_k^{-1}Q_{k-1})\tilde{A}_{k-1}(-Q_{k-1}^{-1})(-P_k) - (-Q_k^{-1})(-Q_{k-2})\tilde{A}_{k-2}(-Q_{k-2}^{-1})(-Q_{k-1}^\dagger) &= \\ -Q_k^{-1}Q_{k-1}\tilde{A}_{k-1}Q_{k-1}^{-1}P_k - Q_k^{-1}Q_{k-2}\tilde{A}_{k-2}Q_{k-2}^{-1}Q_{k-1}^\dagger&. \end{aligned} \tag{A.24}$$

After rearranging and insertion of the unity $Q_k^{-1}Q_k$,

$$Q_k\tilde{A}_kQ_k^{-1}Q_k + Q_{k-1}\tilde{A}_{k-1}Q_{k-1}^{-1}P_k + Q_{k-2}\tilde{A}_{k-2}Q_{k-2}^{-1}Q_{k-1}^\dagger = 0. \tag{A.25}$$

Let $x_{k+1} = Q_k^{-1}\tilde{A}_k^TQ_k$. Note that $|x_{k+1}| = |\tilde{A}_k|$. Also note that the matrix P_k is symmetric by construction. Transposing Eq. (A.25) and inserting the definition of x_k yields

$$Q_{k-1}x_{k-1} + P_kx_k + Q_k^\dagger x_{k+1} = 0, \tag{A.26}$$

which may also be written $\mathrm{Sx} = 0$. By virtue of Theorem1, the determinant $|\mathrm{S}|$ of Eq. (A.16) is now given by

$$|\mathrm{S}| = (-1)^{mn}|\mathrm{Q}||x_{n+1}|, \tag{A.27}$$

with the initial conditions,

$$\begin{aligned} x_1 &= Q_0^{-1}\tilde{A}_0^T Q_0 = Q_1^{-1}(1)Q_1 = 1, \\ x_0 &= Q_1^{-1}\tilde{A}_{-1}^T Q_1 = Q_1^{-1}(0)Q_1 = 0. \end{aligned} \tag{A.28}$$

This completes the proof.

Theorem 3 *The determinant of the symmetric tridiagonal m-block matrix* S *of order n is given by*

$$|\mathrm{S}| = (-1)^{mn}|\mathrm{Q}|\frac{|y_{n+1}|}{|y_1|}, \tag{A.29}$$

with y *being the m-block vector satisfying* $\mathrm{Sy} = 0$*, and* $y_0 = 0$*.* Q_n *and* y_{n+1} *are arbitrary.*

Proof of Theorem 3 Let $\mathrm{x} = \mathrm{y}y_1^{-1}$. Then $x_0 = 0$, $x_1 = 1$. Since $\mathrm{Sx} = \mathrm{Sy}y_1^{-1} = 0$, the proof is complete once we note that $x_{n+1} = y_{n+1}y_1^{-1}$.

Discussion 3.1 Theorem3 states that it is possible to evaluate the determinant by solving a set of homogeneous equations with different boundaries, and then combine them into a determinant the size of the boundary.

Theorem 4 *Let* S *and* $\mathrm{S}^{(0)}$ *be two symmetric tridiagonal m-block matrices of order n. Then*

$$\frac{|\mathrm{S}|}{|\mathrm{S}^{(0)}|} = \frac{|\mathrm{Q}|}{|\mathrm{Q}^{(0)}|}\frac{1}{|1 + u_1^{-1}x_1|}, \tag{A.30}$$

where x *is the m-block vector that satisfies*

$$\mathrm{S}(\mathrm{x} + \mathrm{u}) = 0 \tag{A.31}$$

with boundary conditions $x_0 = x_{n+1} = 0$*,* Q_n *is arbitrary, and* u *is any m-block that satifies* $\mathrm{S}^{(0)}\mathrm{u} = 0$*,* $u_0 = 0$*.*

Proof of Theorem 4 Let y of Theorem3 satisfy $\mathrm{Sy} = 0$, $y_0 = 0$, $y_{n+1} = u_{n+1}$. Require that $S^{(0)}u = 0$, $u_0 = 0$. Then, by virtue of Theorem3 we have

$$\frac{|\mathrm{S}|}{|\mathrm{S}^{(0)}|} = \frac{|G_{n+1}|}{|y_1|}\frac{|u_1|}{|u_{n+1}|}\frac{|\mathrm{Q}|}{|\mathrm{Q}^{(0)}|} = \frac{|\mathrm{Q}|}{|\mathrm{Q}^{(0)}|}\frac{|u_1|}{|y_1|}. \tag{A.32}$$

Let y be $\mathrm{y} = \mathrm{x} + \mathrm{u}$, $\mathrm{S}(\mathrm{x} + \mathrm{u}) = 0$, $x_0 = x_{n+1} = 0$. Then

$$\frac{|u_1|}{|y_1|} = \frac{|u_1|}{|u_1 + x_1|} = \frac{1}{|1 + u_1^{-1}x_1|}, \tag{A.33}$$

which completes the proof.

Discussion 4.1 We may always choose u_1 to be unitary, $u_1^{-1} = u_1^\dagger$. This seems innocent, but actually further reduces the computational complexity. We can assume that $u_1^\dagger x_1$, which is the linear response of the system, is sparse; it is really unnatural that when applying a dipole field, the system responds with a large quadropole field, etc. Hence, the computationl complexity of Eq. (A.30) may be approximated with $\mathcal{O}(m^2)$, rather than $\mathcal{O}(m^3)$. The analysis of Theorem1 may be simplified. Assume $u_1^\dagger x_1$ is p-sparse. Then the total complexity of $|\mathrm{S}|$ is $\mathcal{O}(dN^{2-1/d} + pN^{2(1-1/d)})$, which in three dimensions becomes $\mathcal{O}(N^{5/3})$.

Definition 3 Let a *symmetric, isotropic, second-order differential operator* $\hat{S}$ in d dimensions be given by

$$\hat{S} = \sum_{i=1}^{d} \partial_i \hat{\epsilon} \partial_i, \tag{A.34}$$

where $\hat{\epsilon}$ is any operator. If along any axis, $\hat{\epsilon}$ is *diagonal*, we shall call $\hat{S}$ axi-local, and denote that direction the *local axis.*

Theorem 5 *Let $\hat{S}$ be a symmetric, isotropic, axi-local second-order differential operator in a d-dimensional space. Let* S *be the discretisized form of $\hat{S}$, with n points along the local axis. Then* S *is a symmetric tridiagonal (N/n)-block matrix of order n.*

Proof of Theorem 5 Along the local axis, the operator takes the form of a one-dimensional second-order differential operator, which only couples to nearest neighbors. Let the number of points along this local axis be n. Now enumerate the N discrete points of S in blocks x_k, so that all points in one block only couples to two other blocks, x_{k-1} and x_{k+1}. Those blocks are then of size (N/n), which completes the proof.

Discussion 5.1 The application of the ideas presented here should be realizable for two-dimensional systems. It is probably best to use brute force on Theorem2, rather than trying to sophisticate the algorithms too much. Especially since the integral over k is replaced by a slightly large operation count – $\mathcal{O}(N^{3/2})$ for the whole thing, compared to N times the number of k-points.

In summary, this approach should be very useful for atom-atom interactions as well as atom-jellium interactions, or any two-dimensional system.