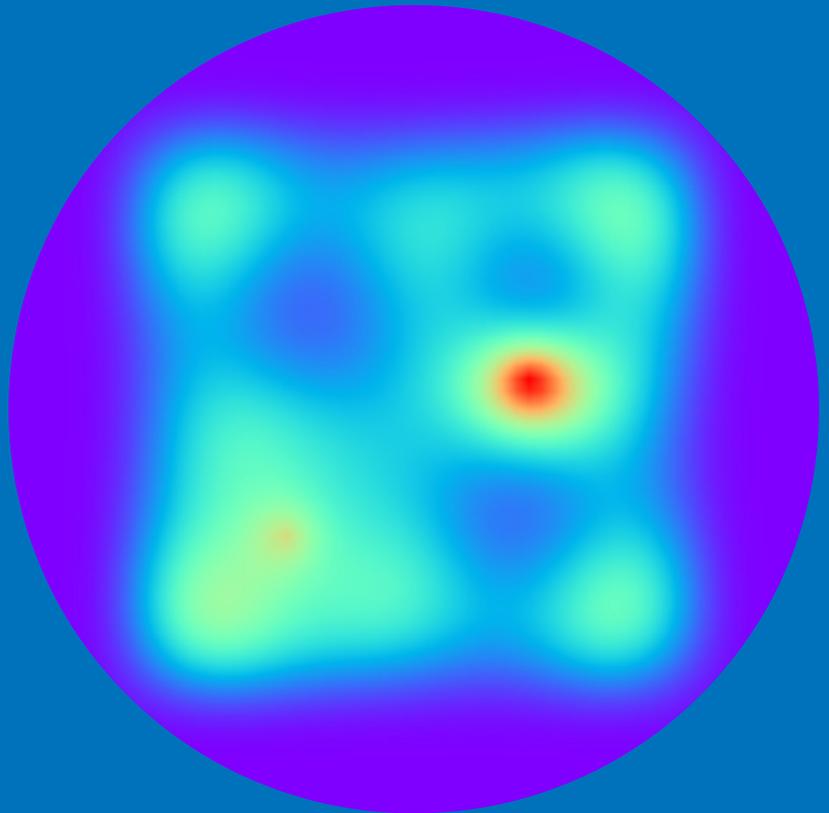


Direct Minimization and Acceleration of Electronic Structure Calculations

Kurt Baarman



Direct Minimization and Acceleration of Electronic Structure Calculations

Kurt Baarman

Doctoral dissertation for the degree of Doctor of Science in
Technology (Doctor of Philosophy) to be presented with due
permission of the School of Science for public examination and
debate in Auditorium L at the Aalto University School of Science
(Espoo, Finland) on the 17th of August 2012 at 12 noon.

Aalto University
School of Science
Department of Mathematics and Systems Analysis

Supervising professor

Prof. Timo Eirola

Thesis advisor

Prof. Timo Eirola

Preliminary examiners

Prof. Elena Celledoni

Norwegian University of Science and Technology
Norway

Dr. Volker Blum

Fritz Haber Institute of the Max Planck Society
Germany

Opponents

Prof. Sverker Holmgren

Uppsala University
Sweden

Aalto University publication series

DOCTORAL DISSERTATIONS 99/2012

© Kurt Baarman

ISBN 978-952-60-4721-8 (printed)

ISBN 978-952-60-4722-5 (pdf)

ISSN-L 1799-4934

ISSN 1799-4934 (printed)

ISSN 1799-4942 (pdf)

<http://urn.fi/URN:ISBN:978-952-60-4722-5>

Unigrafia Oy

Helsinki 2012

Finland



Author

Kurt Baarman

Name of the doctoral dissertation

Direct Minimization and Acceleration of Electronic Structure Calculations

Publisher School of Science**Unit** Department of Mathematics and Systems Analysis**Series** Aalto University publication series DOCTORAL DISSERTATIONS 99/2012**Field of research** Mathematics**Manuscript submitted** 17 April 2012**Date of the defence** 17 August 2012**Permission to publish granted (date)** 7 June 2012**Language** English **Monograph** **Article dissertation (summary + original articles)****Abstract**

This dissertation investigates numerical methods for direct minimization and acceleration of electronic structure calculations. The focus is on methods for Kohn-Sham density functional theory and its extension to fractionally occupied electronic orbitals.

The methods are derived in the setting of an abstract discretization of the electronic structure problem and then numerically verified. Verification is accomplished with genuine electronic structure codes or for a model problem capturing the nonlinearity originating from electron-electron interactions.

The dissertation demonstrates that the quasi-Newton method is a fast and robust accelerator for the self consistent Kohn-Sham equations and that intrinsic inclusion of the geometric constraints improve the rate of convergence for direct minimization methods. It is also shown that ensemble density functional theory enables convergence of metallic systems without enforced broadening of the Fermi level. Furthermore, simultaneous updates of the electronic orbitals and occupation numbers are shown to reduce the number of iterations necessary for convergence of ensemble density functional theory.

Keywords Electronic structure calculation, acceleration, direct minimization, density functional theory, ensemble density functional theory, Stiefel manifold

ISBN (printed) 978-952-60-4721-8**ISBN (pdf)** 978-952-60-4722-5**ISSN-L** 1799-4934**ISSN (printed)** 1799-4934**ISSN (pdf)** 1799-4942**Location of publisher** Espoo**Location of printing** Helsinki**Year** 2012**Pages** 108**urn** <http://urn.fi/URN:ISBN:978-952-60-4722-5>

Författare

Kurt Baarman

Doktorsavhandlingens titel

Direct Minimization and Acceleration of Electronic Structure Calculations

Utgivare Högskolan för teknikvetenskaper**Enhet** Institutionen för matematik och systemanalys**Seriens namn** Aalto University publication series DOCTORAL DISSERTATIONS 99/2012**Forskningsområde** Matematik**Inlämningsdatum för manuskript** 17.04.2012 **Datum för disputation** 17.08.2012**Beviljande av publiceringstillstånd (datum)** 07.06.2012 **Språk** Engelska **Monografi** **Sammanläggningsavhandling (sammandrag plus separata artiklar)****Sammandrag**

Denna avhandling undersöker numeriska metoder för direkt optimering och acceleration av elektronstruktursberäkningar med tyngdpunkt på Kohn-Shams täthetsfunktionalteori samt utvidgad täthetsfunktionalteori.

Metoderna härleds för en diskretiserad abstrakt elektronstruktursmodell och verifieras numeriskt. Verifikationen utförs med ett autentisk täthetsfunktionalprogram eller för ett modellproblem som återger svårigheter vilka förekommer i elektronstruktursberäkningar.

Avhandlingen visar att sekantmetoder kan användas framgångsrikt för att söka en konsistent lösning till Kohn-Shams ekvationer samt att inbyggt beaktande av geometriska villkor minskar mängden iterationer som krävs vid direkt optimering av systemets totala energi. Vidare demonstreras att utvidgad täthetsfunktionalteori möjliggör beräkning av metalliska system utan att en fiktiv temperatur behöver införas och att samtidig uppdatering av elektronskal och skalens ockupationstal förbättrar konvergens i jämförelse med sekventiell uppdatering.

Nyckelord Elektronstrukturberäkning, acceleration, direkt minimering, Stiefelmångfald, täthetsfunktionalteori

ISBN (tryckt) 978-952-60-4721-8**ISBN (pdf)** 978-952-60-4722-5**ISSN-L** 1799-4934**ISSN (tryckt)** 1799-4934**ISSN (pdf)** 1799-4942**Utgivningsort** Esbo**Tryckort** Helsingfors**År** 2012**Sidantal** 108**urn** <http://urn.fi/URN:ISBN:978-952-60-4722-5>

Preface

I would like to thank my supervisor Prof. Timo Eirola for his guidance and for sharing his numerical expertise. Dr. Ville Havu has always offered his support and his interdisciplinary insight has been invaluable. Discussions with Dr. Joost VandeVondele from the University of Zurich has increased my perspective of electronic structure calculations and the Swiss alps.

It has been an honor to have Prof. Elena Celledoni from the Norwegian University of Science and Technology and Dr. Volker Blum from the Fritz Haber Institute as preliminary examiners of this thesis. Their in-depth comments are highly appreciated.

I have had the privilege to visit the group of Prof. Jürg Hutter at the University of Zurich. This visit was very instructive and was made possible by financial support from the Magnus Ehrnrooth foundation.

My first steps towards scientific computing was under the supervision of Prof. Rolf Stenberg. I am grateful for that opportunity.

The working environment has been both engaging and lively. I am especially grateful to Dr. Mika Juntunen for motivational discussions.

I am indebted to friends and family both in Finland and abroad. Their support has made this possible.

Helsinki, June 21, 2012,

Kurt Baarman

Contents

Preface	1
Contents	3
List of Publications	5
Author's Contribution	7
1. Introduction	9
2. Density Functional Theory	13
2.1 Self-consistent Kohn-Sham equations	14
2.2 Direct minimization of the free energy	18
2.3 Ensemble density functional theory	20
3. Numerical Methods for Electronic Structure Calculations	23
3.1 Unconstrained methods	23
3.1.1 Direct inversion of the iterative subspace	24
3.1.2 Quasi-Newton method	25
3.1.3 Nonlinear conjugate gradient method	27
3.2 Orthogonally constrained optimization	28
3.2.1 Update and transport operators	28
3.2.2 Constrained quasi-Newton method	30
3.2.3 Constrained nonlinear conjugate gradient method . .	32
3.2.4 Geometric integration	33
3.2.5 Optimal damping algorithm	33
3.3 Ensemble optimization	34
4. Concluding Remarks	37
4.1 Publication I	37
4.2 Publication II	38

4.3 Publication III	39
4.4 Publication IV	39
Bibliography	41
Publications	45

List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.

I K. Baarman, T. Eirola, and V. Havu. Robust acceleration of self-consistent field calculations for density functional theory. *The Journal of Chemical Physics*, 134, 134109; doi:10.1063/1.3574836 , April 2011.

II K. Baarman and J. VandeVondele. A comparison of accelerators for direct energy minimization in electronic structure calculations. *The Journal of Chemical Physics*, 134, 244104; doi:10.1063/1.3603445, June 2011.

III K. Baarman, T. Eirola, and V. Havu. Direct minimization of electronic structure calculations with Householder reflections. *arXiv:1204.1204*, 16 pages, April 2012.

IV K. Baarman, V. Havu, and T. Eirola. Direct minimization for ensemble electronic structure calculations. *arXiv:1204.1205*, 20 pages, April 2012.

Author's Contribution

Publication I: “Robust acceleration of self-consistent field calculations for density functional theory”

The author is responsible for the implementation of the quasi-Newton methods described in the paper. The numerical examples and major parts of the writing is also due to the author.

Publication II: “A comparison of accelerators for direct energy minimization in electronic structure calculations”

The author is responsible for development of the step length estimate and the implementation of the QN method. The majority of the numerical experiments and major parts of the writing is also due to the author.

Publication III: “Direct minimization of electronic structure calculations with Householder reflections”

The author is responsible for the adaption and implementation of the numerical methods for the manifold. The numerical examples and major parts of the writing is also due to the author.

Publication IV: “Direct minimization for ensemble electronic structure calculations”

The author is responsible for the development and implementation of the simultaneous optimization approach. The numerical examples and major parts of the writing is also due to the author.

1. Introduction

Electronic structure calculations are an important tool which allows scientists and engineers to better understand physical and chemical properties of molecules and materials. Electrons govern many physical phenomena such as electric conductivity and chemical bonding. They also take part in thermal conductivity and determine many central properties of a periodic material including the crystal structure, the lattice parameters, and the bulk modulus. Advances in computational power and numerical methods during the closing decade of the 20th century have made it possible to computationally determine these properties with an accuracy comparable to experimental results. Today, electronic structure calculations can be used to interpret experimental results and to predict the properties of new materials.

Computational science is a field concerned with numerical simulations of mathematical models. Mathematical models originate from several applied disciplines, such as physics, chemistry, engineering, and finance. They assist scientists and engineers to understand phenomena, make predictions, and design products. A simulation requires a mathematical model that captures the important properties and interactions of the system under investigation. The interesting property of a mathematical model is often infinite dimensional and must be reduced to a finite dimensional approximation. This can for example be accomplished by approximating the model with a finite set of functions or by approximating the model at a finite number of points. The next step is to choose a suitable numerical method to solve the problem and finally to validate and interpret the set of numbers given by the computation.

Electronic structure calculations determine the ground state electronic configuration of an atomic system. In principle the electronic ground state is completely determined by the electronic Schrödinger equation,

but the size of the resulting numerical model quickly grows and becomes intractable for systems beyond a few electrons. Scientists are often interested in the properties of systems with hundreds or thousands of electrons which cannot be modeled in practice by the Schrödinger equation. Density functional theory (DFT) reduces the size of the electron structure model and makes it possible to model systems far beyond the reach of the Schrödinger equation.

The price to pay for this reduction of the model size is that DFT gives rise to a nonlinear system. While a linear problem can be solved directly, a nonlinear system must be solved iteratively. The calculations required at each iterative step are computationally expensive and it is therefore important to reduce the number of iterations required to solve the nonlinear system.

Electronic structure calculations are also important for ab initio molecular dynamics (MD) simulations. In classical MD simulations the effective interactions between atoms are determined by empirical or semi-empirical potentials, while the atomic interactions in ab initio MD simulations are obtained directly from the electronic and nuclear configuration. The commonly used Born-Oppenheimer approximation is a simplifying assumption that makes it possible to calculate the electronic ground state independently of the nuclear motion. Despite this simplification, ab initio MD simulations are computationally demanding as it is necessary to determine the electronic configuration at each step of the simulation. Nevertheless, the use of electronic structure calculations to replace the empirical and semi-empirical atomic interaction potentials has increased the predictive power of MD simulations [12, 40, 56].

The focus of this thesis is on direct minimization and numerical acceleration of electronic structure calculations. The methods are presented in the setting of an abstraction of the physical model where the electron density or electronic orbitals are replaced with a discretized representation appropriate for the formulation of the model. While the methods are developed in an abstract context, electronic structure calculations remains the motivation and numerical experiments are always performed with authentic electronic structure codes or on model problems capturing the nonlinear effects present in DFT. Many of the results can also be applied to other large nonlinear equations and optimization problems arising in science and engineering.

The main contribution of this thesis is the application of quasi-Newton

(QN) acceleration to the self-consistent field (SCF) solution of the Kohn-Sham equations and the development of dedicated methods for direct minimization of the Kohn-Sham energy and Helmholtz energy of density functional theory calculations. The QN method is compared to the popular direct inversion of the iterative subspace (DIIS) for SCF calculations and with the nonlinear conjugate gradient (NLCG) method for direct energy minimization. In addition, optimization methods that intrinsically enforce the orthogonality constraints are developed and extended to ensemble DFT.

This summary is divided into four chapters: Chap. 1 is the introduction, Chap. 2 reviews density functional theory, Chap. 3 is an overview of numerical methods for electronic structure calculations, and Chap. 4 discusses the articles.

2. Density Functional Theory

The electronic ground state corresponding to the external potential V_{Ext} is the lowest eigenstate of the time independent many-body Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (2.1)$$

where $\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_{n_e}, \sigma_{n_e})$ is the complex valued all-electron wave function, \mathbf{r}_i is the spatial coordinate and σ_i the spin state of the i :th electron, and the index i runs over all electrons. The fermionic electrons have spin $\sigma_i \in \{\uparrow, \downarrow\}$ and the Hamilton operator is

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V_{\text{Ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|}, \quad (2.2)$$

in atomic units, where ∇_i^2 represents the Laplace operator. In addition, the wave function Ψ must be antisymmetric with regards to an exchange of two electrons i and $j \neq i$.

A system with n_e electrons requires $3n_e$ spatial variables to describe Ψ and the size of a discretized problem exponentially grows with n_e . This dramatic growth, the *curse of dimensionality*, makes the all-electron many-body Schrödinger equation intractable for systems beyond a few electrons and makes it necessary to use other methods to determine the electronic ground state.

Figure 2.1 shows an approximate electronic ground state density of an eight electron system. The solution corresponds to a two dimensional model problem detailed in Publication III with eight electrons. The external potential is a regularized Coulombic potential generated by two identical nuclei with charge $Z_4 = 4$ at $(\frac{1}{3}, \frac{1}{3})$ and $Z_4 = 4$ at $(\frac{2}{3}, \frac{13}{24})$. The computation is performed in a unit square with zero boundary conditions corresponding to an infinite potential well. The electron density is concentrated around the nuclei, with delocalized valence orbitals extending further from the nuclei. The core electrons of the nucleus at $(\frac{2}{3}, \frac{13}{24})$ are

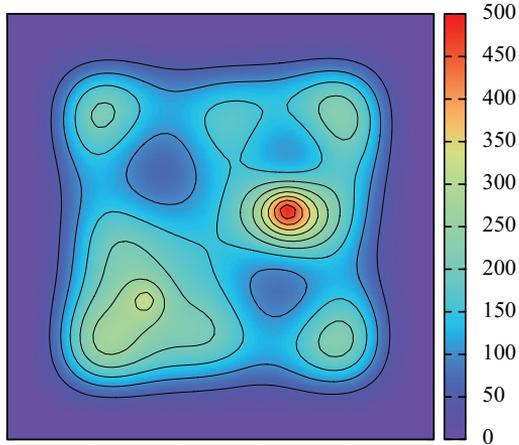


Figure 2.1. Approximate electronic ground state density of a two dimensional system with eight electrons and zero boundary condition in the unit square. The density is computed with a density functional theory approximation using a regularized Hartree effective single particle potential. The two peaks in the electronic density correspond to two Z_4 nuclei at $(\frac{1}{3}, \frac{1}{3})$ and $(\frac{2}{3}, \frac{13}{24})$. The isocurves of the electronic density correspond to the ticks in the colorbar.

significantly more localized than those belonging to the nucleus at $(\frac{1}{3}, \frac{1}{3})$.

This chapter presents an overview of density functional theory: Sec. 2.1 introduces the SCF formulation of DFT, Sec. 2.2 reviews the energy minimization formulation of DFT, and Sec. 2.3 presents ensemble DFT.

2.1 Self-consistent Kohn-Sham equations

While the electronic ground state can in principle be found by solving Eq. (2.1), this is impossible to do in practice for most systems of interest. DFT reduces the size of the electronic structure calculation and is one most successful and versatile methods in quantum chemistry and condensed matter physics. It determines an approximate ground state total energy E and electron spin densities $\rho_\uparrow, \rho_\downarrow$ for a system consisting of n_e interacting electrons in an external potential V_{Ext} . The ground state spin densities are found by solving the one-electron Schrödinger equation [22]

$$\hat{\mathbf{H}}_{\text{KS}}\psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r}), \quad (2.3)$$

where $\hat{\mathbf{H}}_{\text{KS}}$ is the Kohn-Sham Hamiltonian expressed in atomic units

$$\hat{\mathbf{H}}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{Ext}}(\mathbf{r}) + V_{\text{Int}}(\rho, \mathbf{r}) + V_{\text{xc}}^\sigma(\rho_\uparrow, \rho_\downarrow, \mathbf{r}). \quad (2.4)$$

The spin degree of freedom is $\sigma \in \{\uparrow, \downarrow\}$ and α represents the remaining one-electron quantum numbers. The spin densities are

$$\rho_\sigma(\mathbf{r}) = \sum_{\alpha} f_{\alpha\sigma} |\psi_{\alpha\sigma}(\mathbf{r})|^2, \quad (2.5)$$

and the one-electron orbitals $\psi_{\alpha\sigma}$ use the natural normalization

$$\int |\psi_{\alpha\sigma}(\mathbf{r})|^2 d\mathbf{r} = 1. \quad (2.6)$$

Above $f_{\alpha\sigma} \in \{0, 1\}$ is the occupation numbers corresponding to the $\psi_{\alpha\sigma}$ orbital. The occupation number takes the value $f_{\alpha\sigma} = 1$ for the n_e occupied lowest energy single electron orbitals and $f_{\alpha\sigma} = 0$ for higher energy orbitals. This gives the correct total number of electrons

$$\int \rho(\mathbf{r}) d\mathbf{r} = n_e, \quad (2.7)$$

where

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}). \quad (2.8)$$

The internal potential is the classical Hartree potential

$$V_{\text{Int}}(\rho, \mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}', \quad (2.9)$$

and the exchange-correlation term V_{xc}^σ is defined to cover the remaining electron-electron interaction effects.

The numerical methods are described for an abstract version of the SCF problem described by the Kohn-Sham Eqs. (2.3)–(2.5). The general fixed point problem is: find $\mathbf{x} \in \mathbb{R}^n$ such that

$$\mathbf{g}(\mathbf{x}) = \mathbf{x}, \quad (2.10)$$

where \mathbf{x} is a discretization of $(\rho_{\uparrow}, \rho_{\downarrow})$ and \mathbf{g} is an implementation of the interdependent Kohn-Sham equations. For DFT problems it is expensive to compute $\mathbf{g}(\mathbf{x})$ and is often difficult to drive Eq. (2.10) to converge [54]. The fixed point equation is typically rewritten as

$$\mathbf{f}(\mathbf{x}) = \mathbf{0}, \quad (2.11)$$

where $\mathbf{f}(\mathbf{x}) = \mathbf{x} - \mathbf{g}(\mathbf{x})$. This form is better suited to approximate the derivative and accelerate the SCF iteration. The task is then to construct a sequence of vectors $\{\mathbf{x}_k\}$ such that

$$\lim_{k \rightarrow \infty} \|\mathbf{f}(\mathbf{x}_k)\| = \mathbf{0}. \quad (2.12)$$

Conservation of the number of electrons n_e in the system requires that

$$\mathbf{b}^T \mathbf{x} = n_e, \quad (2.13)$$

where $\mathbf{b} \in \mathbb{R}^n$ depends on the discretization of $(\rho_\uparrow, \rho_\downarrow)$.

Several discretizations are available, such as atomic orbital bases, plane-waves, finite element, finite difference grids, and wavelets. Atomic orbital bases represent the solution as a linear combination of atomic solutions including numeric atomic orbitals [7] and Gaussians [37, 60]. They can be efficient, but their accuracy suffers if the solution is not well represented by perturbed atomic solutions. Plane-waves bases [31, 37] and the finite difference methods [20, 44, 57] are uniform discretizations of the space and work well with Fourier techniques. However, the uniform space discretization requires large numbers of degrees of freedom to accurately resolve the sharp features near nuclei. Finite element [33, 57] and wavelet bases [57] are not as widely used in DFT calculations, but make it possible to efficiently concentrate computational effort near nuclei. In general, the finite difference method is very easy to implement but not as flexible as the discretizations relying on a basis.

The Kohn-Sham equations, (2.3)–(2.5), are interdependent and can only be solved by finding a solution that satisfies the equations simultaneously. This simultaneous solution is called a self-consistent field (SCF) solution. To find the SCF solution it is necessary to begin with an initial guess and iteratively improve this. The fixed point iteration is a simple way to do this: the electron orbitals of the individual atoms can be used to evaluate ρ_σ from Eq. (2.5). The electron orbitals corresponding to this initial guess can then be found from Eq. (2.3), which in turn makes it possible to update ρ_σ . This process is repeated until the change in electronic orbitals and spin densities between successive iterations is sufficiently small. Unfortunately, ρ_σ is expensive to compute as it requires several of the lowest eigenpairs of \hat{H}_{KS} in (2.4).

An alternative procedure to compute ρ_σ is to find the subspace spanned by the lowest orbitals $\psi_{\alpha\sigma}$ [5, 62]. This subspace is sufficient to determine ρ_σ as it is invariant under a unitary transformation of $\psi_{\alpha\sigma}$. Subspace methods do not require the lowest eigenpairs of \hat{H}_{KS} to be computed. Instead, they rely on a polynomial filtering to suppress eigenvectors corresponding to high eigenvalues and consequently require that operations with \hat{H}_{KS} are inexpensive.

The simple fixed point iteration generally fails to find a solution for a SCF problem without under-relaxation and is generally prohibitively slow with sufficient under-relaxation. To remedy this, SCF iterations make use of methods known as accelerators or mixers—numerical methods de-

signed to reduce the number of iterations necessary to achieve convergence [54]. In addition to reducing the number of SCF iterations an accelerator must be robust and require only modest computational resources.

The ground state solution of the Kohn-Sham equations is in principle equivalent to the all-electron wave function and can be used to reconstruct Eq. (2.1) [27, 28, 34–36]. In practice however, the exchange-correlation term is unknown and must be replaced with an approximation. Due to this approximation the DFT electron density becomes an approximation of the actual electronic density given by the many-body Schrödinger equation. While the energy contribution of the exchange-correlation functional is typically only a fraction of the total energy, it is often larger than the chemical bonding energy of the system. For this reason accurate approximation of the exchange-correlation functional is crucial for the accuracy of DFT calculations [22].

Several approximations of the unknown exact Kohn-Sham exchange-correlation functional are available and the optimal choice generally depends on the particular simulation. The local density approximation (LDA) is popular in physics and is derived for the homogeneous electron gas [49, 50]. Other widely used functionals include the local spin density approximation (LSDA), which is an extension of LDA to spin polarized systems, and the generalized gradient approximation (GGA), which accounts for the gradients of the spin densities [48]. Finally, hybrid functionals combine exact Hartree-Fock exchange with other exchange-correlation functionals [55], but fall outside the scope of Kohn-Sham density functional theory.

Valence electrons are responsible for chemical bonding and electric conductivity. The valence electrons are not as closely bound to the nuclei as core electrons and they require less energy to excite. For this reason their impact on material properties is significant and it is often sufficient to model only the valence orbitals. In DFT calculations a conventional method to do this is to eliminate the core electrons from the model and replace the full Coulombic potential of the nuclei with a pseudopotential that covers the combined effect of the core electrons and the nuclei [22]. This approximation has the dual benefit of reducing the size of the model and improving the conditioning of the system. The pseudopotential is chosen to coincide with the Coulombic potential outside a cutoff radius. An illustration of the smoothing effect of a pseudopotential is given in Fig. 2.2.

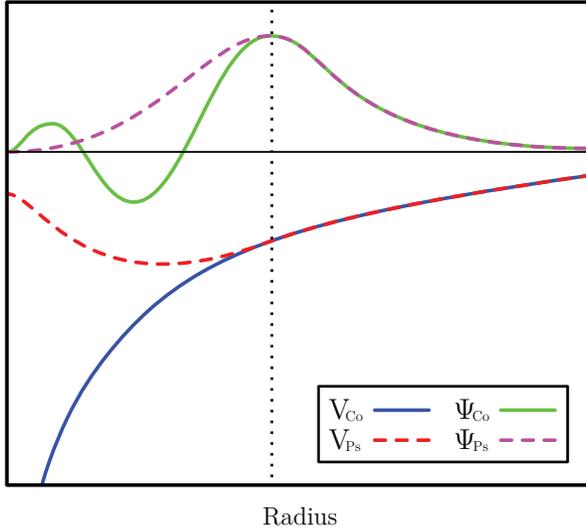


Figure 2.2. The Coulombic potential V_{Co} is replaced with an effective pseudopotential V_{Ps} seen by the valence electrons that differs from V_{Co} close to the nucleus. The pseudopotential leads to a smoother orbital Ψ_{Ps} which numerically behaves better than the oscillating orbital Ψ_{Co} corresponding to V_{Co} .

2.2 Direct minimization of the free energy

The electronic ground state minimizes the total energy of the system. This property leads to an alternative formulation of the DFT model, where the goal is to find a set of single electron orbitals $\psi_{\alpha\sigma}$ minimizing the Kohn-Sham energy

$$E(\{\psi_{\alpha\sigma}\}) = K(\{\psi_{\alpha\sigma}\}) + \int \rho(\mathbf{r})V_{\text{Ext}}(\mathbf{r})d\mathbf{r} + U(\rho) + E_{\text{xc}}(\rho_{\uparrow}, \rho_{\downarrow}), \quad (2.14)$$

of the system and satisfying the orthonormality constraint

$$\int |\psi_{\alpha\sigma}(\mathbf{r})\psi_{\beta\sigma}(\mathbf{r})|d\mathbf{r} = \delta_{\alpha\beta}. \quad (2.15)$$

Here the kinetic energy component is

$$K(\{\psi_{\alpha\sigma}\}) = \sum_{\alpha\sigma} f_{\alpha\sigma} \int \psi_{\alpha\sigma}^*(\mathbf{r}) \hat{\mathbf{p}}^2 \psi_{\alpha\sigma}(\mathbf{r})d\mathbf{r}, \quad (2.16)$$

where the kinetic energy operator is $\hat{\mathbf{p}}^2 = -\frac{1}{2}\nabla^2$ and the energy corresponding to the electrostatic Hartree potential is

$$U(\rho) = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}d\mathbf{r}'. \quad (2.17)$$

The exchange-correlation energy E_{xc} is again an approximation of the electron-electron interactions that are not included in U . The spin densities ρ_{σ} (2.5) and total density ρ (2.8) are computed as for the Kohn-Sham Eqs. (2.3)–(2.5).

The electronic ground state density given by the total energy (2.14) is identical to the SCF solution of the Kohn-Sham equations. The one-electron Schrödinger Eq. (2.3) is derived from the energy formulation via the variational form [47]. First, the orthonormality constraints are included by Lagrange multipliers $\epsilon_{\alpha\beta\sigma}$ which gives the Lagrange function

$$\Omega = E - \sum_{\alpha\beta\sigma} \epsilon_{\alpha\beta\sigma} \left(\int |\psi_{\alpha\sigma}(\mathbf{r})\psi_{\beta\sigma}(\mathbf{r})| d\mathbf{r} - \delta_{\alpha\beta} \right). \quad (2.18)$$

Varying Ω around the minimizing set of orbitals leads to the equations

$$\hat{\mathbf{H}}_{\text{Eff}} \psi_{\alpha\sigma}(\mathbf{r}) = \sum_{\alpha\beta} \epsilon_{\alpha\beta\sigma} \psi_{\beta\sigma}(\mathbf{r}), \quad (2.19)$$

where the effective Hamiltonian is

$$\hat{\mathbf{H}}_{\text{Eff}} = -\frac{1}{2}\nabla^2 + V_{\text{Ext}}(\mathbf{r}) + V_{\text{Int}}(\rho, \mathbf{r}) + V_{\text{xc}}^{\sigma}(\rho_{\uparrow}, \rho_{\downarrow}, \mathbf{r}). \quad (2.20)$$

Equation (2.3) is recovered in canonical form from Eq. (2.19) by a unitary transformation of the electronic orbitals $\psi_{\alpha\sigma}$ that diagonalizes $\epsilon_{\alpha\beta\sigma}$. Note that the electronic orbitals given by Eq. (2.14) do not necessarily correspond to the orbitals given by the lowest eigenstates of the single electron Schrödinger Eq. (2.3).

As for the SCF formulation it is possible to consider numerical methods for a more abstract version of the direct minimization problem given by a discretization of Eq. (2.14). That is, solve

$$\min_{\mathbf{X} \in \mathcal{M}} E(\mathbf{X}), \quad (2.21)$$

where the columns of \mathbf{X} corresponds to an orthonormal discretization of the electronic orbitals and the manifold

$$\mathcal{M} = \{\mathbf{X} \in \mathbb{R}^{m \times n} \mid \mathbf{X}^T \mathbf{X} = \mathbf{I}\}, \quad (2.22)$$

is called the Stiefel manifold [1, 19]. Here m is the degrees of freedom of the discretization of a single electron orbital and $n = n_e$ is the number of electrons in the system. The tangent space corresponding to the Stiefel manifold is

$$\mathcal{T}_{\mathbf{X}} \mathcal{M} = \{\mathbf{Y} \in \mathbb{R}^{m \times n} \mid \mathbf{Y} = \mathbf{X}\mathbf{A} + \mathbf{Z} \text{ where } \mathbf{A}^T = -\mathbf{A} \text{ and } \mathbf{Z}^T \mathbf{X} = \mathbf{0}\}. \quad (2.23)$$

A unitary transformation of the electronic orbitals which leaves the occupied subspace intact does not affect ρ_{σ} and E , Eqs. (2.5) and (2.14). The discretized problem inherits this property and Eq. (2.21) satisfies the homogeneity condition:

$$E(\mathbf{X}) = E(\mathbf{X}\mathbf{Q}), \quad (2.24)$$

when $\mathbf{Q} \in \mathbb{R}^{n \times n}$ is unitary. The homogeneity condition indicates that $E(\mathbf{X})$ is invariant under an orthogonal rotation of the columns of \mathbf{X} , and Eq. (2.23) can be simplified by setting $\mathbf{A} = \mathbf{0}$ as it describes a subspace rotation of the electronic orbitals. The orthonormality constraint (2.15) together with the homogeneity condition defines the Grassmann manifold, and the effective tangent space corresponding to this is

$$\mathcal{T}_{\mathbf{X}}\mathcal{M}_H = \{\mathbf{Y} \in \mathbb{R}^{m \times n} \mid \mathbf{Y}^T \mathbf{X} = \mathbf{0}\}, \quad (2.25)$$

and the associated orthogonal projector onto $\mathcal{T}_{\mathbf{X}}\mathcal{M}_H$ is

$$\mathbf{P} = \mathbf{I} - \mathbf{X}\mathbf{X}^T. \quad (2.26)$$

The projected gradient needed for the minimization is then

$$\mathbf{F}_k = (\mathbf{I} - \mathbf{X}\mathbf{X}^T)\nabla E(\mathbf{X}_k). \quad (2.27)$$

An advantage of the direct minimization approach is that it avoids the eigenvalue decomposition that is typically necessary at each step of the SCF iteration [54]. Furthermore, the direct approach is also appealing on an intuitive level as energy is a fundamental physical quantity. The drawback is the necessity to enforce the orthogonality constraint (2.15), which requires more sophisticated numerical methods.

2.3 Ensemble density functional theory

The standard DFT model does not converge well for systems where the occupied and unoccupied parts of the eigenvalue spectrum are not separated by sufficiently large gap [2, 56]. Ensemble DFT improves the rate of convergence for these systems by introducing fractional occupation of electronic orbitals which results in a smoother transition from occupied to unoccupied orbitals.

These fractional occupation numbers are accommodated by replacing the Kohn-Sham energy (2.14) with the Helmholtz energy [41]

$$A(\{\psi_{\alpha\sigma}\}) = E(\{\phi_{\alpha\sigma}\}, \{f_{\alpha\sigma}\}) - TS(\{f_{\alpha\sigma}\}), \quad (2.28)$$

where $0 \leq f_{\sigma\alpha} \leq 1$ is the occupation of the orbital $\psi_{\alpha\sigma}$, $T \geq 0$ is the absolute temperature, and $S(\{f_{\alpha\sigma}\})$ is the entropy. The entropic term is

$$S(\{f_{\alpha\sigma}\}) = - \sum_{\alpha\sigma} f_{\alpha\sigma} \ln(f_{\alpha\sigma}) + (1 - f_{\alpha\sigma}) \ln(1 - f_{\alpha\sigma}). \quad (2.29)$$

The spin density and kinetic energy terms in (2.28) are identical to those for the direct minimization, Eqs. (2.5) and (2.16), but fractional occupation numbers are allowed.

The discretized abstract version of Eq. (2.28) is

$$\min_{\substack{\mathbf{X} \in \mathcal{M} \\ \mathbf{f} \in \mathcal{F}}} A(\mathbf{X}, \mathbf{f}) \quad (2.30)$$

where \mathcal{M} is defined by Eq. (2.22) and

$$\mathcal{F} = \left\{ \mathbf{f} \in \mathbb{R}^n \mid \sum_{i=1}^n f_i = n_e \text{ and } 0 \leq f_i \leq 1 \ \forall i \in \{1, \dots, n\} \right\}. \quad (2.31)$$

The orbital gradient is

$$\nabla_{\mathbf{X}} A(\mathbf{X}, \mathbf{f}), \quad (2.32)$$

and the gradient with regards to the occupation numbers is

$$\nabla_{\mathbf{f}} A(\mathbf{X}, \mathbf{f}). \quad (2.33)$$

For Eq. (2.30) the homogeneity condition is only satisfied for orbitals with identical occupation numbers. The occupation numbers are in general not identical, which makes it impossible to simplify \mathcal{M} by eliminating \mathbf{A} for ensemble calculations. The tangent space of \mathcal{M} is therefore equal to that given by Eq. (2.23)

$$\mathcal{T}_{\mathbf{X}} \mathcal{M} = \{ \mathbf{Y} \in \mathbb{R}^{m \times n} \mid \mathbf{Y} = \mathbf{X}\mathbf{A} + \mathbf{Z} \text{ where } \mathbf{A}^T = -\mathbf{A} \text{ and } \mathbf{Z}^T \mathbf{X} = \mathbf{0} \}.$$

This gives the orthogonal projector for an arbitrary $\mathbf{W} \in \mathbb{R}^{m \times n}$ onto $\mathcal{T}_{\mathbf{X}} \mathcal{M}$

$$\mathbf{P}_{\mathbf{X}}(\mathbf{W}) = (\mathbf{I} - \frac{1}{2} \mathbf{X}\mathbf{X}^T) \mathbf{W} - \frac{1}{2} \mathbf{X}\mathbf{W}^T \mathbf{X}, \quad (2.34)$$

and the projected orbital gradient

$$\mathbf{F}_k = \mathbf{P}_{\mathbf{X}}(\nabla_{\mathbf{X}} A(\mathbf{X}_k, \mathbf{f}_k)). \quad (2.35)$$

The energy level of a fictitious electronic orbital with occupation exactly one half is known as the Fermi level. A system with well separated energies of the electronic orbitals is constrained to integer occupation numbers at absolute zero.

At positive temperatures the entropic term of the Helmholtz energy drives the system towards fractional occupation of orbitals. Occupation of these higher energy orbitals is simultaneously discouraged by the energy term E in the Helmholtz energy. The relative strength of these two tendencies is governed by the temperature and this determines the electronic configuration.

Ensemble DFT also permits fractional occupation of degenerate and near degenerate orbitals at the Fermi level even at absolute zero resulting in simplified treatment of small gap systems. At this temperature the Helmholtz energy of ensemble DFT is reduced to the regular Kohn-Sham energy, and there is no longer a tendency for the entropy to drive the system towards fractional occupation of electronic orbitals. Nevertheless, it is still possible for nonlinear effects to favor small excitations when fractional occupation numbers are permitted.

A more common method is to use deterministic smearing, or broadening of the Fermi level to improve convergence of small gap systems [7, 42]. A smearing function is used to determine the occupation numbers of the individual electronic orbitals based on their energy level. The width of the fractionally occupied orbital band is determined by the fictitious temperature. Common smearing functions include the Fermi function [42], as well as Gaussian [24] and Methfessel-Paxton [43] smearing schemes. Smearing requires that the electronic orbital energies near the Fermi level are computed to high accuracy for the smearing function to correctly predict the occupation of the orbitals.

3. Numerical Methods for Electronic Structure Calculations

This chapter gives an overview of the numerical methods presented in the articles. The methods are divided into two general classes, methods for acceleration of self consistent field iterations, and methods for direct minimization of the energy. These classes are related in that self consistent field iteration attempt to construct an electron density which gives a vanishing residual and direct minimization methods search for electron orbitals for which the gradient vanishes.

The direct minimization methods are further subdivided into methods for the Grassmann manifold and methods for the Stiefel manifold. In the former case the energy is invariant under subspace rotations of the electronic orbitals and only depends on the space spanned by the electronic orbitals. In the latter case the energy of the system depends on the individual electronic orbitals and it also becomes necessary to optimize with regards to the electronic orbitals.

This chapter is divided into three sections. First, Sec. 3.1 reviews the unconstrained methods. Next, Sec. 3.2 presents constrained methods for direct optimization. Finally, Sec. 3.3 discusses the extension of direct minimization methods to ensemble DFT.

3.1 Unconstrained methods

This section reviews methods for acceleration of the SCF formulation of DFT: Sec. 3.1.1 presents DIIS, Sec. 3.1.2 recalls the QN method, and Sec. 3.1.3 discusses the NLCG method.

3.1.1 Direct inversion of the iterative subspace

DIIS, also known as Pulay’s method [51], is an acceleration method designed to solve (2.11)

$$\mathbf{f}(\mathbf{x}) = 0,$$

when \mathbf{f} can be well approximated by a quadratic vector field. When applied to DFT, \mathbf{x} corresponds to the discretized spin densities and \mathbf{f} to the residual of the SCF implementation of the Kohn-Sham equations. DIIS is based on minimization of the norm of an affine combination of the previous evaluations of $\mathbf{f}(\mathbf{x}_k)$. The coefficients that minimize the norm are then used to construct the next trial density \mathbf{x}_{k+1} . That is, solve

$$\min_{\{c_i\}} \left\| \sum_{i=l}^k c_i \mathbf{f}(\mathbf{x}_i) \right\| = \min_{\{c_i\}} \left\| \sum_{i=l}^k c_i (\mathbf{x}_i - \mathbf{g}(\mathbf{x}_i)) \right\|, \quad (3.1)$$

for $k \geq l$ when \mathbf{g} represents the SCF iteration, Eqs. (2.3)–(2.5), subject to

$$\sum_{i=l}^k c_i = 1, \quad (3.2)$$

and construct the next trial density by

$$\mathbf{x}_{k+1} = \sum_{i=l}^k c_i \mathbf{x}_i. \quad (3.3)$$

The construction of \mathbf{x}_k together with the affine constraint (3.2) on $\{c_i\}$ automatically ensures conservation of electrons, Eq. (2.13).

To ensure the convergence of the DIIS method it is often necessary to use under-relaxation. In this case Eq. (3.3) is substituted with

$$\mathbf{x}_{k+1} = (1 - \beta) \mathbf{x}_k + \beta \sum_{i=l}^k c_i \mathbf{x}_i, \quad (3.4)$$

where $\beta \in]0, 1]$ is the under-relaxation parameter. In principle, β is unconstrained, but $\beta < 1$ makes it possible to solve more challenging problems with DIIS.

DIIS is simple to implement, requires only modest computational resources, and often converges quickly for simple systems [29, 30]. For this reason it has become very popular and is available in nearly all DFT codes. However, DIIS is not particularly robust and occasionally fails to converge for more challenging calculations [58]. The convergence rate of DIIS is sensitive to β , but the correct choice is problem dependent and the dependency can be very nonintuitive. Furthermore, it is not possible to tell in advance whether DIIS will converge successfully for a particular problem.

3.1.2 Quasi-Newton method

Newton's method

$$\mathbf{x}_{k+1} = \mathbf{x}_k - \beta \mathbf{J}(\mathbf{x}_k)^{-1} \mathbf{f}(\mathbf{x}_k), \quad (3.5)$$

is very fast at finding successively better approximations to the solution of a system of equations (2.11)

$$\mathbf{f}(\mathbf{x}) = \mathbf{0},$$

when the Jacobian \mathbf{J} of \mathbf{f} is available and $\beta \in]0, 1]$ is an under-relaxation parameter. The default implementation of Newton's method can fail to converge due to problematic behavior of \mathbf{J} and requires a good initial guess [46]. Nevertheless, for problems where \mathbf{J} is available Newton's method is an extremely fast solver and robustness can be increased through techniques such as backtracking [46]. When Newton's method is applied to DFT, \mathbf{x} corresponds to the discretized spin densities and \mathbf{f} to the SCF implementation (2.11).

While \mathbf{J} is typically not available for DFT problems it is possible to replace \mathbf{J}^{-1} with an approximation \mathbf{G} . The method resulting from this replacement is the QN method and it can retain the superlinear convergence of the Newton method [52]. The update for the QN method is identical to Newton's update

$$\mathbf{x}_{k+1} = \mathbf{x}_k - \beta \mathbf{G}_k \mathbf{f}(\mathbf{x}_k), \quad (3.6)$$

with \mathbf{G}_k approximating \mathbf{J}^{-1} at \mathbf{x}_k .

Several update schemes for \mathbf{G} are available but numerical experience suggests that Broyden's second or *bad* update tends to be more robust for ill conditioned problems [39]. In contrast with the first, or *good*, update the second update is derived directly for \mathbf{J}^{-1} [8, 17, 21]. The updated approximation \mathbf{G}_{k+1} is required to satisfy the secant condition

$$\mathbf{G}_{k+1} \Delta \mathbf{f}_k = \Delta \mathbf{x}_k, \quad (3.7)$$

and the no change condition

$$\mathbf{G}_k \mathbf{q} = \mathbf{G}_{k+1} \mathbf{q} \quad \forall \mathbf{q} \text{ such that } \mathbf{q}^T \Delta \mathbf{f}_k = 0, \quad (3.8)$$

where

$$\Delta \mathbf{f}_k = \mathbf{f}(\mathbf{x}_{k+1}) - \mathbf{f}(\mathbf{x}_k), \quad (3.9)$$

and

$$\Delta \mathbf{x}_k = \mathbf{x}_{k+1} - \mathbf{x}_k. \quad (3.10)$$

The secant condition incorporates the information gained from the most recent evaluation of f and the no change condition ensures that this update does not modify \mathbf{G} in directions that are orthogonal to the evaluated direction. The secant condition and no change condition together give the update formula

$$\mathbf{G}_{k+1} = \mathbf{G}_k + (\Delta \mathbf{x}_k - \mathbf{G}_k \Delta \mathbf{f}_k) \frac{\Delta \mathbf{f}_k^T}{\Delta \mathbf{f}_k^T \Delta \mathbf{f}_k}. \quad (3.11)$$

This update formula enforces conservation of the electrons, Eq. (2.13), by ensuring that $\mathbf{b}^T \mathbf{G}_k \mathbf{f}(\mathbf{x}_k) = 0$ when $\mathbf{b}^T \mathbf{G}_0 \mathbf{f}(\mathbf{x}_0) = 0$. Here \mathbf{b} is determined by the discretization of the spin densities and corresponds to spatial integration. Equation (2.10) ensures that $\mathbf{b}^T \mathbf{f}(\mathbf{x}) = 0$ is satisfied as \mathbf{f} is the difference between two electronic densities.

The update formula for \mathbf{G}_{k+1} can also be derived by requiring that the secant condition (3.7) is satisfied and that the change

$$\|\Delta \mathbf{G}_k\| = \|\mathbf{G}_{k+1} - \mathbf{G}_k\|, \quad (3.12)$$

is minimal in the Frobenius norm. The initial approximation of \mathbf{J}^{-1} is

$$\mathbf{G}_0 = \mu \mathbf{I}, \quad (3.13)$$

where μ scales the search directions that have not been explored.

Newton's method is an improvement over the method of steepest descent (SD). For ill conditioned problems, the direction of steepest descent can be nearly orthogonal to a globally preferable direction. Newton's method scales the search direction by \mathbf{J}^{-1} , which improves the search direction and eliminates the characteristic zig-zag behavior of SD [46]. This beneficial behavior is inherited by the QN method when \mathbf{G} is a good approximation of \mathbf{J}^{-1} .

The Broyden updates of \mathbf{G} improve the approximation in directions that have been sampled but the majority of possible search directions remain unsampled for a typical DFT calculation. In fact, Marks and Luke [39] argue that the QN method should be considered a method that randomly samples a high dimensional space and not a method constructing a deterministic path. Step size in the unsampled directions significantly impacts the rate of convergence and is controlled by μ . For challenging problems μ should in general be smaller than for easy problems [39]. Nevertheless, the QN method is both robust and quick when it is properly implemented.

3.1.3 Nonlinear conjugate gradient method

The conjugate gradient (CG) method can be viewed as a minimization scheme where the objective function is successively minimized along conjugate directions. A set of vectors $\mathbf{p}_1, \dots, \mathbf{p}_k \in \mathbb{R}^n$ are \mathbf{A} -conjugate if they are linearly independent and $\mathbf{p}_i^T \mathbf{A} \mathbf{p}_j = 0$ when $i \neq j$. Minimization along conjugate directions finds a solution to the quadratic problem

$$\min h(\mathbf{x}) = \frac{1}{2} \mathbf{x}^T \mathbf{A} \mathbf{x} - \mathbf{b}^T \mathbf{x}, \quad (3.14)$$

in n steps when an exact line search is used.

In DFT computations the objective function h is not quadratic and the update of the search direction \mathbf{p} must take this into account to approximately preserve conjugacy of the search directions. The initial search direction is the direction of steepest descent

$$\mathbf{p}_1 = -\mathbf{h}_1, \quad (3.15)$$

where $\mathbf{h}_k = \nabla h(\mathbf{x}_k)$ and step length τ_k is determined by solving

$$\min_{\tau} h(\mathbf{x}_k + \tau \mathbf{p}_k). \quad (3.16)$$

The density update is

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \tau_k \mathbf{p}_k, \quad (3.17)$$

and the new conjugate direction is

$$\mathbf{p}_{k+1} = -\mathbf{h}_{k+1} + \gamma_k \mathbf{p}_k, \quad (3.18)$$

where γ_k is often determined by the Polak-Ribière formula

$$\gamma_k = \frac{\mathbf{h}_k^T (\mathbf{h}_{k+1} - \mathbf{h}_k)}{\mathbf{h}_k^T \mathbf{h}_k}. \quad (3.19)$$

The Fletcher-Reeves and Hestenes-Stiefel formulas provide alternatives to the Polak-Ribière formula [46]. All of these are intended to approximately preserve conjugacy of the conjugate vectors for higher order objective functions. For a quadratic objective function the NLCG method is reduced to the standard CG method regardless of the choice of formula.

A common modification of the NLCG method is to restart it at regular intervals. This serves to refresh the algorithm and erase information that is no longer beneficial.

The NLCG method relies on the availability of the gradient of the function to be minimized. The gradient of the total energy with respect to the spin densities \mathbf{x} or the orbitals \mathbf{X} is in general not available for the SCF

formulation of DFT and the orthogonality constraints must be enforced for the direct formulation. For this reason the unconstrained NLCG method requires the constraints and electron conservation to be externally enforced, for example by a parametrization of \mathcal{M} [59] or by a suitable projection onto \mathcal{M} [11]. In this case $\mathbf{x} \in \mathbb{R}^{mn}$ represents the unconstrained discretized electronic orbitals in vector form, as opposed to the matrix representation $\mathbf{X} \in \mathbb{R}^{m \times n}$ assumed in (2.21).

NLCG is robust, computationally inexpensive, and has low memory requirements compared to DIIS and QN methods. Sequential optimization along conjugate directions is an ingenious way to ensure that each iteration is in a substantially different direction and the CG method has given rise to several variants popular for a broad range of problems. However, conjugacy is crucial for the performance of the NLCG method and a high quality line search must be employed at step (3.16). If the line search is not sufficiently accurate the NLCG method quickly loses conjugacy and the rate of convergence suffers. The quality of the line search can become a concern when numerical evaluation of the target function is expensive. Moreover, the requirement to externally enforce the constraints on \mathbf{x} and \mathbf{X} makes the unconstrained NLCG method difficult to implement.

3.2 Orthogonally constrained optimization

This section overviews constrained minimization methods for the direct formulation of DFT (2.21). First, Sec. 3.2.1 presents two alternative update and transport operators. Then, Secs. 3.2.2 and 3.2.3 describes the constrained QN and NLCG for the Stiefel manifold. Finally, Secs. 3.2.4 and 3.2.5 briefly mentions orthogonally constrained integration methods and the optimal damping algorithm.

3.2.1 Update and transport operators

The electronic ground state can be found by minimizing the energy of the system. This requires that the discretization of the electronic orbitals \mathbf{X} satisfies the orthonormality constraint $\mathbf{X}^T \mathbf{X} = \mathbf{I}$ which defines the Stiefel manifold \mathcal{M} . The curvature of \mathcal{M} is taken into account by constructing an update operator for \mathbf{X} and an associated transport operator for matrices in $\mathcal{T}_{\mathbf{X}} \mathcal{M}$. These operators ensure that the orthogonality constraints remain satisfied and make it possible to use information from previous

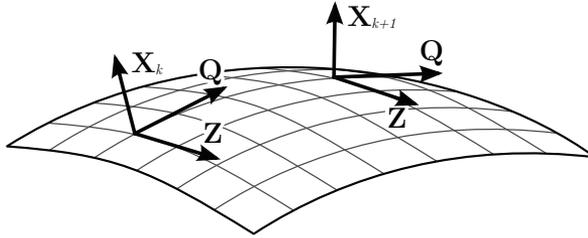


Figure 3.1. The curvature of \mathcal{M} must be taken into account when the matrices belonging to $\mathcal{T}_{\mathbf{X}_k}\mathcal{M}$ are transported to $\mathcal{T}_{\mathbf{X}_{k+1}}\mathcal{M}$ along the geodesic defined by \mathbf{Q} . Here \mathbf{Q} represents the direction of the update and $\mathbf{Z} \in \mathcal{T}_{\mathbf{X}_k}$ satisfies $\mathbf{Z}^T \mathbf{Q} = 0$. Conceptually, \mathbf{Q} and \mathbf{X} are orthogonally projected onto the tangent space and its orthogonal complement respectively after each infinitesimal update of \mathbf{X} . In contrast, \mathbf{Z} remains constant during the update.

evaluations to improve convergence.

An arbitrary vector $\mathbf{Y} \in \mathcal{T}_{\mathbf{X}}\mathcal{M}$ can be decomposed into

$$\mathbf{Y} = \mathbf{X}\mathbf{A} + \mathbf{Q}\mathbf{R}, \quad (3.20)$$

where \mathbf{Q} satisfies $\mathbf{Q}^T \mathbf{X} = 0$, $\mathbf{Q}^T \mathbf{Q} = \mathbf{I}$, and $\mathbf{A}^T = -\mathbf{A}$. When \mathbf{Y} is a search direction given by an optimization procedure such as QN or NLCG, it is possible to construct an update operator

$$\mathbf{U}(\tau) = \begin{bmatrix} \mathbf{X} & \mathbf{Q} \end{bmatrix} \exp \left(\tau \begin{bmatrix} \mathbf{A} & -\mathbf{R}^T \\ \mathbf{R} & \mathbf{0} \end{bmatrix} \right) \begin{bmatrix} \mathbf{X} & \mathbf{Q} \end{bmatrix}^T, \quad (3.21)$$

which rotates \mathbf{X} along the geodesic given by \mathbf{Y} . This operator ensures that $\mathbf{X}_{k+1} = \mathbf{U}(\tau_k)\mathbf{X}_k \in \mathcal{M}$ whenever $\mathbf{X}_k \in \mathcal{M}$. The term $\mathbf{X}\mathbf{A}$ in Eq. (3.20) describes a subspace rotation of the electronic orbitals, while the $\mathbf{Q}\mathbf{R}$ term changes the space spanned by the electronic orbitals.

Both the QN and NLCG methods make use of earlier information to improve the rate of convergence. Due to the curvature of \mathcal{M} it is not possible to simply add two matrices, $\mathbf{Y}_k \in \mathcal{T}_{\mathbf{X}_k}\mathcal{M}$ and $\mathbf{Y}_{k+1} \in \mathcal{T}_{\mathbf{X}_{k+1}}\mathcal{M}$, when the tangent spaces differ. Instead, \mathbf{Y}_k must be transported to $\mathcal{T}_{\mathbf{X}_{k+1}}\mathcal{M}$ before the addition, see Fig. 3.1. This is done with the transport operator

$$\mathbf{T}(\tau) = \mathbf{I}_m + \begin{bmatrix} \mathbf{X} & \mathbf{Q} \end{bmatrix} \left(\exp \left(\tau \begin{bmatrix} \mathbf{A} & -\mathbf{R}^T \\ \mathbf{R} & \mathbf{0} \end{bmatrix} \right) - \mathbf{I}_{2n} \right) \begin{bmatrix} \mathbf{X} & \mathbf{Q} \end{bmatrix}^T, \quad (3.22)$$

which maps a matrix $\mathbf{Y} \in \mathcal{T}_{\mathbf{X}}\mathcal{M}$ to the corresponding matrix in $\mathcal{T}_{\mathbf{U}(\tau)\mathbf{X}}\mathcal{M}$. To enable optimization routines to make use of the information from previous evaluations of ∇E and $\nabla_{\mathbf{X}}A$ the matrices associated with $\mathcal{T}_{\mathbf{X}_k}\mathcal{M}$ are transported to $\mathcal{T}_{\mathbf{X}_{k+1}}\mathcal{M}$ together with the update of \mathbf{X}_k and $\tau_k \in \mathbb{R}$.

Instead of \mathbf{U} , it is possible to use an alternative update operator \mathbf{H} based on the Householder reflector. Univariate descent methods update \mathbf{X}

through individual reflections and breaks down the optimization problem into several line searches [13]. This is advantageous when the successive line searches are relatively inexpensive to solve. Several reflections through orthogonal planes can also be combined into one Householder update to reduce the necessary number of line searches. This alternative update operator to (3.21) based on the Householder transform is

$$\mathbf{H}(\tau) = \mathbf{I} - 2\mathbf{V}(\tau)\mathbf{V}(\tau)^T, \quad (3.23)$$

where $\mathbf{V}(\tau)^T\mathbf{V}(\tau) = \mathbf{I}$.

When the energy satisfies the homogeneity condition, Eq. (2.24), $\mathbf{A} = \mathbf{0}$ and Eq. (3.20) simplifies to

$$\mathbf{Y} = \mathbf{QR}. \quad (3.24)$$

Then $\mathbf{V}(\tau)$ in Eq. (3.23) can be determined from

$$\mathbf{V}(\tau) = \begin{bmatrix} \mathbf{Q} & \mathbf{X} \end{bmatrix} \exp \left(\tau \begin{bmatrix} \mathbf{0} & \frac{1}{2}\mathbf{R} \\ -\frac{1}{2}\mathbf{R}^T & \mathbf{0} \end{bmatrix} \right) \begin{bmatrix} \mathbf{I} \\ \mathbf{0} \end{bmatrix}. \quad (3.25)$$

As for the update operator \mathbf{U} the historical information obtained from the evaluations of the gradients must be transported together with the update of \mathbf{X} . The transport operator corresponding to $\mathbf{H}(\tau)$ takes the form

$$\mathbf{T}_{\mathbf{H}}(\tau) = \mathbf{I} - \mathbf{H}(\tau)\mathbf{V}(\tau)\mathbf{V}(\tau)^T - \mathbf{V}(\tau)\mathbf{V}(\tau)^T. \quad (3.26)$$

The update operators \mathbf{U} and \mathbf{H} are interchangeable when used together with the associated transport operator, \mathbf{T} or $\mathbf{T}_{\mathbf{H}}$, for direct minimization with integer occupation numbers. Fractional occupation numbers do not satisfy the homogeneity condition, Eq. (2.24), and \mathbf{A} does consequently not vanish. In this case \mathbf{U} (3.21) is the appropriate update operator as it takes the subspace rotations represented by \mathbf{A} into account.

3.2.2 Constrained quasi-Newton method

The constrained QN method is used for minimization of the Kohn-Sham energy E , (2.21), or the Helmholtz energy A , (2.30), for fixed occupation numbers. For these problems the gradients with respect to the electronic orbitals $\mathbf{X} \in \mathcal{M}$ (2.22) are available and $\mathbf{G} \in \mathbb{R}^{m \times m}$ approximates the inverse Hessian of E or A . In contrast, the QN method for the SCF problem (2.11) attempts to find a density $\mathbf{x} \in \mathbb{R}^m$ such that $\mathbf{f}(\mathbf{x}) = \mathbf{0}$. For the SCF problem the Jacobian of \mathbf{f} with respect to \mathbf{x} is unknown and \mathbf{G} approximates the inverse Jacobian.

The effective tangent spaces $\mathcal{T}_{\mathbf{X}}\mathcal{M}_H$ (2.25) and $\mathcal{T}_{\mathbf{X}}\mathcal{M}$ (2.23) of the electronic orbitals differ for minimization of E or A respectively. This makes it necessary to choose the orthogonal projector, (2.26) or (2.34), associated with the tangent space. The choice between the update operators \mathbf{U} (3.21) and \mathbf{H} (3.23) also depends on the energy to be minimized. The update operator \mathbf{H} is derived under the assumption that the effective tangent space is $\mathcal{T}_{\mathbf{X}}\mathcal{M}_H$, whereas \mathbf{U} works for both $\mathcal{T}_{\mathbf{X}}\mathcal{M}_H$ and $\mathcal{T}_{\mathbf{X}}\mathcal{M}$. The QN methods for minimization of E and A are nearly identical, and work for both as long as the correct projector and update operator is used. Publication IV describes how the occupation numbers can be included in the update formula for \mathbf{G} , but this section presents the unweighted variant.

The three necessary changes compared to the unconstrained QN method are: the update of \mathbf{X}_k must be done with an update operator \mathbf{U} or \mathbf{H} , the secant and no change conditions hold for matrices in $\mathcal{T}_{\mathbf{X}}\mathcal{M}_H$, and the information from the previous evaluations must be transported to the tangent space associated with the updated \mathbf{X}_{k+1} . The update of \mathbf{G} is determined by a formula which is closely related to Broyden's second update [21]. The secant condition

$$\mathbf{G}_{k+1}\Delta\mathbf{F}_k = \Delta\mathbf{X}_k, \quad (3.27)$$

is simultaneously satisfied for all electronic orbitals, where

$$\Delta\mathbf{F}_k = \mathbf{F}_{k+1} - \mathbf{T}(\tau_k)\mathbf{F}_k, \quad (3.28)$$

and

$$\Delta\mathbf{X}_k = \mathbf{P}_{\mathbf{X}_{k+1}}(\mathbf{X}_{k+1} - \mathbf{X}_k). \quad (3.29)$$

Here the orthogonal projector $\mathbf{P}_{\mathbf{X}_k}$ is given by Eq. (2.26) or (2.34) and the projected gradient \mathbf{F}_k is given by Eq. (2.27) or (2.35) depending on whether the homogeneity condition is satisfied. The update of \mathbf{G} is then determined by requiring that the updated approximation only changes in directions for which new information is obtained. The no-change condition

$$\mathbf{G}_k\mathbf{q} = \mathbf{G}_{k+1}\mathbf{q} \quad \forall \mathbf{q} \in \text{Null}(\Delta\mathbf{F}_k^T), \quad (3.30)$$

together with the secant condition gives Broyden's second generalized update formula [21]

$$\mathbf{G}_{k+1} = \mathbf{G}_k + (\Delta\mathbf{X}_k - \mathbf{G}_k\Delta\mathbf{F}_k)(\Delta\mathbf{F}_k^T\Delta\mathbf{F}_k)^{-1}\Delta\mathbf{F}_k^T. \quad (3.31)$$

The search direction at step k is then

$$\mathbf{Y}_k = -\mathbf{G}_k\mathbf{F}_k, \quad (3.32)$$

and the step length τ_k is determined by

$$\min_{\tau} E(\mathbf{U}(\tau)\mathbf{X}_k). \quad (3.33)$$

In practice τ_k is determined by optimization of a quadratic approximation of E along the search direction \mathbf{Y} . This quadratic approximation p can for example be determined by solving the system of equations

$$\begin{aligned} p(0) &= E(\mathbf{X}), \\ p(\tau_e) &= E(\mathbf{T}(\tau_e)\mathbf{X}), \\ p'(0) &= (\mathbf{Y}, \nabla E(\mathbf{X})), \end{aligned} \quad (3.34)$$

where τ_e is a trial step length. A more detailed presentation of the line search and selection of τ_e is given in Publication II and Publication IV.

3.2.3 Constrained nonlinear conjugate gradient method

The constrained NLCG method must also enforce the orthonormality constraint (2.15) and requires similar changes as the QN method [19]. As for the constrained QN method presented in Sec. 3.2.2 the NLCG method attempts to find $\mathbf{X} \in \mathcal{M}$ (2.22) that minimizes E or A with the correct choice of orthogonal projector and update operator.

The initial search direction remains the direction of steepest descent given by Eq. (2.27) or (2.35)

$$\mathbf{Y}_1 = -\mathbf{F}_1, \quad (3.35)$$

and the step length τ_k is chosen to minimize the total energy $E(\mathbf{X})$, where \mathbf{X} is the discretization of the electronic orbitals, along the search direction

$$\min_{\tau} E(\mathbf{U}(\tau)\mathbf{X}_k). \quad (3.36)$$

As before, the minimization step is replaced with the minimization of a quadratic approximation of E , but \mathbf{U} is used to approximate $E(\mathbf{X})$ along a path on \mathcal{M} . After the τ_k has been determined \mathbf{X} is updated

$$\mathbf{X}_{k+1} = \mathbf{U}(\tau_k)\mathbf{X}_k, \quad (3.37)$$

and the new conjugate direction associated with $\mathcal{T}_{\mathbf{X}}\mathcal{M}$ is determined

$$\mathbf{Y}_{k+1} = -\mathbf{F}_{k+1} + \gamma_k \mathbf{T}(\tau_k)\mathbf{Y}_k, \quad (3.38)$$

where

$$\gamma_k = \frac{(\mathbf{F}_{k+1}, \mathbf{F}_{k+1} - \mathbf{T}(\tau_k)\mathbf{F}_k)}{(\mathbf{F}_k, \mathbf{F}_k)}. \quad (3.39)$$

3.2.4 Geometric integration

Orthogonal integration schemes designed for solving ordinary differential equations (ODE) on the Stiefel manifold are available, but remain relatively rare in the electronic structure community. The minimization problem described by Eq. (2.21) can be reformulated as an ODE:

$$\dot{\mathbf{X}} = -\nabla E(\mathbf{X}), \quad (3.40)$$

for an initial condition $\mathbf{X}_0 \in \mathcal{M}$ (2.22) where ∇ is defined to ensure that $\nabla E(\mathbf{X}) \in \mathcal{T}_{\mathbf{X}}\mathcal{M}$ (2.23). Orthogonal integration methods can then be used to find the critical point that corresponds to a minimum of E .

A special consideration for DFT models is that m is large and evaluation of $\dot{\mathbf{X}}$ is expensive. These properties rule out many intrinsic integration schemes such as Crouch-Grossman and Runge-Kutta methods which demand operations with $m \times m$ matrices [16,45]. Higher order methods that eliminate $m \times m$ matrix operations still require multiple evaluations of $\dot{\mathbf{X}}$ which can become prohibitively expensive [14]. The choice of coordinates can also be based on a QR factorization and polar decompositions [18] or Lie groups [32]. An overview of geometric numerical integration techniques can be found in [38].

3.2.5 Optimal damping algorithm

The optimal damping algorithm (ODA) is a hybrid optimization procedure combining SCF with direct minimization of the Kohn-Sham energy. It relies on optimization over a convex set to ensure that electron numbers are conserved. The convex set is given by the density matrices $\mathbf{X}_k \mathbf{X}_k^T$ and $\mathbf{g}(\mathbf{X}_k \mathbf{X}_k^T)$, where \mathbf{g} is an SCF step for the density matrix. ODA is a fixed point density mixing scheme with optimal under-relaxation determined by minimizing [9,10]

$$\min_{\beta \in [0,1]} E((1 - \beta)\mathbf{X}_k \mathbf{X}_k^T + \beta \mathbf{g}(\mathbf{X}_k \mathbf{X}_k^T)), \quad (3.41)$$

where E is the density matrix dependent energy. For Kohn-Sham DFT ODA can converge to state corresponding to a system with fractional occupation [9]. However, ODA requires the expensive SCF step to be computed.

3.3 Ensemble optimization

Ensemble DFT requires minimization of the Helmholtz energy with regards to both the electronic orbitals \mathbf{X} and their occupation \mathbf{f} . This is typically done by keeping one variable fixed while optimizing with regards to the other [41].

Minimization of the Helmholtz energy with regards to the occupation numbers \mathbf{f} makes it necessary to ensure that \mathbf{f} remains in the physically feasible set \mathcal{F} (2.31). To ensure this, it is not possible to simply use the negative gradient as the search direction for optimization of A with regards to \mathbf{f} . When all occupation numbers are fractional it is enough to require that the search direction \mathbf{y} satisfies $\sum_{i=1}^n y_i = 0$ and that the step is sufficiently small to conserve the number of electrons. This can be achieved by orthogonal projection of $\nabla_{\mathbf{f}} A$

$$\mathbf{y} = - \left(\mathbf{I} - \frac{\mathbf{c}\mathbf{c}^T}{\mathbf{c}^T\mathbf{c}} \right) \nabla_{\mathbf{f}} A, \quad (3.42)$$

where all entries of \mathbf{c} are unity. However, all occupation numbers are in general not fractional and a simple projection fails to account for the physical requirements imposed on the occupation. In this case \mathbf{y} is determined by minimizing the quadratic objective function

$$\min_{\mathbf{y}} \|\mathbf{y} + \nabla_{\mathbf{f}} A(\mathbf{X}, \mathbf{f}_k)\|, \quad (3.43)$$

subject to the constraints

$$y_i \geq 0 \text{ if } f_i^k = 0, \quad (3.44)$$

$$y_i \leq 0 \text{ if } f_i^k = 1, \quad (3.45)$$

and

$$\sum_{i=1}^n y_i = 0. \quad (3.46)$$

Here y_i indicates the i :th entry of \mathbf{y} and f_i^k the i :th entry of \mathbf{f}_k .

Equation (3.43) can be solved with interior point methods [46]. After \mathbf{y} has been determined a line search is used to determine the positive step length

$$\min_{\sigma \leq \sigma_{\max}} A(\mathbf{X}, \mathbf{f}_k + \sigma \mathbf{y}), \quad (3.47)$$

where σ_{\max} is chosen to ensure that

$$0 \leq f_i^k + \sigma_{\max} y_i \leq 1 \quad \forall i, \quad (3.48)$$

remains satisfied. In practice a quadratic approximation of A along the search direction is constructed and σ_k is chosen to minimize this.

The direct optimization methods for the Stiefel manifold described in Sec. 3.2 can be combined with the optimization with regards to the occupation numbers described above. This is done by solving

$$\min_{\tau, \sigma} A(\mathbf{U}(\tau)\mathbf{X}_k, \mathbf{f}_k + \sigma\mathbf{y}), \quad (3.49)$$

which determines τ_k and σ_k and simultaneously updating both \mathbf{X} and \mathbf{f} . As before, the search is done by minimizing a quadratic approximation of A . Now A is approximated by a quadratic surface

$$p(\tau, \sigma) = c_1\tau^2 + c_2\sigma^2 + c_3\tau\sigma + c_4\tau + c_5\sigma + c_6. \quad (3.50)$$

To determine $p(\tau, \sigma)$, A and its gradients are evaluated at $(\mathbf{X}_k, \mathbf{f}_k)$ and at the trial point $(\mathbf{U}(\tau_t)\mathbf{X}_k, \mathbf{f}_k + \sigma_t\mathbf{y})$. The resulting system of equations is insufficient to uniquely determine $p(\tau, \sigma)$, as it is linearly dependent. This leaves two options: Eq. (3.50) can be modified, or A can be evaluated at a second trial point

$$(\tau_{t_2}, \sigma_{t_2}) \notin \{\gamma(\tau_t, \sigma_t) \mid \gamma \in \mathbb{R}\}. \quad (3.51)$$

The best option to determine $p(\tau, \sigma)$ depends on the implementation of the procedures computing A and its gradients.

Instead of using gradient information to minimize A it is possible to base the minimization scheme on smearing. This scheme minimizes the occupation for a fixed set of electronic orbitals and requires the energy of the individual orbitals to be computed [23, 41]. The updated occupation \mathbf{f}_{k+1} is given by the solution to

$$\min_{\sigma \in [0,1]} A(\mathbf{X}, (1 - \sigma)\mathbf{f}_k + \sigma\mathbf{f}_F), \quad (3.52)$$

where \mathbf{f}_F is the occupation given by the Fermi smearing function. This procedure ensures that $\mathbf{f}_{k+1} \in \mathcal{F}$ by optimization along the convex combination of \mathbf{f}_k and \mathbf{f}_F .

4. Concluding Remarks

This chapter reviews the four publications that form the main contribution of this dissertation. Publication I demonstrates the robustness of QN methods with Broyden type updates and Publication II documents a comparison of several direct minimizers with parametrized orthogonality constraints. Publication III presents direct optimization methods that intrinsically enforce the orthogonality constraints and Publication IV describes simultaneous optimization of the electronic orbitals and occupation numbers for ensemble DFT.

4.1 Publication I

Publication I demonstrates the robustness of the QN method with Broyden's second update when applied to the electronic density. Density based acceleration has the advantage that the discretized density is independent of the representation used for the approximation. The publication compares the DIIS method with the QN method and shows that the QN method is more robust and converges quickly even when DIIS completely fails to find a solution. In addition, the convergence rate of the QN method is comparable to DIIS for the remaining models. Publication I also includes a technical discussion on recursive implementation of Broyden's second update and highlights the importance of the weighting of the initial approximation of the inverse Jacobian.

The models considered cover a wide range of problem types in electronic ground state calculations. They include single molecules as well as a metal surface and a periodic system. A particularly challenging case is the spin-polarized Co_3 in a linear configuration. Each Co atom has an uneven number of electrons and the Co_3 molecule has several degenerate or near degenerate electron orbitals near the Fermi surface. For this reason

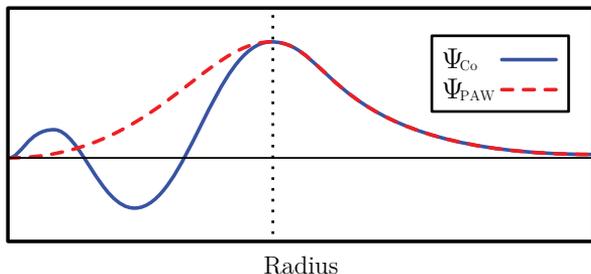


Figure 4.1. The electronic orbital Ψ_{Co} corresponding to a Coulombic potential is related to a PAW orbital Ψ_{PAW} by a linear transformation. The smoothing operation leads to an electron orbital with better numerical behavior.

the convergence of the valence electron orbitals becomes challenging.

The work presented in Publication I is carried out with GPAW [25,26]. GPAW is a real space finite difference DFT code that makes use of projector augmented waves (PAW) to simplify orbital behavior near the nuclei [20,44]. PAWs are related to pseudopotential techniques, but instead of using an effective potential, a linear operator is used to transform the electronic orbitals inside some critical radius [6,53], see Fig. 4.1. The description of the nuclear configuration for GPAW is done with ASE [3,4,26].

4.2 Publication II

Publication II investigates methods for direct energy minimization in electronic structure calculations. The unconstrained DIIS, QN, and NLCG methods are compared for the direct problem when orthogonality of the electronic orbitals is approximately preserved through an orbital transformation [59]. The publication also documents an adaptive weight estimator for the initial approximation of the inverse Jacobian. This adaptive weight estimator makes it possible to eliminate the line search step and reduce the cost of each optimization iteration for the QN method.

The results show that the line search free QN method remains a robust choice for electronic structure calculations. However, while the performance and robustness of the NLCG method is often comparable to the more complex QN method the NLCG method is parameter independent. Nevertheless, NLCG fails for the challenging linear Co_3 molecule, while QN successfully converges.

The methods are implemented and compared for the QUICKSTEP electronic structure code available as part of the CP2K suite of programs [15,

26,61]. QUICKSTEP makes use of an atom-centered hybrid Gaussian and plane-wave basis with a pseudopotential replacing the effective potential generated by the nuclei and core electrons [37].

4.3 Publication III

Publication III represents a shift in focus towards direct minimization where the orthonormality constraints are intrinsic to the energy optimization scheme. It explores updates of the electronic orbitals with a Householder reflection that simultaneously reflects the orbitals in several planes. The article also considers practical calculations where the orbitals are represented in an nonorthonormal basis. For these, the orthonormality constraint $\mathbf{X}^T \mathbf{X} = \mathbf{I}$ is replaced with an S-orthonormality constraint

$$\mathbf{X}^T \mathbf{S} \mathbf{X} = \mathbf{I}, \quad (4.1)$$

where \mathbf{S} is a symmetric and positive definite matrix. This matrix is called the overlap matrix in the electronic structure community.

The Householder reflector ensures that the S-orthonormality constraint on the orbitals remains satisfied and that the orbitals consequently remain on the manifold determined by these constraints. It is also demonstrated that the matrix exponential necessary to construct the reflector can be replaced with a unitary second order approximation without decreasing performance.

The methods are numerically evaluated on a model problem corresponding to an electronic structure calculation where the exchange-correlation effect and spin degree of freedom are neglected. The results show that the QN and NLCG methods based on the Householder update significantly outperform the projected NLCG reference method. The QN method performs slightly better than the NLCG method when the parameters of the QN method are correctly set. Nevertheless, the parameter independent NLCG method is more robust overall. Furthermore, it is found that the S-orthonormal basis only has a small impact on the number of iterations required for convergence as long as \mathbf{S} is well conditioned.

4.4 Publication IV

Publication IV continues the development of optimization schemes for direct energy minimization by intrinsic enforcement of the geometric con-

straints. The optimization routines are extended to the ensemble DFT formulation which permits fractional occupation of the electronic orbitals. Ensemble DFT makes it possible to compute states that minimize the Helmholtz energy at positive temperatures and offers an alternative to smearing schemes for metallic systems.

The numerical demonstrations are carried out on a model problem closely related to the model problem introduced in Publication III with the addition of an entropic term. The Helmholtz energy requires minimization with regards to both the electronic orbitals and the occupation of these orbitals. This is typically done separately for each variable while the other variable is kept fixed. It is shown that simultaneous updates of both variables is feasible and reduces the number of steps necessary for convergence.

For metallic systems at zero temperature the Helmholtz energy reduces to the Kohn-Sham energy which tends to discourage fractional occupation numbers. However, fractional occupation numbers are not forbidden and these are encountered for systems with degenerate or near degenerate orbitals at the Fermi level. In contrast, smearing schemes require highly accurate calculation of orbital energies and a fictitious positive temperature to correctly predict fractional occupation.

Bibliography

- [1] P.-A. Absil, R. Mahony, and R. Sepulchre. *Optimization Algorithms on Matrix Manifolds*. Princeton University Press, 2008.
- [2] J. F. Annett. Efficiency of algorithms for Kohn-Sham density-functional theory. *Comput. Mater. Sci.*, 4:23, 1995.
- [3] The latest version of ASE can be publicly accessed and anonymously downloaded from <http://wiki.fysik.dtu.dk/ase>.
- [4] S. R. Bahn and K. W. Jacobsen. An object-oriented scripting interface to a legacy electronic structure code. *Comput. Sci. Eng.*, 4:56, 2002.
- [5] C. Bekas, E. Kokiopoulou, and Y. Saad. Computation of large invariant subspaces using polynomial filtered Lanczos iterations with applications in density functional theory. *SIAM J. Matrix Anal. Appl.*, 30:397, 2008.
- [6] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50:17953, 1994.
- [7] V. Blum, R. Gehrke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler. Ab initio molecular simulations with numeric atom-centered orbitals. *Comp. Phys. Commun.*, 180:2175, 2009.
- [8] C. G. Broyden. A class of methods for solving nonlinear simultaneous equations. *Math. Comp.*, 19:577, 1965.
- [9] E. Cancès. Self-consistent field algorithms for Kohn-Sham models with fractional occupation numbers. *J. Chem. Phys.*, 114:10616, 2001.
- [10] E. Cancès and C. Le Bris. Can we outperform the DIIS approach for electronic structure calculations. *Int. J. Quantum Chem.*, 79:82, 2000.
- [11] E. Cancès and K. Pernal. Projected gradient algorithms for Hartree-Fock and density matrix functional theory calculations. *J. Chem. Phys.*, 128:134108, 2008.
- [12] R. Car and M. Parinello. Unified approach for molecular dynamics and density-functional theory. *Phys. Rev. Lett.*, 55:2471, 1985.
- [13] E. Celledoni and S. Fiori. Descent methods for optimization on homogeneous manifolds. *Mathematics and Computers in Simulation*, 79:1298, 2008.

- [14] E. Celledoni and B. Owren. A class of intrinsic schemes for orthogonal integration. *SIAM J. Numer. Anal.*, 40:2069, 2002.
- [15] The latest version of CP2K can be publicly accessed and anonymously downloaded from <http://www.cp2k.org/>.
- [16] P. E. Crouch and R. Grossman. Numerical integration of ordinary differential equations on manifolds. *J. Nonlinear Sci.*, 3:1, 1993.
- [17] J. E. Dennis, Jr. and J. J. Moré. Quasi-Newton methods: Motivation and theory. *SIAM Rev.*, 19:46, 1977.
- [18] L. Dieci and E. S. Van Vleck. Orthonormal integrators based on Householder and Givens transformations. *Future Gener. Comp. Sy.*, 19:363, 2003.
- [19] A. Edelman, T. A. Arias, and S. T. Smith. The geometry of algorithms with orthogonality constraints. *SIAM J. Matrix Anal. Appl.*, 20:303, 1998.
- [20] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsarlis, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, J. Schłötz, K. S. Thygesen, and K. W. Jacobsen. Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method. *J. Phys.: Condens. Matter*, 22:253202, 2010.
- [21] H.-r. Fang and Y. Saad. Two classes of multiseccant methods for nonlinear acceleration. *Numer. Linear Algebra Appl.*, 16:197, 2009.
- [22] C. Fiolhais, F. Nogueira, and M. Marques, editors. *A Primer in Density Functional Theory*. Springer, 2003.
- [23] C. Freysoldt, S. Boeck, and J. Neugebauer. Direct minimization technique for metals in density functional theory. *Phys. Rev. B*, 79:241103, 2009.
- [24] C.-L. Fu and K.-M. Ho. First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to Nb and Mo. *Phys. Rev. B*, 28:5480, 1983.
- [25] The latest version of GPAW can be publicly accessed and anonymously downloaded from <http://wiki.fysik.dtu.dk/gpaw>.
- [26] A description of the GPL licence can be found at <http://www.gnu.org/licenses/gpl.html>.
- [27] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864, 1964.
- [28] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133, 1965.
- [29] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mat. Sci.*, 6:15, 1996.

- [30] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54:11169, 1996.
- [31] G. Kresse and J. Hafner. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B*, 48:13115, 1993.
- [32] S. Krogstad. A low complexity lie group method on the Stiefel manifold. *BIT*, 43:107, 2003.
- [33] L. Lehtovaara, V. Havu, and M. Puska. All-electron density functional theory and time-dependent density functional theory with high-order finite elements. *J. Chem. Phys.*, 131:054103, 2009.
- [34] M. Levy and J. P. Perdew. Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. Shape of the correlation potential and diamagnetic susceptibility of atoms. *Phys. Rev. A*, 32:2010, 1985.
- [35] E. H. Lieb. Density functionals for coulomb systems. *Int. J. Quantum Chem.*, 24:243, 1983.
- [36] E. H. Lieb and S. Oxford. Improved lower bound on the indirect coulomb energy. *Int. J. Quantum Chem.*, 19:427, 1981.
- [37] G. Lippert, J. Hutter, and M. Parrinello. A hybrid Gaussian and plane wave density functional scheme. *Molec. Phys.*, 92:477, 1997.
- [38] C. Lubich, E. Hairer, and G. Wanner. *Geometric Numerical Integration*. Springer, 2006.
- [39] L. D. Marks and D. R. Luke. Robust mixing for ab initio quantum mechanical calculations. *Phys. Rev. B*, 78:075114, 2008.
- [40] D. Marx and J. Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, 2009.
- [41] N. Marzari, D. Vanderbilt, and M. C. Payne. Ensemble density-functional theory for ab initio molecular dynamics of metals and finite-temperature insulators. *Phys. Rev. Lett.*, 79:1337, 1997.
- [42] N. D. Mermin. Thermal properties of the inhomogeneous electron gas. *Phys. Rev.*, 137:A1441, 1965.
- [43] M. Methfessel and A. T. Paxton. High precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B*, 40:3616, 1989.
- [44] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen. Real-space grid implementation of the projector augmented wave method. *Phys. Rev. B*, 71:035109, 2005.
- [45] H. Munthe-Kaas. High order Runge-Kutta methods on manifolds. *Appl. Numer. Math.*, 29:115, 1999.
- [46] J. Nocedal and S. J. Wright. *Numerical Optimization*. Springer, 2006.
- [47] R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, 1989.

- [48] J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 78:1396, 1997.
- [49] J. P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 45:13244, 1992.
- [50] J. P. Perdew and A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23:5048, 1981.
- [51] P. Pulay. Convergence acceleration in iterative sequences: The case of SCF iteration. *Chem. Phys. Lett.*, 73:393, 1980.
- [52] L. Qi. On superlinear convergence of quasi-Newton methods for nonsmooth equations. *Oper. Res. Lett.*, 20:223, 1997.
- [53] C. Rostgaard. The Projector Augmented-wave Method. Available from https://wiki.fysik.dtu.dk/gpaw/paw_note.pdf.
- [54] Y. Saad, J. R. Chelikowsky, and S. M. Shontz. Numerical methods for electronic structure calculations of materials. *SIAM Review*, 52:3, 2010.
- [55] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Chem. Phys.*, 98:11623, 1994.
- [56] F. Tassone, F. Mauri, and R. Car. Acceleration schemes for ab initio molecular-dynamics simulations and electronic-structure calculations. *Phys. Rev. B*, 50:10561, 1994.
- [57] T. Torsti, T. Eirola, J. Enkovaara, T. Hakala, P. Havu, V. Havu, T. Höynälänmaa, J. Ignatius, M. Lyly, I. Makkonen, T. T. Rantala, J. Ruokolainen, K. Ruotsalainen, E. Räsänen, H. Saarikoski, and M. J. Puska. Three real-space discretization techniques in electronic structure calculations. *Phys. Stat. Sol. (b)*, 243:1016, 2006.
- [58] T. van Voorhis and M. Head-Gordon. A geometric approach to direct minimization. *Mol. Phys.*, 100:1713, 2002.
- [59] J. VandeVondele and J. Hutter. An efficient orbital transformation method for electronic structure calculations. *J. Chem. Phys.*, 118:4365, 2003.
- [60] J. VandeVondele and J. Hutter. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.*, 127:114105, 2007.
- [61] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter. QUICKSTEP: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.*, 167:103, 2005.
- [62] Y. Zhou, Y. Saad, M. L. Tiago, and J. R. Chelikowsky. Self-consistent-field calculations using Chebyshev-filtered subspace iteration. *J. Comp. Phys.*, 219:172, 2006.



ISBN 978-952-60-4721-8
ISBN 978-952-60-4722-5 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934
ISSN 1799-4942 (pdf)

Aalto University
School of Science
Department of Mathematics and Systems Analysis
www.aalto.fi

**BUSINESS +
ECONOMY**

**ART +
DESIGN +
ARCHITECTURE**

**SCIENCE +
TECHNOLOGY**

CROSSOVER

**DOCTORAL
DISSERTATIONS**