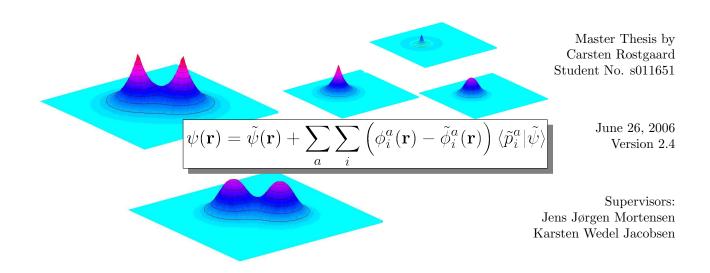# Exact Exchange in Density Functional Calculations

An implementation in the projector augmented wave method

Master Thesis by
Carsten Rostgaard
Student No. s011651

$$\psi(\mathbf{r}) = \tilde{\psi}(\mathbf{r}) + \sum_a \sum_i \left(\phi_i^a(\mathbf{r}) - \tilde{\phi}_i^a(\mathbf{r}) \right) \langle \tilde{p}_i^a | \tilde{\psi} \rangle$$

Supervisors:
Jens Jørgen Mortensen
Karsten Wedel Jacobsen

Preface

This thesis is submitted in candidacy for the cand.polyt degree (Master of Science in Engineering) at the Technical University of Denmark (DTU). The work presented here has been performed between September 2005 and June 2006, at the Center for Atomic-scale Materials Physics (CAMP), Department of Physics, DTU, with Professor Karsten Wedel Jacobsen and Ph.D. Jens Jørgen Mortensen as supervisors.

I sincerely thank my supervisors Jens Jørgen Mortensen and Karsten Wedel Jacobsen for helpful guidance and for introducing me to this subject, which has proven a stimulating challenge. Especially thanks to Jens Jørgen Mortensen for guiding me through the many lines of code in his program and helping me debug my own contributions.

The process of my work had a high initial barrier, having to learn a new programming language, and trying to understand both the role of exact exchange in density functional theory and the technicalities of the projector augmented wave method. The diversity of being able to shift between doing practical implementations and digging deeper into the theory of electronic structure calculations, was very inspiring and helped ward of stagnation during the 10 months of working on the subject.

Also a warm thanks to my office mates Souheil Saadi, Jeppe Gavnholt, Heine A. Hansen, Mads Engelund, and Anja Toftelund for providing a both social and intellectually stimulating working environment.

Lyngby, June 2006
Carsten Rostgaard

Abstract

This thesis discuss the theoretical and practical aspects of the exact treatment of exchange, within density functional theory. The specific type of density functional scheme, is the projector augmented wave (PAW) method. The exact treatment of exhange plays an important role for an accurate description of the electronic structure of matter.

The PAW method is a pseudopotential-like approach, in which explicit calculations are only performed on a pseudized version of the valence states. The advantage of PAW over other psedopotential methods is, that it offers access to the all-electron wave functions, through a linear transformation. This is important, as exact exchange involves overlap integrals of all states, so access to the core states is essential.

The results of applying the method indicates that the valence-core exchange interactions play an important role, thus justifying the use of the PAW method instead of ordinary pseudopotential approaches, where such contributions would be inaccessible.

Resumé

Dette projekt omhandler de teoretiske og praktiske aspekter ved beregning af eksakt exchange i tæthedsfunktional beregninger. Dette er gjort indenfor PAW (projector augmented wave) metoden. Bestemmelse af eksakt exchange er vigtigt for en nøjagtig beskrivelse af materialers elektroniske struktur.

PAW metoden er af pseudopotential karakter, hvor de egentlige beregninger kun omfatter udglattede versioner af valenstilstandene. Fordelen ved PAW frem for andre pseudopotential metoder er, at den giver adgang til de fulde bølgefunktioner ved en lineær transformation af de udglattede versioner. Dette er vigtigt, idet eksakt exchange involverer overlap-integraler af alle kombinationer af bølgefunktioner, så information om kernetilstandene er nødvendig for en korrekt beskrivelse.

Beregninger udført i rapporten indikerer at valens-kerne vekselvirkning udgør en vigtig del af exchange energien. Dette retfærdiggør brugen af PAW i stedet for andre pseudopotential metoder, hvor sådanne vekselvirkninger ville være utilgængelige.

Contents

Chapter 1

Introduction

Electronic Structure Calculations

Electronic structure calculations are the source of many *ab initio*, or first principles, calculations in condensed matter physics.

In principle the full time dependent relativistic Schrödinger equation holds the promise of accurate calculations of all properties of any material from the specification of the atomic number of the constituents, their initial state, and the externally applied forces and electromagnetic fields only. In practice the equations to be solved are much too complicated to solve for all but the simplest of systems. Separating the motion of nuclei and electrons in accordance with the Born-Oppenheimer approximation, it turns out that most physics are well described by the electronic structure of the considered system.

If one restricts focus to the ground-state properties of time independent systems, one can make use of Density Functional Theory (DFT), which offers a large computational simplification of the many-electron problem. DFT also exists in a time dependent version (TDDFT), but this is rather more involved, and will not be discussed in this text. See e.g. [1, chapter 4] for a nice review. Ground-state properties span a very important class of properties for solids and molecules, as this is the natural state of matter. Among these are for example equilibrium crystal structures and lattice constants, molecular binding lengths, cohesive-, atomization-, and ionization energies, electron affinities, reaction sites of catalysts, energy barriers for e.g. diffusion, dissociation and adsorption, Young's and bulk moduli, etc.

In this text all calculations on electronic structure are done within the framework of density functional theory.

Exact Exchange and the Projector Augmented Wave Method

Although in principle exact, DFT requires knowledge of an unknown energy functional, termed the exchange-correlation (xc) functional. The energy contribution of the xc-functional to the total energy is relatively minor, usually less than 1%, but plays an important part in derived quantities, for example it constitutes 50% of the binding energy of N_2.

Usually sufficient accuracy can be obtained by local density-functional approximations of the xc-functional. There is however a limit to what can be described by such local approximations. An exact expression for the exchange part of the xc-functional is actually available, so to go beyond the local xc approximations an exact treatment of exchange seems natural. Energetically exchange is the dominant part of exchange-correlation (total correlation energy is typically only 10% of the size of exchange, although it might be more important for binding energies), and in any case an exact treatment of more parts of the total energy functional is esthetically appealing. Unfortunately including non-local parts of the exchange energy is incompatible with local correlation, as the large cancellation of the long range behaviors of the true non-local correlation and exact exchange

is not described properly. Several procedures have been proposed to correct this problem, some of which are reviewed in this text.

Inclusion of a fraction of exact exchange has a beneficial effect on atomization energies, bond lengths, band gaps and excitation energies of most molecules and insulating solids. This is the motivation for my work on implementing exact exchange calculations in the program GPAW, which is a DFT calculator developed at CAMP [2].

Determination of exact exchange requires access to the core orbitals, so an all electron method is essential for the correct description. As evaluating the Fock integrals inherent in exact exchange is already a very time consuming process, the traditional all electron methods are not very attractive for an implementation. This motivates the choice of the projector augmented wave method (PAW), which offers the speed of pseudopotential approaches, while maintaining the accuracy of all electron methods, specifically, the access to full all electron potentials an Kohn-Sham orbitals.

Consistent with the title of my project, the initial chapters of this report presents different approaches, and reasons, for including exact exchange in density functional calculations. The main result of the analytic section, and my personal contribution to the subject, was the derivation of how the non-local Fock operator and the exact exchange energy functional should be expressed in the PAW formalism. These are the two main ingredients of most exact exchange methods.

Parallel to the analytic work, some software development has been done to implement the method in GPAW. Currently, the working parts of the code include non-self-consistent evaluation of the exchange energy for isolated systems only. The energy evaluation has been implemented both in an atomic calculator, and the full PAW version for comparison of results. Comparisons have also been performed with equivalent exchange calculations in the literature (using other than PAW methods).

Applying exact exchange perturbatively, only total energy evaluations are obtainable. The orbitals and KS eigen values will just be those of the xc-functional used to reach self-consistency of the Kohn-Sham equations. The real strength of exact exchange is that it improves the eigenvalue spectrum, and thereby also the band gap, predicted by the DFT procedure, so a self-consistent evaluation is essential. For a self-consistent inclusion of exact exchange, a specific method must be chosen, the simplest of which is the hybrid Hartree-Fock-Kohn-Sham (HF-KS) method. Work on implementing this specific method has been initiated, but is not finished.

Outline of the Thesis

Chatpers 1 and 2 introduces the subject of electronic structure calculations.

Chapter 3 provides the theoretical background of density functional theory, including a description of the hybrid Hartree-Fock Kohn-Sham scheme for inclusion of exact exchange, and a discussion of the role of exchange and correlation.

Chapter 4 describes the theory and some practical issues of how to handle infinite systems.

Chapter 5 is a review of different methods for handling orbital dependent functionals in the standard Kohn-Sham scheme.

Chapter 6 and 7 presents the theoretical and practical aspects of the projector augmented wave method. This is also where I derive the expressions for how exact exchange is represented in the PAW formalism, and is thus the main part of my analytic work.

Chapter 8 shows the numerical results, which is mainly tests and benchmarking of the implemented code.

Notation

The unit system used in this theoretical part, is atomic units. In this unit system $e = \hbar = a_0 = m_e = 1$, and all electromagnetic expressions are written in cgs form (using Gauss and statvolt for

magnetic and electric field strengths respectively). In SI units kinetic energies/operators would have a prefactor of $\hbar^2/m_e$ and potential terms would have a prefactor of $e^2/4\pi\epsilon_0$, as compared to equations given in atomic units.

I use a capital Ψ to indicate interacting and Φ for non-interacting many-body wave functions. Consistently I denote, everywhere but in the PAW chapters, single particle wave functions (which are by nature non-interacting) by a lower case ϕ. In the PAW chapters however, to conform to standard literature, the Kohn-Sham wave functions are denoted by ψ while ϕ indicates arbitrary basis set functions. Hopefully this explanation will prevent most confusion caused by this choice.

The term locality is used both in the meaning that a density-functional potential can depend on density locally around the point in which it is evaluated, and in the meaning that a potential is multiplicative. GGA approximations of the xc-potential are local in both regards, the Fock potential is non-local in both regards, while the exact exchange potential obtained with for instance the optimized effective potential method is a multiplicative potential, but still non-local in the sense that it depends on the global structure of the density.

Chapter 2

Basic Wave Function Theory

2.1 The Many-Body Problem

The many-body problem is basically the complication of solving the Schrödinger equation for systems involving many particles. The starting point of many problems in condensed matter physics, is the description of systems offered by the non-relativistic, time-independent Schrödinger equation

$$\widehat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle \tag{2.1}$$

where $\widehat{H}$ is the Hamiltonian operator, n is a complete set of quantum state labels, E_n are the eigenenergies, and $|\Psi_n\rangle$ are the full many-body eigenstates depending on both electron and nuclei coordinates. In absence of externally applied fields, the Hamiltonian is

$$\widehat{H} = \sum_i \frac{\widehat{P}_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq j} \frac{Q_i Q_j}{|\widehat{R}_i - \widehat{R}_j|} \tag{2.2}$$

where the sums are over all electrons and nuclei, and m_i, Q_i, $\widehat{P}_i$ and $\widehat{R}_i$ are the mass, charge, momentum- and position operator of the i'th particle (electron or nuclei) respectively. The prefactor of $1/2$ on the second term is present to compensate for double counting.

A great simplification of the many-body problem is achieved by the Born-Oppenheimer approximation, in which the electrons are assumed to respond instantaneously to the movement of the much heavier nuclei. This allows for the nuclei to be considered as static classical potentials. In this case, the Hamiltonian describing the many-electron problem, can be decomposed as a kinetic contribution of the electrons, $\widehat{T}$, a contribution from the electron-electron interaction potential, $\widehat{V}_{ee}$, one from the electron-nuclei interaction potential, $\widehat{V}_{en}$, and one from the nuclei-nuclei interaction potential, $\widehat{V}_{nn}$. In position representation the explicit form of $\widehat{H}$ for a system of N electrons and M nuclei is

$$\begin{aligned}
\widehat{H} &= \widehat{T} + \widehat{V}_{ee} + \widehat{V}_{en} + \widehat{V}_{nn} \\
&= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,k} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \frac{1}{2}\sum_{l\neq k} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}
\end{aligned} \tag{2.3}$$

where the indices $i,j \in 1,\ldots,N$ and $k,l \in 1,\ldots,M$. ∇^2 is the Laplacian with respect to the electron coordinates, Z is the atomic number of the nuclei and $\mathbf{r}$ and $\mathbf{R}$ are the coordinates of the electrons and nuclei respectively. Note that the terms, $\widehat{V}_{ee}$ and $\widehat{V}_{nn}$, are positive due to the coulomb repulsion of charges of the same sign, whereas $\widehat{V}_{en}$ is negative due to the attraction of charges of different sign.

In the Born-Oppenheimer approximation, the relevant wave functions are the electronic wave functions describing the quantum state of the electrons, which only depends explicitly on the electron coordinates

$$\langle \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N |\Psi_n\rangle = \Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{2.4}$$

It does however still depend parametrically on the nuclei coordinates, which is essential if one wishes to determine the forces on the atoms. Note that here and in the remainder of this text, the spin coordinate has been suppressed for notational convenience. For a discussion on the changes introduced by inclusion of spin, see section 2.4. The many-electron wave function must (as all fermionic systems) be antisymmetric under the exchange of electron coordinates, i.e.

$$\Psi(\ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = -\Psi(\ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots) \tag{2.5}$$

As the nuclei are fixed, the term $\widehat{V}_{en}$ in the Hamiltonian, determines an external potential in which the electrons reside, and could equally well include additional external potentials. To allow for this more general case, $\widehat{V}_{en}$ will in the future be denoted $\widehat{V}_{\text{ext}}$.

The term $\widehat{V}_{nn}$ in (2.3) represents an additive constant to the total energy, and will for notational simplicity be omitted in the rest of this text; one can think of it as a constant included in the external potential. The total Hamiltonian for the electronic system in the static potential from the fixed nuclei, will thus in the remainder of this text be written as

$$\widehat{H} = \widehat{T} + \widehat{V}_{ee} + \widehat{V}_{ext} \tag{2.6}$$

It should be remembered, when applying (2.6), that in the case of large external (or internal) fields, the non-relativistic approximation might break down. The core electrons of heavy atoms for example, have very high kinetic energies due to their tight orbits, and as such should be described relativistically.[1]

Light atoms, e.g. hydrogen, or systems in general for which $\nabla_{\mathbf{R}} \psi$ or $\nabla_{\mathbf{R}}^2 \psi$ are not small, are not well described by the Born-Oppenheimer approximation. And of course only time-independent potentials are described by the time-independent Schrödinger equation.

Even when invoking these assumptions, the many-electron problem still requires solving an eigenvalue problem of $3N$ variables, and is not readily solved in the form above.

2.2 Wave Functions and Their Interpretation

The arbitrary multiplicative constant involved when solving a differential equation of the form $\widehat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$ is fixed by the normalization requirement that

$$\langle \Psi | \Psi \rangle = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 = 1 \tag{2.7}$$

The remaining degrees of freedom involved in solving a second order partial differential equation, i.e. the boundary conditions, are discussed in section 4.2.

For a system in a specific state Ψ_n, we interpret $|\Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2$ as the probability density of finding particle 1 at $\mathbf{r}_1$ particle 2 at $\mathbf{r}_2$, etc.[2]. Thus the normalization (2.7) indicates that the probability of finding all electrons somewhere in space is unity.

For a system in a specific state Ψ_n, the expectation value of a given observable $\widehat{\mathcal{O}}$ is:

$$\langle \widehat{\mathcal{O}} \rangle = \langle \Psi_n | \widehat{\mathcal{O}} | \Psi_n \rangle = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \Psi_n^*(\mathbf{r}_1, \ldots, \mathbf{r}_N) \widehat{\mathcal{O}} \Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.8}$$

For example

$$E_n = \langle \Psi_n | \widehat{H} | \Psi_n \rangle = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \Psi_n^*(\mathbf{r}_1, \ldots, \mathbf{r}_N) \widehat{H} \Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.9}$$

To determine expectation values, we need to know the state of the considered system. Usually we will constrict our attention to the ground-state $|\Psi_0\rangle$, which is the state occupied at zero temperature (the state with the smallest eigenvalue $E_n = E_0$).

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[1] As only the valence electrons are chemically important, different schemes are typically applied to avoid explicit calculations on the core states altogether. For a specific scheme, see section 6.

[2] As the particles are indistinguishable, and there are $N!$ distinct permutations of N particles, one should perhaps rather say that $N!|\Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \ldots d\mathbf{r}_N$ is the probability of finding any of the particles in the volume element $d\mathbf{r}_1 \ldots d\mathbf{r}_N$ centered at $\mathbf{r}_1 \ldots \mathbf{r}_N$

2.2.1 One and Two Particle Density Operators

The electron density describes the probability density of finding an electron at position $\mathbf{r}$. The associated operator, and its expectation value are given by

$$\hat{n} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.10a}$$

$$n(\mathbf{r}) = \langle \Psi_n | \hat{n} | \Psi_n \rangle = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \tag{2.10b}$$

In a similar fashion, we can define a two electron density by:

$$\hat{\rho}_2 = \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) = \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\hat{n}(\mathbf{r}) \tag{2.11a}$$

$$\rho_2(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{\rho}_2 | \Psi \rangle = N(N-1) \int d\mathbf{r}_3 \dots d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2 \tag{2.11b}$$

which we interpret as the probability of finding an electron at $\mathbf{r}$ *and* one at $\mathbf{r}'$, $P(\mathbf{r} \wedge \mathbf{r}')$. From basic probability theory, it is well known that the joint probability can be found as the product of the isolated event times the conditional event, i.e. $P(\mathbf{r} \wedge \mathbf{r}') = P(\mathbf{r})P(\mathbf{r}'|\mathbf{r})$ or

$$\rho_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n_2(\mathbf{r}, \mathbf{r}') \tag{2.12}$$

where $n_2(\mathbf{r}, \mathbf{r}')$ is the conditional probability density of finding an electron at $\mathbf{r}'$ given that one is present at $\mathbf{r}$. Clearly, if one is present at $\mathbf{r}$ the number of electron elsewhere is $N - 1$, i.e. we have the sum rule:

$$\int d\mathbf{r}' n_2(\mathbf{r}, \mathbf{r}') = N - 1 \tag{2.13}$$

note that the nature of the two coordinates of n_2 are different due to the definition (2.12).

One can also define a pair correlation function $g(\mathbf{r}, \mathbf{r}')$ and a correlation hole n_{xc}[3] by

$$\rho_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})\left(n(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}')\right) \tag{2.14}$$

The pair correlation function is symmetric in its arguments, and describes the correlation of the two events $P(\mathbf{r} \wedge \mathbf{r}') = P(\mathbf{r})P(\mathbf{r}')g(\mathbf{r}, \mathbf{r}')$. For uncorrelated events $g(\mathbf{r}, \mathbf{r}') = 1$. The exchange-correlation hole describes how much the conditional event differs from the isolated event. For completely uncorrelated events, $n_{xc} = 0$. From (2.13) it is clear that

$$\int d\mathbf{r}' n_{xc}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}' \left(n_2(\mathbf{r}, \mathbf{r}') - n(\mathbf{r}')\right) = -1 \tag{2.15}$$

From the expression for the two particle density (2.11b) we see that the expectation value of the electron-electron interaction operator $\widehat{V}_{ee}$ can be written as

$$\begin{aligned} \langle \Psi | \widehat{V}_{ee} | \Psi \rangle &= \langle \Psi | \tfrac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle \\ &= \frac{1}{2} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \rho_2(\mathbf{r}, \mathbf{r}') \\ &= \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \tag{2.16}$$

where the first term is just the classical electrostatic energy of a charge distribution, the Hartree energy $U_H[n(\mathbf{r})]$, and the last term is a purely quantum mechanical contribution describing the coulombic repulsion of individual electrons.

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[3] The correlation hole is indexed xc for future convenience, as the convention in density-functional theory is to divide the correlation of electrons into an 'exchange' part and a 'correlation' part.

2.3   The Non-Interacting Many-Body Problem

The electron-electron repulsion $\widehat{V}_{ee}$ sums over all distinct pairs of electrons, making them intricately correlated. This correlation is very difficult to handle in any simple way. For this reason, we now turn to the important special case of the general Hamiltonian (2.6), in which there is no electron-electron interaction, i.e.:

$$\widehat{H}_{\text{Non}} = \widehat{T} + \widehat{V}_{ext} \tag{2.17}$$

This system can be described by the N identical single particle systems, described by

$$\hat{h}_i = -\tfrac{1}{2}\nabla_i^2 + v(\mathbf{r}_i) \tag{2.18a}$$

$$\hat{h}_i|\phi_n\rangle = \epsilon_n|\phi_n\rangle \tag{2.18b}$$

where v is the external potential of the many body system, $\langle\mathbf{r}_i|\phi_n\rangle = \phi_n(\mathbf{r}_i)$ are the eigenstates of $\hat{h}_i$, and ϵ_n are the corresponding eigenvalues (or -energies). Here and in the remainder of this text it is understood that the eigenfunctions and -values are ordered such that $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \ldots$.

The many-body system consisting of all N particles would, for non-interacting particles, be described by:

$$\widehat{H}_{\text{Non}} = \sum_i \hat{h}_i \tag{2.19a}$$

$$\widehat{H}_{\text{Non}}|\Phi_0\rangle = E_0|\Phi_0\rangle \tag{2.19b}$$

Where the ground state many-body wave function of the non-interacting system, $|\Phi_0\rangle$, is a slater determinant of the N lowest single particle eigenstates:

$$\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \vdots & \ddots & \\ \phi_N(\mathbf{r}_1) & & \phi_N(\mathbf{r}_N) \end{vmatrix} \tag{2.20}$$

and

$$E_0 = \langle\Phi_0|\widehat{H}_{\text{Non}}|\Phi_0\rangle = \sum_n f_n\epsilon_n \tag{2.21}$$

is the total energy of the non-interacting system. f_n are the occupation numbers.

The electron density of the non-interacting system is:

$$n(\mathbf{r}) = \langle\Phi_0|\sum_i \delta(\mathbf{r} - \mathbf{r}_i)|\Phi_0\rangle = \sum_n f_n|\phi_n(\mathbf{r})| \tag{2.22}$$

Note that interacting wave functions are indicated by ψ and non-interacting by ϕ. Lower case letters indicate single particle wave functions, while upper case letters mark many-body wave functions.

2.4   Spin

Unless stated otherwise, the spin coordinate is suppressed in all equations of this thesis. The procedure for generalizing the equations to inclusion of spin is reviewed in this section, as this will be needed for some considerations.

To include spin, the spatial coordinate must be supplemented by an additional spin coordinate

$$\mathbf{r} \rightarrow \mathbf{r}\sigma \tag{2.23}$$

while the spin state is simply implicitly included in the state index n.

The coordinate transformation implies that e.g.

$$\int d\mathbf{r} \rightarrow \sum_\sigma \int d\mathbf{r} \tag{2.24}$$

$$\delta(\mathbf{r} - \mathbf{r}') \rightarrow \delta_{\sigma,\sigma'}\delta(\mathbf{r} - \mathbf{r}') \tag{2.25}$$

If a single particle Hamiltonian does not depend upon spin, the eigenstates will be simple products of Cartesian functions with spinors [3]

$$\phi_n(\mathbf{r}, \sigma) = \phi_n(\mathbf{r})\chi_{\sigma_n}(\sigma) \tag{2.26}$$

where the spinor is simply a Kronecker delta $\chi_{\sigma_n}(\sigma) = \delta_{\sigma_n,\sigma}$.

In this way, the spin-density becomes

$$n(\mathbf{r}) = \sum_n f_n |\phi_n(\mathbf{r})|^2 \rightarrow n(\mathbf{r}\sigma) = \sum_n f_n \delta_{\sigma_n,\sigma} |\phi_n(\mathbf{r})|^2 \tag{2.27}$$

And the total density is just $n(\mathbf{r}) = \sum_\sigma n(\mathbf{r}\sigma)$.

The direct and exchange products transform according to

$$\iint d\mathbf{r}d\mathbf{r}' \phi_n^*(\mathbf{r})\phi_n(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_{n'}(\mathbf{r}') \rightarrow \iint d\mathbf{r}d\mathbf{r}' \sum_{\sigma\sigma'} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_{n'}(\mathbf{r}')\delta_{\sigma,\sigma_n}\delta_{\sigma',\sigma_{n'}}\delta_{\sigma,\sigma_n}\delta_{\sigma',\sigma_{n'}}$$

$$= \iint d\mathbf{r}d\mathbf{r}' \phi_n^*(\mathbf{r})\phi_n(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_{n'}(\mathbf{r}')$$

$$\iint d\mathbf{r}d\mathbf{r}' \phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}') \rightarrow \iint d\mathbf{r}d\mathbf{r}' \sum_{\sigma\sigma'} \phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}')\delta_{\sigma,\sigma_n}\delta_{\sigma,\sigma_{n'}}\delta_{\sigma',\sigma_n}\delta_{\sigma',\sigma_{n'}}$$

$$= \iint d\mathbf{r}d\mathbf{r}' \delta_{\sigma_n,\sigma_{n'}} \phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}')$$

$$\tag{2.28}$$

The Hartree energy is not really changed, as

$$
\begin{aligned}
U_H &= \tfrac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&\rightarrow \tfrac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \sum_{\sigma\sigma'} \frac{n(\mathbf{r}\sigma)n(\mathbf{r}'\sigma')}{|\mathbf{r} - \mathbf{r}'|} \\
&= \tfrac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{\left(\sum_\sigma n(\mathbf{r}\sigma)\right)\left(\sum_{\sigma'} n(\mathbf{r}'\sigma')\right)}{|\mathbf{r} - \mathbf{r}'|} \\
&= \tfrac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\end{aligned}
\tag{2.29}
$$

i.e. the densities are replaced by total densities (the sum of the spin densities).

Chapter 3

Density Functional Theory

Density-functional theory (DFT) is an, in principle, exact method for obtaining the ground state energy of a system, offering an alternative method to solving for the fully interacting many-body wave function. As the name implies, DFT relies on the density rather than the wave functions to provide information on a system. The basis for DFT is the Hohenberg-Kohn (HK) theorems [4], which tells us that all ground state properties of a system can be regarded as functionals of the ground state density. This is obviously of great numerical importance, as the basis of all calculations are thus centered on a single real-valued function of three coordinates as opposed to the complex valued wave functions of $3N$ coordinates required to describe the N particle problem in the traditional Schrödinger approach.

Although in principle exact, DFT requires knowledge of a universal, but in general unknown functional known as the HK functional $F[n]$, which in practice must be approximated. In 1965 Kohn and Sham [5] developed a self-consistent scheme for approximating $F[n]$, and determining the ground state density. Although to date still the most widely used DFT scheme, KS-DFT is not the only way of doing DFT. The simplest version of DFT is Thomas-Fermi (TF) theory, and more general formulations which encompass both KS and TF theory exist. One such formulation will be discussed in section 3.2.

The father of DFT, Walter Kohn, received the Nobel prize in 1999 [6], for his seminal work on the theory.

3.1 Hohenberg-Kohn Theory
- The Ground State Energy

The total energy of the state Ψ is $\langle\Psi|\widehat{H}|\Psi\rangle$. By the variational principle, the ground state energy is the minimum of the expectation value of the Hamiltonian

$$E_0 = \min_{\Psi}\langle\Psi|\widehat{H}|\Psi\rangle \tag{3.1}$$

where $\widehat{H} = \widehat{T} + \widehat{V}_{ee} + \widehat{V}_{\text{ext}}$ is the full many-electron Hamiltonian, and $|\Psi\rangle$ is any normalized ($\langle\Psi|\Psi\rangle = 1$) antisymmetric many-electron wave function.

The minimization (3.1) can be written as

$$
\begin{aligned}
E_0 &= \min_{\Psi} \langle \Psi | \widehat{H} | \Psi \rangle \\
&= \min_{n(\mathbf{r}) \to N} \left[\min_{\Psi \to n} \langle \Psi | \widehat{T} + \widehat{V}_{ee} + \widehat{V}_{\text{ext}} | \Psi \rangle \right] \\
&= \min_{n(\mathbf{r}) \to N} \left[\min_{\Psi \to n} \langle \Psi | \widehat{T} + \widehat{V}_{ee} | \Psi \rangle + \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right] \\
&= \min_{n(\mathbf{r}) \to N} \left[F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right] \\
&= \min_{n(\mathbf{r}) \to N} E[n]
\end{aligned}
\tag{3.2}
$$

where $\min_{\Psi \to n}$ means minimizing over all antisymmetric wave functions producing the same electron density, $n(\mathbf{r})$, and $\min_{n(\mathbf{r}) \to N}$ is a minimization over all densities which integrates to the total number of electrons, N. We see that the system specific part, $\langle \Psi | \widehat{V}_{\text{ext}} | \Psi \rangle$, is independent of the specific form of the wave function, as long as it produces the density $n(\mathbf{r})$, and that the system independent part can be collected in the universal (HK) functional

$$
F[n] \equiv \min_{\Psi \to n} \langle \Psi | \widehat{T} + \widehat{V}_{ee} | \Psi \rangle
\tag{3.3}
$$

Note that any of the possibly degenerate wave functions producing $n(\mathbf{r})$ while minimizing $\langle \widehat{T} + \widehat{V}_{ee} \rangle$ is equally valid in the minimization above.

Equation (3.2) also defines the energy functional

$$
E[n] = F[n] + \int d\mathbf{r} \, n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})
\tag{3.4}
$$

which when minimized yields both the ground state density $n_0(\mathbf{r})$ and the ground state energy $E_0 = E[n_0]$.

The minimization of the energy functional is be done with the normalization condition $\int d\mathbf{r} n(\mathbf{r}) = N$, i.e. that the total number of electrons is fixed. The Euler-Lagrange equation for the minimization is[1]

$$
\delta \left\{ F[n] + \int d\mathbf{r} \, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) - \mu \int d\mathbf{r} \, n(\mathbf{r}) \right\} = 0
$$
$$
\Downarrow
$$
$$
\frac{\delta F[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \mu
\tag{3.5}
$$

where the conservation of electrons is enforced by the introduced Lagrange multiplier μ, which is adjusted such that $\int d\mathbf{r} n(\mathbf{r}) = N$. μ can be recognized as the chemical potential of the system.

Equation (3.5) plays a central role in DFT, as it establishes a correspondence between the external potential and the ground state density, given that the explicit form of the HK functional is known. The correspondence is not strictly unique, as there might be several densities satisfying (3.5) and resulting in the same (minimal) value of eq. (3.4), i.e. there might be degenerate ground states. Furthermore the potential can only be determined up to an arbitrary additive constant, as a constant shift of v_{ext} is compensated by an identical shift of the chemical potential (a constant shift does not affect the position of the extremes of a functional). This additive constant is obviously irrelevant, as a constant shift of the potential corresponds to the same physical system.

We have thus arrived at the two most important theorems of density functional theory, first stated by Hohenberg and Kohn in 1964 [4] and therefore referred to as the HK theorems:

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[1]Formally the Euler-Lagrange equation is a condition for (local) extremes of a functional, so one should check that the result is indeed a (global) minimum.

1 The ground state electron density

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{3.6}$$

uniquely determines the potential in which the electrons reside (up to an arbitrary additive constant). In the degenerate case, any of the degenerate densities can be used to, in principle, determine the potential.

2 The ground state energy functional is subject to a variational principle, being minimal at the true ground state density only.

The first following from eq. (3.5) and the second from the minimization (3.2).

Since two systems can only differ by the external potential and the total number of electrons, and since $\int n(\mathbf{r})d\mathbf{r} = N$, theorem **1** states that all information about the ground state is contained in the 3 dimensional real-valued density, including the $3N$ variable complex valued ground state wave function. Which is obviously a quite remarkable result.

Theorem **2** implies that if one were able to write down the explicit form of the system independent functional $F[n]$ once and for all, the problem of determining any ground-state property of a given system, would simply be a matter of minimizing the functional $E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$ and then evaluating the observable as a functional of the minimizing density $n(\mathbf{r})$. The only problem is that $F[n]$ is not known explicitly.

Note that the procedure above follows the constrained search principle of Levy [7], in which the only assumption on the wave functions in the minimization (3.3) is that it should be antisymmetric and produce the density $n(\mathbf{r})$, i.e. it should be N-representable. In the original proof of Hohenberg and Kohn [4] they had to restrict the minimization to wave functions that where ν-representable, i.e. the density should be realizable for a real system in *some* external potential.

3.2   The Generalized Kohn-Sham Scheme

The main idea of all DFT schemes is to construct a model system with the same ground state (g.s.) electron density as the real system, solve the Schrödinger equation for this, and then evaluate the total g.s. energy (or any other g.s. property) as a functional of the determined g.s. density. It is known from the HK theorem that all observables can be represented in this way, but not how, so the functional form has to be approximated in practice. If the model system describes most of the energetics of the real system, it is useful to derive the energy functional for the model system, and then only approximate the remaining part.

The scheme presented here is a generalization of the scheme proposed by Kohn and Sham in [5], following the procedure described in [8] and [9].

We start by separating the HK functional according to

$$F[n] = F_s[n] + Q_s[n] \tag{3.7}$$

where $F_s[n]$ is the HK functional of the model system, and $Q_s[n]$ is some approximated density-functional defined by the above. The HK functional of the real system is $F[n] = \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \widehat{T} + \widehat{V}_{ee} | \Psi \rangle$. If we restrict our attention to model systems described by Slater type wave functions, the HK functional of the model system can be written as

$$F_s[n] = \min_{\Phi \to n(\mathbf{r})} S[\Phi] = \min_{\{\phi\} \to n(\mathbf{r})} S[\{\phi\}] \tag{3.8}$$

where the minimization is restricted to Slater type wave functions only, and $S[\Phi]$ is a suitable functional of this determinant defining the model system. For example $S[\Phi] = \langle \Phi | \widehat{T} | \Phi \rangle$ results in the KS scheme, and $S[\Phi] = \langle \Phi | \widehat{T} + \widehat{V}_{ee} | \Phi \rangle$ in the Hartree-Fock Kohn-Sham (HF-KS) scheme.

We now define an effective external potential for the model system, such that the minimizing density of the energy functional of the model system

$$E_s[n] = F_s[n] + \int d\mathbf{r} v_s(\mathbf{r})n(\mathbf{r}) \tag{3.9}$$

is the same as that of the real system. Doing this, we can simply evaluate the true energy functional using the ground state of the model system according to

$$\begin{aligned} E_0 &= E[n_0] \\ &= F[n_0] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n_0(\mathbf{r}) \\ &= F_s[n_0] + Q_s[n_0] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n_0(\mathbf{r}) \end{aligned} \tag{3.10}$$

For the real- and the model system to have the same ground state density, the Euler-Lagrange equations (3.5) of the two minimizations

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \mu \qquad\qquad \frac{\delta F_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu \tag{3.11}$$

must be equivalent (any difference between the two chemical potentials, can be absorbed in the definition of $v_s(\mathbf{r})$). This implies choosing $v_s(\mathbf{r})$ according to

$$v_s(\mathbf{r}) = \frac{\delta(F[n] - F_s[n])}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = \frac{\delta Q_s[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) = v_Q(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \tag{3.12}$$

where $v_Q(\mathbf{r}) = \delta Q_s[n]/\delta n(\mathbf{r})$. Note that here it has been assumed that there exists an effective potential such that the ground state density is identical for the two systems. Following the general procedure of KS theory this is left as an unproven assumption.

With the effective potential of (3.12), we see that we can get the total energy by:

$$E_0 = F_s[n_0] + Q_s[n_0] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n_0(\mathbf{r}) = E_s[n_0] + Q_s[n_0] - \int d\mathbf{r} v_Q(\mathbf{r})n_0(\mathbf{r}) \tag{3.13}$$

where the term $Q_s[n_0] - \int d\mathbf{r} v_Q(\mathbf{r})n_0(\mathbf{r})$ is sometimes referred to as the double counting correction term. To evaluate this energy expression, we just need the ground state density, which we get from the minimization of the energy functional of our model system $E_s[n]$, i.e. by performing the minimization

$$E_0^s = \min_{n(\mathbf{r}) \to N} \left\{ F_s[n] + \int d\mathbf{r} v_s(\mathbf{r})n(\mathbf{r}) \right\} = \min_{\Phi \to N} \left\{ S[\Phi] + \int d\mathbf{r} v_s(\mathbf{r})n[\Phi](\mathbf{r}) \right\} \tag{3.14}$$

Which is equivalent to finding the eigenstate of lowest energy of

$$\left[\widehat{O}_s + \hat{v}_s \right] |\Phi_0\rangle = E_0^s |\Phi_0\rangle \tag{3.15}$$

where $\widehat{O}_s|\Phi\rangle = \frac{\partial S[\Phi]}{\partial \langle\Phi|}$, or equivalently the N lowest states of the generalized Kohn-Sham (GKS) equations

$$\left[\hat{o}_s + v_s(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n \tag{3.16}$$

with $f_n \hat{o}_s \phi_n(\mathbf{r}) = \frac{\delta S[\{\phi\}]}{\delta \phi_n^*(\mathbf{r})}$, and

$$E_0^s = \sum_n f_n \epsilon_n + \langle\Phi|\frac{\partial S}{\partial \langle\Phi|}|\Phi\rangle - \sum_n \langle\phi_n|\frac{\partial S}{\partial \langle\phi_n|}|\phi_n\rangle, \qquad n_0(\mathbf{r}) = \sum_n f_n |\phi_n(\mathbf{r})|^2 \tag{3.17}$$

Note that the operator $\hat{o}_s$ can be both non-local and state dependent in general.

A self consistent approach is needed for solving the GKS equations (3.16), as both operators $\hat{o}_s$ and $\hat{v}_s$ are functionals of the orbitals, i.e. depend on the solution of the GKS equation itself.

To summarize, the self-consistent GKS approach to the ground state energy is:

Preliminary steps:

1. Choose a model functional $S[\Phi] = S[\{\phi\}]$

2. Determine $\hat{o}_s = 1/f_n|\phi_n\rangle \cdot \partial S/\partial\langle\phi_n|$

3. Approximate $Q_s[n] = F[n] - F_s[n]$ and $v_Q[n](\mathbf{r}) = \delta Q_s/\delta n(\mathbf{r})$

Self-consistent field (SCF):

1. Guess initial states, $\{\phi\}$ and density $n(\mathbf{r})$ e.g. from atomic orbitals

   (a) Determine $v_s[n](\mathbf{r}) = v_Q[n](\mathbf{r}) + v_{\text{ext}}(\mathbf{r})$ and $\hat{o}_s[\{\phi\}]$

   (b) Find the N lowest energy eigen states of $[\hat{o}_s + v_s(\mathbf{r}) - \epsilon_n]\phi_n(\mathbf{r}) = 0$

   (c) Calculate $n(\mathbf{r}) = \sum_i f_n|\phi_n(\mathbf{r})|^2$

   (d) Repeat step $a - c$ until $n(\mathbf{r})$ has converged

2. Calculate total energy by either of the expressions

$$E[n] = F_s[n] + Q_s[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) , \qquad E[n] = E_0^s + Q_s[n] - \int d\mathbf{r} v_Q(\mathbf{r})n(\mathbf{r})$$

It can be shown, that first order errors in both v_{ext} and $n(\mathbf{r})$ only appear to second order in $E[n]$ [34].

The scheme can be thought of as mapping the N-particle interacting many-electron problem to a single particle problem with N occupied states that needs to be solved self-consistently. This represents a major simplification, as is clearly illustrated by the example of Kohn in his Nobel lecture [6].

Note that like F, the functionals F_s and Q_s are universal functionals, so in principle only a single (sufficiently accurate) choice of model system and a consistent approximation for Q_s is needed.

3.2.1 Choosing the Model System

There are several ways to define the model system. This section describes a few of the most widely used procedures.

The Standard Kohn-Sham Scheme

The standard Kohn-Sham scheme is recovered if we choose as the model system, a free-electron system, i.e. $S[\Phi] = \langle\Phi|\widehat{T}|\Phi\rangle$. This non-interacting system is also the only system for which we know that the ground state is a Slater determinant. The remaining contributions to the HK functional is then

$$Q_s[n] = F[n] - F_s[n] = \langle\Psi_{n(\mathbf{r})}^{\min}|\widehat{T} + \widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min}\rangle - \langle\Phi_{n(\mathbf{r})}^{\min}|\widehat{T}|\Phi_{n(\mathbf{r})}^{\min}\rangle \tag{3.18}$$

where $|\Psi_{n(\mathbf{r})}^{\min}\rangle$ is the interacting many-electron wave function that minimize $\langle\Psi|\widehat{T} + \widehat{V}_{ee}|\Psi\rangle$ while producing the density $n(\mathbf{r})$, and $|\Phi_{n(\mathbf{r})}^{\min}\rangle$ is the non-interacting many-electron wave function (Slater determinant), that minimize $\langle\Phi|\widehat{T}|\Phi\rangle$, while still producing the same density $n(\mathbf{r})$.

The expectation value of the electron-electron interaction with respect to a Slater determinant can be evaluated explicitly (see appendix A for a derivation) giving

$$\langle\Phi|\widehat{V}_{ee}|\Phi\rangle = U_H[n] + E_x[n] \tag{3.19}$$

where

$$U_H[n] = \tfrac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.20a}$$

$$E_x[n] = -\tfrac{1}{2} \sum_{nn'} f_n f_{n'} \int d\mathbf{r} d\mathbf{r}' \frac{\phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.20b}$$

Here f_α are the occupation numbers, and $\phi_\alpha(\mathbf{r})$ are the single particle wave functions constituting Φ.

Using (3.19), Q_s is expanded as

$$
\begin{aligned}
Q_s[n] &= \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Phi_{n(\mathbf{r})}^{\min} \rangle \\
&= \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle + \left(\langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \right) \\
&= U_H[n] + E_x[n] + E_c[n]
\end{aligned}
\tag{3.21}
$$

where the correlation energy functional $E_c[n]$ is defined by the above expression, and accounts for everything that is not described by the first term, i.e.

$$E_c[n] \equiv \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \tag{3.22}$$

The procedure corresponds to expressing the full HK functional by

$$
\begin{aligned}
F[n] &= \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle \\
&= \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle + E_c[n] \\
&= T_s[n] + U_H[n] + E_x[n] + E_c[n]
\end{aligned}
\tag{3.23}
$$

where T_s is the kinetic energy of an imagined non-interacting electron gas with the same total density as the real system, U_H is the Hartree energy representing a mean-field approximation of the electron-electron interaction. The physical significance of the last two terms E_x and E_c is less obvious, and will be discussed in section 3.3.

This choice of model system leads to the operator $\hat{o}_s = \hat{t} = -\tfrac{1}{2}\nabla^2$, and the effective potential

$$v_Q(\mathbf{r}) = u_H(\mathbf{r}) + v_x(\mathbf{r}) + v_c(\mathbf{r})$$

where $u_H(\mathbf{r}) = \delta U_H[n]/\delta n(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ is the Hartree potential, $E_{xc} = E_x + E_c$ is the exchange-correlation energy, and $v_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$ is the local exchange-correlation potential.

There is no explicit expression for the correlation energy functional and it must be approximated by some suitable functional, and from this, its functional derivative $v_c(\mathbf{r})$ must be determined. As the exchange energy functional is only an implicit functional of the density, its functional derivative is not easily determined. Typically approximations which are explicit functionals of the density are made for both E_c and E_x, such that their functional derivatives are easily found. Besides the difficulties of forming the functional derivative of of an implicit functional there is also an empirical argument for making approximations of the combined exchange-correlation. It turns out, *a posteriori*, that there is a large degree of cancellation between the long range effects of E_x and E_c, such that local approximations for both actually performs better than treating exchange exactly and correlation only locally.

For a discussion of how to construct the functional derivative of orbital dependent functionals, see chapter 5.

From (3.16) we get the Kohn-Sham equations

$$\left[-\tfrac{1}{2}\nabla^2 + u_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \right] \phi_n = \epsilon_n \phi_n \tag{3.24}$$

and the total energy expression:

$$
\begin{aligned}
E &= T_s[n] + U_H[n] + E_{xc}[n] + \int d\mathbf{r}\, n(\mathbf{r})v_{\text{ext}}(\mathbf{r}) \\
&= \sum_n f_n \epsilon_n - U_H[n] + E_{xc}[n] - \int d\mathbf{r}\, n(\mathbf{r})v_{xc}(\mathbf{r})
\end{aligned}
\tag{3.25}
$$

consistent with the standard expressions.

Hybrid Hartree-Fock Kohn-Sham Schemes

In hybrid Hartree-Fock-Kohn-Sham (HF-KS) schemes, a fraction of the electron-electron inter-action is included in the model system. Thus $S[\Phi] = \langle \Phi | \widehat{T} + a\widehat{V}_{ee} | \Phi \rangle$ where a is some number between 0 and 1. From this, we identify Q_s as

$$
\begin{aligned}
Q_s[n] &= F[n] - F_s[n] \\
&= \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + a\widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \\
&= (1-a)\langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle + \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \\
&= (1-a)(U_H[n] + E_x[n]) + E_c[n]
\end{aligned}
$$

This defines the operator $\hat{o}_s = -\nabla^2/2 + a(\hat{u}_H + \hat{v}_x^{\text{NL}})$ and the local potential $v_Q(\mathbf{r}) = (1-a)(u_H(\mathbf{r}) + v_x(\mathbf{r})) + v_c$. Note that the non-local exchange potential differs from the local potential in that $\hat{v}_x^{\text{NL}} | \phi_n \rangle = \partial E_x / f_n \partial \langle \phi_n |$ in general differs from $\hat{v}_x(\mathbf{r}) = \delta E_x / \delta n(\mathbf{r})$.

From (3.16) we get the generalized Kohn-Sham equations

$$
\left[-\tfrac{1}{2}\nabla^2 + u_H(\mathbf{r}) + a\hat{v}_x^{\text{NL}} + (1-a)v_x^s(\mathbf{r}) + v_c^s(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \right] \phi_n = \epsilon_n \phi_n
\tag{3.26}
$$

and the total energy expression:

$$
\begin{aligned}
E &= T_s[n] + U_H[n] + aE_x^{\text{exact}}[\Phi] + (1-a)E_x[n] + E_c[n] + \int d\mathbf{r} n(\mathbf{r})v_{\text{ext}}(\mathbf{r}) \\
&= \sum_n f_n \epsilon_n - U_H[n] - aE_x^{\text{exact}}[\Phi] + (1-a)E_x[n] + E_c[n] - \int d\mathbf{r}((1-a)v_x(\mathbf{r}) + v_c(\mathbf{r}))n(\mathbf{r})
\end{aligned}
\tag{3.27}
$$

A feature of the hybrid HF-KS schemes is that like in ordinary KS schemes, the eigenvalue corresponding to the highest occupied orbital (HOMO) is equal to the exact ionization energy I of the real system [9]

$$
\epsilon_N = -I
\tag{3.28}
$$

In the $a = 0$ limit, the hybrid HF-KS scheme reduce to the KS scheme, and at $a = 1$ the scheme is equivalent to Hartree-Fock, if the correlation functional is approximated by $E_c[n] = 0$.

Thomas-Fermi Theory

The basic idea behind DFT is to evaluate every observable as a functional of the ground state density, yet in the schemes described above, an auxiliary model system is introduced, for which the GKS eigenvalue problem must be solved to find the orbitals, which are then used to determine the density.

In Thomas-Fermi (TF) theory, the construction of a model system is skipped, and the full HK functional is approximated directly by some explicit density functional (corresponding to letting $S = 0$ and approximate Q_s).

Modeling the nuclei density by a homogeneous background charge (a jellium), the eigenstates of the non-interacting (Kohn-Sham) Hamiltonian becomes plane waves, for which it can be shown show that the kinetic- and exchange energies become

$$T_s = \frac{3V}{10}(3\pi^2)^{2/3} n_0^{5/3} \qquad\qquad E_x = -\frac{3V}{4\pi}\left(3\pi^2\right)^{1/3} n_0^{4/3}$$

where n_0 is the (homogeneous) density of the electrons and V is the volume of the system.

The basic idea of Thomas-Fermi theory is that if the charge density is not uniform, but varies slowly, the energy expressions will be the same as above, but evaluated locally and then integrated over space. Thus the approximation for the kinetic energy functional, $T_s[n]$, and the exchange functional, $E_x[n]$, becomes:

$$T_s[n] = \int d\mathbf{r}\,\frac{3}{10}(3\pi^2)^{2/3} n^{5/3}(\mathbf{r}) \qquad\qquad E_x[n] = -\int d\mathbf{r}\,\frac{3}{4\pi}\left(3\pi^2\right)^{1/3} n^{4/3}(\mathbf{r})$$

Neglecting correlation altogether, the total energy functional thus becomes

$$E[n] = T_s[n] + U_H[n] + V_{\text{ext}}[n] + E_x[n]$$
$$= \int d\mathbf{r}\,\frac{3}{10}(3\pi^2)^{2/3} n^{5/3}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r}\,n(\mathbf{r})v_{\text{ext}}(\mathbf{r}) - \int d\mathbf{r}\,\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3}(\mathbf{r})$$

Making explicit density-functional approximations of all components of the HK theorem is a major simplification, as the minimization of the energy functional can then be done directly by applying the Euler-Lagrange equation $\delta E[n]/\delta n(\mathbf{r}) = \mu$, where μ is a Lagrange multiplier (the chemical potential), which is adjusted such that $\int d\mathbf{r} n(\mathbf{r}) = N$. This results in

$$\frac{1}{2}(3\pi^2)^{2/3} n^{5/3}(\mathbf{r}) + \int d\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{ext}}(\mathbf{r}) - \left(\frac{3}{\pi}\right)^{1/3} n^{4/3}(\mathbf{r}) = \mu \qquad (3.29)$$

From which the ground state density can be determined, and thereby also the ground state energy.

Unfortunately the Thomas-Fermi model makes very poor predictions of the energetics of real systems. The problem is that the kinetic energy is the dominant energy term, making it crucial that this is described correctly, but assuming that the electron structure is a homogeneous electron gas, all information on the formation of electronic shells near the nuclei, is obviously lost. Such structure is naturally included, when the kinetic energy is determined by solving the Schrödinger equation of a real system (free electron gas), as in the KS scheme.

The original model proposed independently by Thomas in 1927 [10] and Fermi in 1928 [11] included only the kinetic part, and among other failures predicts that formation of molecules is always energetically unfavorable, i.e. that all molecules are unstable. The inclusion of the exchange term was done by P. A. M. Dirac in 1930 [12], and the resulting model makes even worse results. Because of the computational advantages of the model, several attempts have been made to improve the model, but none coming close in accuracy to KS-type schemes. For a nice review of different TF models, and the systems they can describe see [13].

It should be noted that TF theory predates DFT, which is based on the two articles by Hohenberg and Kohn [4] from 1964 and by Kohn and Sham [5] from 1965, by more than three decades.

3.2.2   Comparison of KS and hybrid HF-KS Schemes

To compare the KS scheme with the hybrid HF-KS schemes, we compare the two energy expressions:

$$E^{\text{KS}} = T^{\text{KS}}[n] + U_H[n] + E_x^{\text{KS}}[n] + E_c^{\text{KS}}[n] + \int d\mathbf{r}\,n(\mathbf{r})v_{\text{ext}}(\mathbf{r})$$

$$E^{\text{Hy},a} = T^{\text{Hy},a}[n] + U_H[n] + aE_x^{\text{exact}}[\Phi^{\text{Hy},a}] + (1-a)E_x^{\text{Hy},a}[n] + E_c^{\text{Hy},a}[n] + \int d\mathbf{r}\,n(\mathbf{r})v_{\text{ext}}(\mathbf{r})$$

There is a subtle difference between the functionals that the approximated exchange and correlation functionals of the two methods are designed to model. This difference stems from the difference between the KS and the hybrid HF-KS orbitals. We can express the hybrid functionals in terms of the KS functionals by

$$E_x^{\text{Hy},a} = E_x^{\text{KS}} + \Delta E_x \ , \qquad \Delta E_x = \langle \Phi^{\text{Hy},a}|\widehat{V}_{ee}|\Phi^{\text{Hy},a}\rangle - \langle \Phi^{\text{KS}}|\widehat{V}_{ee}|\Phi^{\text{KS}}\rangle \tag{3.30}$$

$$E_c^{\text{Hy},a} = E_c^{\text{KS}} + \Delta E_c \ , \qquad \Delta E_c = \langle \Phi^{\text{KS}}|\widehat{T} + \widehat{V}_{ee}|\Phi^{\text{KS}}\rangle - \langle \Phi^{\text{Hy},a}|\widehat{T} + \widehat{V}_{ee}|\Phi^{\text{Hy},a}\rangle \tag{3.31}$$

Usually the density functional approximations for the exchange and correlation used in hybrid schemes are just those established within KS theory. The error caused by this is

$$\begin{aligned}\Delta E_{xc}^{\text{Hy},a} &= (1-a)\Delta E_x + \Delta E_c \\ &= \langle \Phi^{\text{KS}}|\widehat{T} + a\widehat{V}_{ee}|\Phi^{\text{KS}}\rangle - \langle \Phi^{\text{Hy},a}|\widehat{T} + a\widehat{V}_{ee}|\Phi^{\text{Hy},a}\rangle\end{aligned}$$

Using the Hellmann-Feynman theorem, and that $\Delta E_{xc}^{\text{Hy},0} = 0$, this can be written as

$$\begin{aligned}\Delta E_{xc}^{\text{Hy},a} &= \int_0^a d\alpha \left[\langle \Phi^{\text{KS}}|\widehat{V}_{ee}|\Phi^{\text{KS}}\rangle - \langle \Phi^{\text{Hy},\alpha}|\widehat{V}_{ee}|\Phi^{\text{Hy},\alpha}\rangle \right] \\ &= \int_0^a d\alpha \left[E_x^{\text{exact}}[\Phi^{\text{KS}}] - E_x^{\text{exact}}[\Phi^{\text{Hy},\alpha}] \right]\end{aligned} \tag{3.32}$$

which is believed to be small in general [9]. From the success of the hybrid HF-KS methods using standard xc functionals, it might seem that these are actually better approximations of $E_{xc}^{\text{Hy},a}$ than the functional E_{xc}^{KS} which they where designed to approximate.

3.3   Exchange and Correlation

The Hartree and Exchange terms of the total energy is defined by the expression (3.19):

$$U_H[n] + E_x[n] = \langle \Phi_{n(\mathbf{r})}^{\min}|\widehat{V}_{ee}|\Phi_{n(\mathbf{r})}^{\min}\rangle \tag{3.33}$$

If one considers the electron-electron interaction as a perturbation to the non-interacting Hamiltonian, we can interpret the above quantity as the first order correction to the total energy due to this perturbation. The explicit form of U_H is

$$U_H[n] = \tfrac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \tfrac{1}{2} \sum_{nn'} f_n f_{n'} \int d\mathbf{r}d\mathbf{r}' \frac{\phi_n^*(\mathbf{r})\phi_n(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_{n'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.34}$$

which is just the classical electrostatic energy of the charge density $n(\mathbf{r})$. This interaction clearly includes a spurious self-interaction of each state with itself.

The explicit form of the exchange energy is

$$E_x[n] = -\tfrac{1}{2} \sum_{nn'} f_n f_{n'} \delta_{\sigma_n \sigma_{n'}} \int d\mathbf{r}d\mathbf{r}' \frac{\phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.35}$$

Here spin has been included, according to the prescription in section 2.4, as it is crucial for the interpretation of exchange.

The object 'a Slater determinant' is constructed to satisfy the antisymmetry principle, which is the principle leading to Pauli repulsion, so this effect is expected to show in the expression $\langle \Phi|\widehat{V}_{ee}|\Phi\rangle$. In the exchange energy, (3.35), we see that the diagonal terms, $n = n'$, exactly cancels the self-interaction of the Hartree term, and is thus just a classical correction of this. The remaining $n \neq n'$ parts of E_x is a direct consequence of Pauli repulsion. It can be seen that E_x correlates pairs of states with parallel spin, and gives a large negative value for any such pair, which have non-zero overlap. This is because, in the true ground state, the Pauli exclusion principle would

tend to keep any two electrons of parallel spin apart in space, thus the true ground state would have a much smaller electrostatic energy than in the non-interacting case if this has overlapping states of equal spin. All other many-electron effects are represented by the correlation functional. In some texts exchange is referred to as static correlation, and correlation as dynamic correlation.

Note that if we write the exchange energy as

$$E_x[n] = -\frac{1}{2} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \sum_\sigma \left| \sum_n \delta_{\sigma,\sigma_n} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}') \right|^2 \tag{3.36}$$

we see that it is always negative,

$$E_x[n] < 0 \tag{3.37}$$

The correlation functional was defined in equation (3.22) as

$$E_c[n] = \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \tag{3.38}$$

i.e. it is everything that is not accounted for by using the non-interacting slater determinant to evaluate the total energy. From eq. (3.38), we clearly see that

$$E_c[n] \leq 0$$

as $|\Psi_{n(\mathbf{r})}^{\min}\rangle$ is the wave function that minimizes $\langle \widehat{T} + \widehat{V}_{ee} \rangle$. By rewriting the expression (3.38) as:

$$E_c[n] = \left(\langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Phi_{n(\mathbf{r})}^{\min} \rangle \right) + \left(\langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{V}_{ee} | \Phi_{n(\mathbf{r})}^{\min} \rangle \right) \tag{3.39}$$
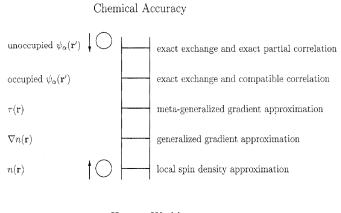
it is seen that the correlation energy consists of a positive kinetic correction (since $\Phi_{n(\mathbf{r})}^{\min}$ is the wave function that minimizes $\langle \widehat{T} \rangle$), and a negative potential correction (since the sum is negative). In the interacting, physical, system, the electrons would be kept apart due to the coulombic repulsion of charged particles. Thus the real system would have a smaller electrostatic energy than the non-interacting system (explaining the negative potential correction), and since the electrons would thereby be restricted to a smaller part of space, they would have a larger kinetic energy.

In the same way that $U_H + E_x$ represents the first order correction to the total energy due to the electron-electron interaction, the correlation energy represents all higher order corrections. Schemes have been devised that construct E_C using perturbation theory, at every level of the KS SCF cycle. Although the perturbation expansion is obviously truncated at some point, the procedure in principle leads to an 'exact' DFT scheme [53]. Unfortunately some physical effects required particular types of perturbative terms to be described to infinite order for the sum to make sense [63].

While the exact behavior of the exchange functional can be studied using the explicit formula (3.35), the exact correlation functional is much harder to obtain information about. The exact behavior of the correlation potential- and energy functionals are only known in certain limiting cases of simple model systems. These are used when constructing density functional approximations for v_c and E_c.

3.3.1 Jacob's Ladder

Many different approximations for the exchange-correlation functional, a few of which are summarized in appendix E, but they can all be placed on one of the five rungs of the Jacob's ladder proposed by Perdew in [14]. The concept is a ladder of accuracy ranging from the Hartree level to the heaven of chemical accuracy. The ladder can be navigated depending on the need for accuracy at the cost of computational effort. The five rungs of the ladder are shown on figure 3.1. The term chemical accuracy refers to the highest accuracy available with current experimental techniques. A few of the key quantities of molecules, and present chemical accuracy, are [52]:

Chemical Accuracy

Figure 3.1: *Jacob's ladder of exchange-correlation functionals. From [14].*

- Binding energies: 1 kcal/mol

- Bond lengths: 0.01 Å

- Vibration frequencies: 10 cm^{-1}

- Excitation energies: 0.1 eV

Exchange-correlation functionals are typically written in the form

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) e_{xc}[n(\mathbf{r})](\mathbf{r})$$

In figure 3.1 the steps of the Jacob's ladder indicates the number of ingredients included in the exchange-correlation energy density e_{xc}. For example a meta-GGA functional would look like

$$E_{xc}^{\mathrm{MGGA}}[n(\mathbf{r})] = \int d\mathbf{r} \; n(\mathbf{r}) \, e_{xc}^{\mathrm{MGGA}}\big(n(\mathbf{r}), \boldsymbol{\nabla} n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})\big) \tag{3.40}$$

where τ is the kinetic energy density

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_n f_n |\boldsymbol{\nabla}\phi_i(\mathbf{r})|^2 \tag{3.41}$$

A useful theoretical tool for understanding the xc-functional (and thereby making it easier to construct good approximations), is that offered by the 'adiabatic connection method', ACM, described in the next section.

3.3.2   The Adiabatic Connection Formula

From the definitions of exchange, (3.33), and correlation, (3.22), the combined functional can be expressed as:

$$E_{xc}[n] = \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Phi_{n(\mathbf{r})}^{\min} \rangle - U_H[n] \tag{3.42}$$

or, using the definition of the exchange correlation hole (2.14)

$$E_{xc}[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \langle \Psi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Psi_{n(\mathbf{r})}^{\min} \rangle - \langle \Phi_{n(\mathbf{r})}^{\min} | \widehat{T} | \Phi_{n(\mathbf{r})}^{\min} \rangle \tag{3.43}$$

It is difficult to make models for how the kinetic energy $\langle\widehat{T}\rangle$ is changed from the real to the KS system, so to avoid the last two terms, the following procedure is applied:

Define $|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle$ as the many-electron wave function that minimizes $\langle\widehat{T}+\lambda\widehat{V}_{ee}\rangle$, while still yielding the ground-state density $n(\mathbf{r})$. I.e. $|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle$ is the ground state of the Hamiltonian $\widehat{T}+\lambda\widehat{V}_{ee}+v_{\lambda}(\mathbf{r})$, where $v_{\lambda}(\mathbf{r})$ is some fictitious external potential adjusted such that $\langle\Psi_{n(\mathbf{r})}^{\min,\lambda}|\hat{n}|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle = n(\mathbf{r})$ for all λ. At $\lambda = 1$, $\Psi_{n(\mathbf{r})}^{\min,1} = \Psi_{n(\mathbf{r})}^{\min}$ is identical to the true physical wave function, and $v_{\lambda} = v_{\text{ext}}$ is the true external potential, while at $\lambda = 0$, $\Psi_{n(\mathbf{r})}^{\min,0} = \Phi_{n(\mathbf{r})}^{\min}$ equals the Slater determinant of KS wave functions, and $v_{\lambda} = v_s$ reduce to the KS potential. This is shown in figure 3.2.
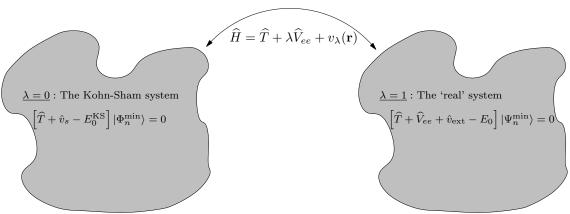
$$0 \leq \lambda \leq 1$$

$$\widehat{H} = \widehat{T} + \lambda\widehat{V}_{ee} + v_{\lambda}(\mathbf{r})$$

$\underline{\lambda = 0}$: The Kohn-Sham system

$$\left[\widehat{T} + \hat{v}_s - E_0^{\text{KS}}\right]|\Phi_n^{\min}\rangle = 0$$

$\underline{\lambda = 1}$: The 'real' system

$$\left[\widehat{T} + \widehat{V}_{ee} + \hat{v}_{\text{ext}} - E_0\right]|\Psi_n^{\min}\rangle = 0$$

Figure 3.2: *The adiabatic connection.*

Using these definitions, (3.43) can be re-expressed as

$$
\begin{aligned}
E_{xc}[n] &= \langle\Psi_{n(\mathbf{r})}^{\min,\lambda}|\widehat{T}+\lambda\widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle\Big|_{\lambda=1} - \langle\Psi_{n(\mathbf{r})}^{\min,\lambda}|\widehat{T}+\lambda\widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle\Big|_{\lambda=0} - U_H[n] \\
&= \int_0^1 d\lambda\frac{d}{d\lambda}\langle\Psi_{n(\mathbf{r})}^{\min,\lambda}|\widehat{T}+\lambda\widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle - U_H[n] \\
&= \int_0^1 d\lambda\langle\Psi_{n(\mathbf{r})}^{\min,\lambda}|\widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min,\lambda}\rangle - U_H[n]
\end{aligned}
\tag{3.44}
$$

where in the last line the Hellmann-Feynman theorem has been applied.

Using (2.16) and that the ground state density is identical for each system along the adiabatic integration path, we get:

$$E_{xc}[n] = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})\bar{n}_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.45}$$

where

$$\bar{n}_{xc}(\mathbf{r},\mathbf{r}') = \int_0^1 d\lambda\, n_{xc}^{\lambda}(\mathbf{r},\mathbf{r}') \tag{3.46}$$

is the coupling-constant averaged exchange-correlation hole.

In the expression (3.45) the kinetic energy contribution has been subsumed by the coupling-constant integration of the exchange-correlation hole, otherwise the expression is identical to (3.43).

Introducing $\mathbf{u} = \mathbf{r}' - \mathbf{r}$, (3.45) can be re-expressed as:

$$E_{xc}[n] = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})\bar{n}_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \frac{N}{2}\int_0^{\infty} du4\pi u^2\langle\bar{n}_{xc}(u)\rangle/u \tag{3.47}$$

where

$$\langle\bar{n}_{xc}(u)\rangle = \int\frac{n(\mathbf{r})d\mathbf{r}}{N}\int\frac{d\hat{\mathbf{u}}}{4\pi}\bar{n}_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u}) \tag{3.48}$$

is the system averaged ($\int n(\mathbf{r})d\mathbf{r}/N$), spherically averaged ($\int d\hat{\mathbf{u}}/4\pi$), and coupling-constant averaged ($\bar{n}_{xc} = \int_0^1 d\lambda n_{xc}^\lambda$) exchange-correlation hole density. From this we see that only the radial part of the exchange-correlation hole is required for an accurate description of the exchange-correlation energy. This explains in part the success of LDA xc-functionals, in their description of the total energy [59]. One must keep in mind however, that the energy is only an integrated property, differential properties like the xc-potential, the response function, KS eigen-energies etc. are more difficult to treat accurately.

The exchange hole is defined by the $\lambda = 0$ limit of the coupling constant integration.

$$n_x(\mathbf{r}, \mathbf{r}') = n_{xc}^{\lambda=0}(\mathbf{r}, \mathbf{r}') \tag{3.49}$$

At this point, the wave function is just The KS Slater determinant, and the exchange hole can be determined explicitly by

$$
\begin{aligned}
n(\mathbf{r})n_x(\mathbf{r}, \mathbf{r}') &= \rho_2^{\lambda=0}(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') \\
&= \langle \Phi_{n(\mathbf{r})}^{\min} | \hat{\rho}_2 | \Phi_{n(\mathbf{r})}^{\min} \rangle - n(\mathbf{r})n(\mathbf{r}') \\
&= -\sum_{nn'} f_n f_{n'} \phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}') \\
&= -\left| \sum_n \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}') \right|^2
\end{aligned}
\tag{3.50}
$$

The derivation follows almost exactly that given in appedix A for exact exchange. From this expression the exchange energy can also be recovered, as

$$E_x[n] = -\frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n_x(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = -\frac{1}{2} \sum_{nn'} f_n f_{n'} \iint d\mathbf{r}d\mathbf{r}' \frac{\phi_n^*(\mathbf{r})\phi_{n'}(\mathbf{r})\phi_{n'}^*(\mathbf{r}')\phi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.51}$$

justifying the definition of the exchange hole.

From the last expression of (3.50) it follows that the exchange hole is negative:

$$n_x(\mathbf{r}, \mathbf{r}') \le 0 \tag{3.52}$$

and since the sum rule (2.15) holds for all values of λ

$$\int d\mathbf{r}' n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') = -1 \Rightarrow \int d\mathbf{r}' n_x(\mathbf{r}, \mathbf{r}') = -1 \Rightarrow \int d\mathbf{r}' \bar{n}_c^\lambda(\mathbf{r}, \mathbf{r}') = 0 \tag{3.53}$$

The connection between the two electron joint probability distribution $\rho_2(\mathbf{r}, \mathbf{r}')$ and the exchange-correlation hole is (2.14):

$$\rho_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})\left(n(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}')\right)$$

as this must be positive, see e.g. (2.11), it follows that

$$n_{xc}(\mathbf{r}, \mathbf{r}') \ge -n(\mathbf{r}')$$

which from the interpretation of the xc-hole as the change in the total density at $\mathbf{r}'$ due to placing an electron at $\mathbf{r}$, can be regarded as as the constraint the the hole cannot remove electrons that are not there initially.

Example - The non-interacting Homogeneous Electron Gas

As an example[2] of an exchange correlation hole, consider a non-interacting homogeneous electron gas. The eigenstates of this system are the plane waves $\phi_{\mathbf{k}\sigma_n}(\mathbf{r}\sigma) = \phi_{\mathbf{k}}(\mathbf{r})\chi_{\sigma_n}(\sigma)$, where

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(-i\mathbf{k} \cdot \mathbf{r})/V$$

---

[2]In this and the following examples, spin will be included according to the prescription of section 2.4.

In this case, it can be shown that

$$n_x(\mathbf{r}\sigma, \mathbf{r}'\bar{\sigma}) = 0$$

$$n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma) = n_x(R) = -\frac{9n}{2(k_F R)^6} \left[\sin(k_F R) - k_F R \cos(k_F R)\right]^2$$

where n is the homogeneous total density, $\bar{\sigma}$ is the spin anti-parallel to σ, and $R = |\mathbf{r} - \mathbf{r}'|$. This function is shown in figure 3.3.
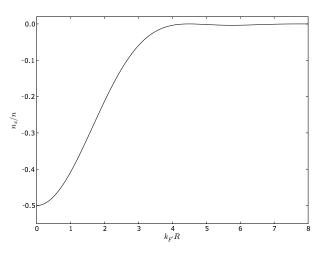

Figure 3.3: *The exchange hole of a homogeneous electron gas*

The hole is entirely due to parallel spin interactions, as exchange does not correlate electrons of opposite spin. The figure shows that if an electron is located at $\mathbf{r}$ the probability density of finding another in the same place is reduced $n/2 = n(\mathbf{r}\sigma)$, as all equal spin electrons are completely repelled. For the true on-top xc-hole $n_{xc}(\mathbf{r}\sigma, \mathbf{r}\bar{\sigma}) = -n(\mathbf{r}\bar{\sigma})$ for the anti-parallel spin also, as two electrons cannot occupy the same place (the Coulomb repulsion would be infinite).

Example - The Hydrogen Molecule

As a further example, the hydrogen molecule is considered in two limiting cases.

The $\lambda = 1$ limit

We cannot solve the interacting system exactly, but if we as an example consider the limit of a very large Hubbard U, i.e. strong repulsion between electrons in the same state, the true many particle state will be the symmetrized product of the atomic orbital on one atom $|1\rangle$ with the atomic orbital of the other atom $|2\rangle$. If we use the general rule for determining the exchange-correlation hole

$$n(\xi)n_{xc}(\xi, \xi') = \langle \Psi | \hat{n}(\xi)\hat{n}(\xi') - \delta(\xi - \xi')\hat{n}(\xi) | \Psi \rangle - n(\xi)n(\xi') \tag{3.54}$$

on this system, and resolve it in the basis of the two atomic orbitals instead of Cartesian space, we get

$$n(i)n_{xc}(i, j) = \langle \Psi | \hat{n}(i)\hat{n}(j) - \delta_{i,j}\hat{n}(i) | \Psi \rangle - n(i)n(j) = -\delta_{i,j}n(i)$$
$$\Rightarrow n_{xc}(i, j) = -\delta_{i,j} \tag{3.55}$$

where it has been used that the ground state is an eigenstate of the number operator in state space.

From this, we see that if the probability of finding an electron in state i given that there is one in state j is completely uncorrelated if $i \neq j$, while it is completely repelled if $i = j$. This shows the same kind of localized xc-hole as for the non-interacting homogeneous electron gas, which can be described accurately by a GGA approximation.

The $\lambda = 0$ limit

In the $\lambda = 0$ limit the system is non-interacting, i.e. the xc-hole is a pure exchange hole. The ground state of the molecule is in this case the Slater determinant giving the binding molecular orbital σ_g, i.e. the determinant of the two states

$$
\begin{aligned}
\phi_1(r\sigma) &= \sigma_g(\mathbf{r})\chi_\uparrow(\sigma) \\
\phi_2(r\sigma) &= \sigma_g(\mathbf{r})\chi_\downarrow(\sigma)
\end{aligned}
\tag{3.56}
$$

From the rule for Slater-determinant x-holes (3.50), we see that:

$$
n(\mathbf{r}\sigma)n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\sum_{nn'} \phi_n^*(r\sigma)\phi_{n'}(r\sigma)\phi_{n'}^*(r'\sigma')\phi_n(r'\sigma) = -\delta_{\sigma\sigma'}|\sigma_g(\mathbf{r})|^2|\sigma_g(\mathbf{r}')|^2
$$

$$
\Rightarrow n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma) = -|\sigma_g(\mathbf{r}')|^2
$$

It is seen that $n_x(\mathbf{r}\sigma, \mathbf{r}'\bar{\sigma}) = 0$, (again this is true because Pauli repulsion only correlates electrons of parallel spin). The sum rule (2.15) is satisfied since

$$
\sum_{\sigma'} \int d\mathbf{r}' n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \int d\mathbf{r}' n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma) = -\int d\mathbf{r}'|\sigma_g(\mathbf{r}')|^2 = -1
\tag{3.57}
$$

For the parallel spin x-hole $n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma) = -|\sigma_g(\mathbf{r}')|^2$. This exchange hole is thus completely delocalized in the sense that if we have an electron in $\mathbf{r}'$, the probability of finding one in $\mathbf{r}$, with the same spin, is the same in all parts of space. Such a delocalized behavior of the xc-hole is impossible to capture in any GGA approach.

3.3.3   Hybrid Functionals: Rationale for Admixture of Exact Exchange

From the adiabatic connection formula, it follows that the exchange-correlation energy can be determined by

$$
\begin{aligned}
E_{xc} &= \underbrace{\langle\Psi_{n(\mathbf{r})}^{\min}|\widehat{V}_{ee}|\Psi_{n(\mathbf{r})}^{\min}\rangle - U_H[n]}_{U_{xc}} + \underbrace{\langle\Psi_{n(\mathbf{r})}^{\min}|\widehat{T}|\Psi_{n(\mathbf{r})}^{\min}\rangle - \langle\Phi_{n(\mathbf{r})}^{\min}|\widehat{T}|\Phi_{n(\mathbf{r})}^{\min}\rangle}_{T_{xc}} \\
&= U_{xc} + T_{xc} \\
&= \int_0^1 d\lambda\, U_{xc}^\lambda
\end{aligned}
$$

I.e. the kinetic part of the correlation energy can be incorporated into a coupling constant integration, over systems with the scaled Coulomb interaction $\lambda/|\mathbf{r} - \mathbf{r}'|$, in an external potential designed such that the one electron density $n(\mathbf{r})$ is held fixed.

The potential xc-energy is related to the xc-hole density by

$$
U_{xc}^\lambda = \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}^\lambda(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
$$

where the xc-hole is defined in terms of the pair density $\rho_2^\lambda(\mathbf{r}, \mathbf{r}')$ by

$$
n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') = \frac{\rho_2^\lambda(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})} - n(\mathbf{r}')
$$

The $\lambda = 0$ end of the coupling constant integration is merely the pure exchange energy of the KS Slater determinant. Unfortunately density functional approximations (DFA) for the xc-hole models this end of the integration quite poorly. This is seen in the example above for the hydrogen molecule; in this case the x-hole was completely delocalized, offering little chance of being properly described by a local or semi-local DFA. According to the authors of [42] there is also strong evidence

that the problems of GGA's in describing multiply-bonded molecules are primarily due to the improper description of the exchange ($\lambda = 0$) limit. On the other hand, in the fully interacting end of the integration $\lambda = 1$, the inclusion of correlation effects tends to make the xc-hole deeper and more localized [1].

The original idea of a hybrid functional proposed by Becke in [45] and further developed in his series on density-functional thermochemistry [46, 47, 48, 49] was to make a two point approximation of the coupling constant integration

$$E_{xc} = \int_0^1 d\lambda\, U_{xc}^\lambda \approx \frac{1}{2}\left(U_{xc}^{\lambda=0} + U_{xc}^{\lambda=1}\right) = \frac{1}{2}\left(E_x^{\text{exact}} + \tfrac{1}{2}U_{xc}^{\lambda=1}\right)$$

using the exact expression in the $\lambda = 0$ limit, and a local DFA for $U_{xc}^{\lambda=1}$. Using his half-and-half hybrid with a Hartree-Fock calculation for the the exchange limit, and the local spin density (LSD) approximation for the interacting limit, he maneged to predict better atomization energies than most GGA's of the time.

A more sophisticated procedure, proposed by Perdew, Ernzerhof, and Burke [42], is to assume that the hybrid functional has the coupling-constant dependence

$$U_{xc,\lambda}^{\text{hyb}} = U_{xc,\lambda}^{\text{DFA}} + (E_x^{\text{exact}} - U_{xc,\lambda}^{\text{DFA}})(1-\lambda)^{n-1}$$

where $n \geq 1$ is an integer. This hybrid has the exact form E_x^{exact} in the exchange limit, and reduces to the DFA in the interacting limit, where the hole is more correctly described by a local DFA. The suggested functional form is shown in figure 3.4.
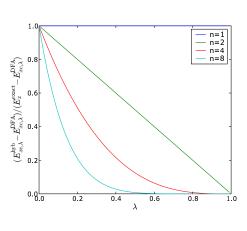
This form implies the hybrid functional

$$E_{xc}^{\text{hyb}} = \int_0^1 d\lambda\, U_{xc,\lambda}^{\text{hyb}} = E_{xc}^{\text{DFA}} + \frac{1}{n}(E_x^{\text{exact}} - E_{xc}^{\text{DFA}})$$

From this it is then argued from a perturbation theory argument [42], why $n = 4$ should be the optimal choice for molecules and insulating solids.

Figure 3.4: *The coupling constant dependence of the hybrid functional*

Hybrid functionals using 1/4 mixing of exact exchange have been termed ACM0 models, indicating that it is an adiabatic-connection-method with 0 empirical parameters. Hybrid functionals including an amount of exact exchange fitted to a data base are denoted ACM1, and hybrids mixing different amounts of exact exchange, DFA exchange and DFA correlation, such as the popular B3LYP, are denoted ACM3 functionals. The PBE0 functional (mixing 25% exact exchange with the PBE functional) has been tested thoroughly in the papers [43, 44] for molecules, and in [37] for solids. The verdict is that that inclusion of exact exchange has a beneficial effect on bond lengths and atomization energies of molecules. For insulating solids lattice constants and bulk moduli are improved, but the atomization energies are made worse. Exact exchange improves band gaps and eigenvalue spectra for most insulating systems, but shows large over-corrections for metals.

Chapter 4

Extended Systems

Although we have seen in the preceding chapter that the problem of solving the Schrödinger equation for N interacting electrons can be reduced to solving N non-interacting single particle KS equations, this is still an immense task for large systems.

A very useful simplification can be made in the case of periodic systems, by the application of Bloch's theorem described in the following section. Bloch theory is essential for the description of infinitely periodic systems, which in principle requires solving the KS equation in an infinitely large domain for an infinity of states. In this case, the Bloch representation of the states, requires only that the KS equation is solved within the unit cell of the system, and only for a representative set of states.

4.1 Bloch Theory

Bloch theory is applicable for non-interacting systems (i.e. systems that can be described by single particle eigenstates), in static potentials. The theorem states that if the considered system has a translational symmetry, i.e. the (static) potential v, satisfy the relation $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{R})$ for all Bravais lattice vectors $\mathbf{R}$, then the set of single particle eigenstates $\{\psi_n\}$, can be represented by a different set of (Bloch) states, $\{\psi_{n,\mathbf{k}}\}$, satisfying the following two equivalent formulations of Bloch's theorem:

$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n,\mathbf{k}}(\mathbf{r}) \tag{4.1a}$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n,\mathbf{k}}(\mathbf{r}) \tag{4.1b}$$

Where $u_{n,\mathbf{k}}(\mathbf{r})$ is a function with the same periodicity as the lattice, i.e. $u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R})$. For the Bloch states, the $\mathbf{k}$ index is termed the Bloch wave vector or crystal momentum, and n the band index. Which of the two formulations (4.1a) and (4.1b) is more convenient, depends on the choice of basis set.

Since two Bloch wave vectors differing by a reciprocal lattice vector are equivalent, we only need to consider vectors within the first Brillouin zone (BZ), which is just the Wigner-Zeitz cell of the reciprocal lattice. Thus the range of $\mathbf{k}$ vectors is inversely proportional to the size of the unit cell. The spectrum of wave vectors is given by the boundary conditions on the edge of the crystal. Periodic or Dirichlet conditions both imply an integer number of waves in the crystal. The density of $\mathbf{k}$ states is thus directly propotional to the volume of the crystal. In total, the number of $\mathbf{k}$ states, N_k, is identical to the total number of unit cells in the crystal, and the number of occupied bands at each $\mathbf{k}$ point, is on average equal to the number of electrons per unit cell, although it can vary slightly between $\mathbf{k}$-points.

The total number of occupied states is, and must obviously be, identical for both Bloch and non-Bloch representation, i.e. equal to the total number of electrons, so in this regard, not much have been gained, but the Bloch representation actually represents several simplifications.

The first is that two states having almost the same $\mathbf{k}$ index are very similar, justifying that the states are only calculated for a representative number of $\mathbf{k}$-points within the first BZ. Especially for infinitely periodic systems there are an infinity of occupied states, which in the Bloch representation translates to a continuum of $\mathbf{k}$-values, but still only a finite number of occupied bands for each $\mathbf{k}$ point. Calculating an observable, e.g. the total energy, for an infinite or finite periodic system thus amounts to picking a representative set of $\mathbf{k}$ vectors, solving the Kohn-Sham equation for the (few) occupied bands, and making an appropriate average over the $\mathbf{k}$ vectors.

Many different schemes for picking a representative set of $\mathbf{k}$ points exists, see e.g. ref. [23, 24].

An additional feature of the Bloch representation is that symmetry properties of the unit cell greatly reduce the number of distinct $\mathbf{k}$ vectors. The only $\mathbf{k}$ vectors needed are those of the irreducible BZ, which is usually only a fraction of the BZ in size; existence of a mirror symmetry for example reduces the BZ by a factor of two.

The Bloch representation also implies a reduction of the basis set necessary for representing the wave functions, as will be demonstrated in the following section.

4.2   Basis Sets and Boundary Conditions

Since the Kohn-Sham equations are second order differential equations, two sets of linearly independent boundary conditions (BC's) must be specified.

The appropriate BC's depend on the the nature of the considered system.

Plain Waves

The advantage of Bloch's theorem, when using plain wave basis sets, is that the function $u_{n,\mathbf{k}}(\mathbf{r})$ of (4.1b) is cell-periodic, and as such can be represented by the *discrete* expansion

$$u_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} \cdot e^{i\mathbf{G}\cdot\mathbf{r}} \quad \Rightarrow \quad \psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} \cdot e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{4.2}$$

where the $\mathbf{G}$'s are reciprocal lattice vectors (i.e. $\mathbf{G}\cdot\mathbf{R} = 2\pi p$, $p \in \mathbb{Z}$). In principle the expansion (4.2) requires an infinite sum, but the low energy (small $\mathbf{G}$ values) terms will typically be dominant, so in practice the expansion is truncated beyond some large $\mathbf{G}$. Had Bloch's theorem not been applied, a plane wave expansion would have to be continuous and would therefore require an infinite basis set despite the truncation of the expansion.

Using plane waves as an expansion results in the particularly simple secular version of the Kohn-Sham equation

$$\sum_{\mathbf{G}'} \left[\tfrac{1}{2}|\mathbf{k}+\mathbf{G}'|^2 \delta_{\mathbf{G}\mathbf{G}'} + V^{\mathrm{eff}}_{\mathbf{G}-\mathbf{G}'} \right] c_{n,\mathbf{k}+\mathbf{G}'} = \epsilon_n \cdot c_{n,\mathbf{k}+\mathbf{G}} \tag{4.3}$$

where $V^{\mathrm{eff}}_{\mathbf{G}}$ are the expansion coefficients of $V_{\mathrm{eff}}(\mathbf{r})$. The term in square brackets represents the Hamiltonian matrix $H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}$. A nice feature is that the kinetic terms are diagonal. For large $\mathbf{G}'$ vectors, the kinetic energy $E_{\mathrm{kin}} = \tfrac{1}{2}|\mathbf{k}+\mathbf{G}'|^2$ will dominate, and the truncation of the plane wave expansion, is usually done by choosing a cutoff energy $E_c = \tfrac{1}{2}|\mathbf{k}+\mathbf{G}_c|^2$, beyond which all terms of (4.3) are truncated. The size of the Hamiltonian matrix is thus (slightly) $\mathbf{k}$ dependent.

Real Space Grids

One can also choose to represent the wave functions on real space grids. When using this representation, one works directly with the (non-periodic) Bloch states $\psi_{n,\mathbf{k}}$, utilizing eq. (4.1a) to obtain the appropriate BC's:

$$e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n,\mathbf{k}}(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r}+\mathbf{R}) \tag{4.4a}$$

$$e^{i\mathbf{k}\cdot\mathbf{R}}\hat{\mathbf{n}}(\mathbf{r}) \cdot \boldsymbol{\nabla}\psi_{n,\mathbf{k}}(\mathbf{r}) = -\hat{\mathbf{n}}(\mathbf{r}+\mathbf{R}) \cdot \boldsymbol{\nabla}\psi_{n,\mathbf{k}}(\mathbf{r}+\mathbf{R}) \tag{4.4b}$$

where $\hat{\mathbf{n}}(\mathbf{r})$ is the (outward) unit normal of the cell boundary at $\mathbf{r}$.

Having specified the two BC's (4.4), the KS equations only have to be solved in between, i.e. in a single unit cell. Had Bloch's theorem not been applied, one would have to solve the KS equation in the entire domain of the crystal.

While the kinetic energy was diagonal in the plain wave representation, the effective KS potential is diagonal in real space (if it is local, i.e. the HF potential is not diagonal in real space either).

Isolated Systems

Choosing a plane wave basis set for the representation of the wave functions requires the application of periodic (Born-Von Karman) boundary conditions, thus in practice making any system infinitely periodic. This is the natural boundary conditions for solids. For isolated systems, e.g. molecules, the appropriate choice is Dirichlet boundary conditions. When using plain waves, Dirichlet boundary conditions can be obtained by embedding the system in a sufficiently large super-cell, such that the wave functions are essentially zero, and has zero gradient, at the boundaries. In this case there will be no difference between the wave functions for different $\mathbf{k}$ values, and typically only the Γ point ($\mathbf{k} = (0, 0, 0)$) is chosen.

Enforcing Dirichlet BC's in real space is not a problem, which is one of the strengths of real space basis sets. Actually one has the freedom to choose more exotic BC's like e.g. chiral boundary conditions, making it possible to represent for example nanotubes with a minimal unit cell.

To represent an isolated system correctly, the unit cell must be big enough that the potential is (practically) zero at the boundaries. As the decay of potentials is generally quite slow, this implies the use of very large cells. In real space, one can do a multipole expansion of the density, and use these to enforce the correct boundary conditions, thus reducing the minimal unit cell to one completely containing the density (which decays must faster than the potential). This procedure also allows one to handle charged systems efficiently, which is non-trivial when using plain waves, as a non-zero charge per unit cell in this case implies an infinite charge in the system (see section 8.3.1).

Chapter 5

Orbital Dependent Functionals

5.1 Direct Functional Derivative The Non-local Hartree-Fock Potential

If one tries to use the usual trick $f_i \hat{v} \phi_i(\mathbf{r}) = \frac{\delta E}{\delta \phi_i^*(\mathbf{r})}$ to obtain the potential $\hat{v}_x$ corresponding to the exact exchange energy expression

$$E_x = -\tfrac{1}{2} \sum_{ij} f_i f_j \iint d\mathbf{r} d\mathbf{r}' \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{5.1}$$

one arrives at the non-local Fock potential operator $\hat{v}_x^{\mathrm{NL}}$ defined by

$$\frac{\delta E_x}{\delta \phi_i^*(\mathbf{r})} = f_i \hat{v}_x^{\mathrm{NL}} \phi_i(\mathbf{r}) \tag{5.2}$$

Resolving the exchange operator in a basis, it can be considered either a non-local potential in real space, $v_x^{\mathrm{NL}}(\mathbf{r}, \mathbf{r}')$, or in state space, v_{ij}^{NL}:

$$\hat{v}_x^{\mathrm{NL}} \phi_i(\mathbf{r}) = \int d\mathbf{r}' v_x^{\mathrm{NL}}(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}') = \sum_j f_j v_{ij}^{\mathrm{NL}}(\mathbf{r}) \phi_j(\mathbf{r}) \tag{5.3}$$

with the two potentials given by

$$v_x^{\mathrm{NL}}(\mathbf{r}, \mathbf{r}') = -\sum_j f_j \frac{\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{5.4a}$$

$$v_{ij}^{\mathrm{NL}}(\mathbf{r}) = -\int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{5.4b}$$

The total energy can be expressed in terms of the potential operator as

$$E_x = \tfrac{1}{2} \sum_i f_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \hat{v}_x^{\mathrm{NL}} \phi_i(\mathbf{r}) = \tfrac{1}{2} \sum_i f_i \langle i | \hat{v}_x^{\mathrm{NL}} | i \rangle \tag{5.5}$$

One can also define an exchange energy density

$$v_x^{\mathrm{Sla}}(\mathbf{r}) = \frac{1}{n(\mathbf{r})} \sum_{ij} f_i f_j \int d\mathbf{r}' \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{n(\mathbf{r})} \sum_i f_i \phi_i^*(\mathbf{r}) \hat{v}_x^{\mathrm{NL}} \phi_i(\mathbf{r}) \tag{5.6}$$

which for historic reasons is termed the Slater potential [60]. In terms of this, the total exchange energy is

$$E_x = \tfrac{1}{2} \int d\mathbf{r} n(\mathbf{r}) v_x^{\mathrm{Sla}}(\mathbf{r}) \tag{5.7}$$

In the Kohn-Sham scheme, the exchange-correlation potential is required to be local, so for inclusion of exact exchange in this scheme, different methods for obtaining the (local) exchange potential must be applied. In the hybrid HF-KS schemes, described in section 3.2.1, the non-locality of the exchange potential is not a problem, but this method redefines the nature of the correlation functional, thus making the well established and thoroughly tested correlation functionals of KS theory unusable. In reality the difference between KS and HF-KS correlation functionals can be argued to be small (see section 3.2.2), and using non-local exchange potentials with KS correlation potentials is the standard way of doing exact exchange in e.g. GAUSSIAN and VASP.

The following sections describe different procedures for obtaining local potentials from general orbital dependent energy functionals.

5.2   Optimized Effective Potential

The optimized effective potential (OEP) method, also known as the optimized potential method (OPM) provides the procedure for constructing a multiplicative potential from an arbitrary state dependent energy functional. The final equation states that the exchange correlation potential can be found as the solution of an integral equation involving summations over all (occupied as well as unoccupied) states, making the method cumbersome to handle numerically. The method can be used both as a method for making very accurate descriptions of potentials, or as the starting point for making numerically faster approximations. A few such methods will be discussed in the following sections.

The starting point is to apply the chain-rule of functional derivative's twice

$$v(\mathbf{r}) = \frac{\delta E[\{\phi\}]}{\delta n(\mathbf{r})} = \sum_i \int d\mathbf{r}' \int d\mathbf{r}'' \left[\frac{\delta E}{\delta \phi_i(\mathbf{r}'')} \frac{\delta \phi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} + c.c. \right] \frac{\delta v_s(\mathbf{r}')}{\delta n(\mathbf{r})} \tag{5.8}$$

where the sum is over all states i, although it can be restricted to occupied orbitals if E only depends on occupied orbitals (since then $\delta E / \delta \phi_i(\mathbf{r}'')$ is zero for all the unoccupied orbitals).

The term $\frac{\delta E}{\delta \phi_i(\mathbf{r})}$ is easily evaluated for an explicitly orbital dependent functional. The functional derivative $\delta \phi_i(\mathbf{r}'')/\delta v_s(\mathbf{r}')$ is a first-order quantity, and as such can be evaluated exactly using first order perturbation theory

$$\frac{\delta \phi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} = \phi_i^*(\mathbf{r}') G_i(\mathbf{r}', \mathbf{r}'') \tag{5.9}$$

with the Green's function

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}')}{\epsilon_i - \epsilon_j} \tag{5.10}$$

The last remaining functional derivative $\delta v_s(\mathbf{r}')/\delta n(\mathbf{r})$ is the inverse of the response function, $\chi_s(\mathbf{r}', \mathbf{r})$, which for a system of non-interacting electrons is

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_i f_i \phi_i^*(\mathbf{r}) G_i(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}') + c.c. \tag{5.11}$$

Acting with the response function on both sides of (5.8) , and collecting the terms, yields the integral equation

$$\sum_i f_i \int d\mathbf{r}' \phi_i^*(\mathbf{r}) G_i(\mathbf{r}, \mathbf{r}') \left(v(\mathbf{r}') - \hat{v}^{\mathrm{NL}} \right) \phi_i(\mathbf{r}') + c.c. = 0 \tag{5.12}$$

with the, possibly but not necessarily, non-local potential $\hat{v}^{\mathrm{NL}}$ defined by

$$f_i \hat{v}^{\mathrm{NL}} \phi_i(\mathbf{r}) = \frac{\delta E}{\delta \phi_i^*(\mathbf{r})} \tag{5.13}$$

If the energy functional also depend on the KS eigenvalues, there would be an additional term $\sum_i \frac{\delta\epsilon_i}{\delta v_s(\mathbf{r})}\frac{\partial E}{\partial\epsilon_i} = \sum_i |\phi_i(\mathbf{r})|^2 \partial E/\partial\epsilon_i$ on the right hand side of (5.12). The part

$$\int d\mathbf{r}' G_i(\mathbf{r}, \mathbf{r}') \left(v(\mathbf{r}') - \hat{v}^{\mathrm{NL}}\right) \phi_i(\mathbf{r}')$$

is sometimes denoted the orbital shift $\psi_i(\mathbf{r})$ [64]. It is the first order shift of the orbitals with the local potential, towards those with the non-local potential. In terms of the orbital shifts, the OEP equation is $\sum_i f_i \psi_i^*(\mathbf{r})\phi_i(\mathbf{r}) + c.c. = 0$.

The OEP equation (5.12) is quite difficult to solve numerically. First of all it is an integral equation, and secondly the summation in the Green's function (5.10) run over all states, occupied as well as unoccupied. The denominator of the Green's function will obviously increase monotonically, so highly excited states becomes less important, but in practice a large number of unoccupied states have to be included to obtain convergence. The difficulties of solving the integral equation is illustrated by the fact that it has so far only been solved directly for spherically averaged isolated atoms.

5.3   Approximations to the Optimized Potential Method

In the Krieger-Li-Iafrate (KLI) approximation [57], the energy difference in the denominator of the Green's function is approximated by a constants $\epsilon_l - \epsilon_k = \Delta\bar{\epsilon}$. Using the closure relation $\sum_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ the Green's function thus becomes $G_i(\mathbf{r}, \mathbf{r}') \approx (\delta(\mathbf{r}-\mathbf{r}') - \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}'))/\Delta\bar{\epsilon}$. When this is done, the actual value of the constant disappears, and the resulting equations are

$$\begin{aligned}
v(\mathbf{r}) &= \frac{1}{2n(\mathbf{r})} \sum_i f_i \phi_i^*(\mathbf{r}) \left(\langle i|\hat{v} - \hat{v}^{\mathrm{NL}}|i\rangle + \hat{v}^{\mathrm{NL}}\right) \phi_i(\mathbf{r}) + c.c. \\
&= \frac{1}{n(\mathbf{r})} \sum_i f_i \left[\phi_i^*(\mathbf{r})\hat{v}^{\mathrm{NL}}\phi_i(\mathbf{r}) + |\phi_i(\mathbf{r})|^2 \langle i|\hat{v} - \hat{v}^{\mathrm{NL}}|i\rangle\right]
\end{aligned} \tag{5.14}$$

where

$$\langle i|\hat{v} - \hat{v}^{\mathrm{NL}}|i\rangle = \int d\mathbf{r}\phi_i^*(\mathbf{r}) \left(v(\mathbf{r}) - \hat{v}^{\mathrm{NL}}\right) \phi_i(\mathbf{r}) \tag{5.15}$$

The approximation of a constant energy denominator in $G_i(\mathbf{r}, \mathbf{r}')$ might seem crude, but it turns out that the exact same equation can be derived using a mean-field approximation (the only approximation done is neglecting a term which when averaged over the density is zero).

For the exact exchange potential, the KLI equation can be written as

$$v_x(\mathbf{r}) = v_x^{\mathrm{Sla}}(\mathbf{r}) + \sum_i f_i \frac{|\phi_i(\mathbf{r})|^2}{n(\mathbf{r})} \langle i|\hat{v}_x - \hat{v}_x^{\mathrm{NL}}|i\rangle \tag{5.16}$$

A different approximation of the OEP equation for exact exchange can be reached, by assuming that the orbitals of HF and exact exchange only DFT are identical. This approximation leads to the equation

$$v_x(\mathbf{r}) = v_x^{\mathrm{Sla}}(\mathbf{r}) + \sum_{ij} f_i f_j \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})}{n(\mathbf{r})} \langle j|\hat{v}_x - \hat{v}_x^{\mathrm{NL}}|i\rangle \tag{5.17}$$

which is known as the localized Hartree-Fock (LHF) method [51].

The equations (5.16) and (5.17) only define the potential to within a constant. The usual asymptotic behavior $v_x(\mathbf{r} \to \infty) = 0$ is recovered if one neglects the HOMO term in the summation of (5.16) or the HOMO-HOMO term of (5.17).

Since $v(\mathbf{r})$ appears on both sides of the KLI equation (5.14), the potential has to be determined by a self-consistent approach in general. In the case of exact exchange one can derive a set of linear equations determining the constants $\langle i|\hat{v}|i\rangle$, thus making it possible to solve (5.16) in one evaluation.

Besides KLI, and LHF there exists several other ways of determining approximations of the local exchange potential, see e.g. [54, 52] for nice reviews, or [50, 53] for specific methods. Recently (2003) Perdew and Kümmel proposed an iterative approach for solving the OEP equation [55, 56]. Starting from e.g. the KLI potential, they claim that a converged solution of the OEP equation can be reached within 4-5 iterations of their scheme. This makes the OEP potential obtainable for practical calculations, and has even revealed some surprising behaviors of the exact OEP potential on nodal surfaces of the HOMO orbital.

5.4 Screened Exchange

A fundamental problem with including exact exchange instead of the local approximations in the xc-functional, is that it is incompatible with local correlation approximations. Because of the success of local xc-functionals, we know that there must be a large degree of cancellation between the long range effects of exchange and correlation. This can not be exploited when using a non-local exchange functional and a local correlation functional. This problem can either be resolved by making a proper non-local approximation for the correlation, or to screen the exchange, such that it becomes local. The last procedure is obviously the simplest way of handling the problem, although it will remove some of the required features of exact exchange, i.e. the self-interaction correction is no longer complete, the $1/r$ decay of the exchange potential is no longer captured correctly, etc. Nevertheless functionals using screened exchange, seems to perform remarkably better than ordinary exact exchange calculations in a wide range of areas. In addition, the computational cost of evaluating exact exchange is improved by screening, as fewer $\mathbf{k}$ points are needed for convergence, and in calculations using localized basis sets, the locality can be exploited to neglect the exchange integrals involving states which are distant in space.

The most successful implementation of screened exchange, is that of Heyd, Scuseria, and Ernzerhof [38, 39]. In their approach, the Coulomb kernel is decomposed in a short range (SR) and a long range (LR) part using the errorfunction:

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\omega r)}{r}}_{SR} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{LR}$$

where ω is an adjustable screening length. Next, the hybrid method

$$E_x^{\text{GGA}} \to a E_x^{\text{exact}} + (1-a) E_x^{\text{GGA}}$$

is only performed on the short ranged part of the separated xc-functional

$$E_{xc}^{\text{HSE}} = a E_x^{\text{exact, SR}} + (1-a) E_x^{\text{GGA, SR}} + E_x^{\text{GGA, LR}} + E_c^{\text{GGA}}$$

this method reduces to the original GGA in the $\omega \to \infty$ limit, and the hybrid version in the $\omega = 0$ limit. The only complication is that in order to screen the Coulomb kernel of the GGA exchange functional, it has to be put in the form

$$E_x^{\text{GGA}} = \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{n_{xc}^{\text{GGA}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

such that there is a potential which can be screened. This is not necessarily the standard form of the considered GGA functional, so further approximations has to be made, i.e. numerical expansions of the analytic form of the functional. The authors have applied their method to the PBE functional, and the resulting functional is called HSE03. This screened hybrid functional has been tested extensively in the articles [40, 41], and shown to give good results.

5.5   Conclusion

To include exact exchange self-consistently in the SCF, one must in some way have access to the exchange potential. In the hybrid HF-KS schemes of section 3.2.1, the exchange potential is simply the non-local Fock potential of Hartree-Fock theory, this however redefines the nature of the correlation functional, making established approximations less usable. In Kohn-Sham theory, the exchange-correlation potential must be a local multiplicative potential. Constructing a local potential from an orbital dependent functional is a quite complicated, i.e. computationally time consuming, process and approximations are needed to make the approach feasible in practice. Construction of the local exchange potential can be achieved at several levels, climbing the following ladder of accuracy (and complexity):

- Slater potential: $v_x(\mathbf{r}) = v_x^{\mathrm{Sla}}(\mathbf{r})$

- KLI: $v_x(\mathbf{r}) = v_x^{\mathrm{Sla}}(\mathbf{r}) + \sum_i f_i |\phi_i(\mathbf{r})|^2 \langle i|\hat{v}_x - \hat{v}_x^{\mathrm{NL}}|i\rangle / n(\mathbf{r})$

- LHF: $v_x(\mathbf{r}) = v_x^{\mathrm{Sla}}(\mathbf{r}) + \sum_{ij} f_i f_j \phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) \langle j|\hat{v}_x - \hat{v}_x^{\mathrm{NL}}|i\rangle / n(\mathbf{r})$

- OEP: $\sum_i f_i \int d\mathbf{r}' \phi_i^*(\mathbf{r}) G_i(\mathbf{r}, \mathbf{r}') \left(v_x(\mathbf{r}') - \hat{v}_x^{\mathrm{NL}}\right) \phi_i(\mathbf{r}') + c.c. = 0$

where the OEP level can also be reached by an iterative scheme from one of the lower rungs of the ladder [55].

Chapter 6

Projector Augmented Wave Method

By the requirement of orthogonality, the wave functions have very sharp features close to the core, as all the states are non-zero in this region. Further out only the valence states are non-zero, resulting in much smoother wave functions in this region. The oscillatory behavior in the core regions, requires a very large set of plane waves, or equivalently a very fine grid, to be described correctly. One way of solving this problem is the use of pseudopotentials in which the collective system of nuclei and core electrons are described by an effective, much smoother, potential. The KS equations are then solved for the valence electrons only. The pseudopotentials are constructed such that the correct scattering potential is obtained beyond a certain radius from the core. This method reduces the number of wave functions to be calculated, since the pseudo potentials only have to be calculated and tabulated once for each type of atom, so that only calculations on the valence states are needed. It justifies the neglect of relativistic effects in the KS equations, since the valence electrons are non-relativistic (the pseudopotentials describing core states are of course constructed with full consideration of relativistic effects). The technique also removes the unwanted singular behavior of the ionic potential at the lattice points.

The drawback of the method is that all information on the full wave function close to the nuclei is lost. This can influence the calculation of certain properties, such as hyperfine parameters, and electric field gradients. Another problem is that one has no before hand knowledge of when the approximation yields reliable results.

A different approach is the augmented-plane-wave method (APW), in which space is divided into atom-centered augmentation spheres inside which the wave functions are taken as some atom-like partial waves, and a bonding region outside the spheres, where some envelope functions are defined. The partial waves and envelope functions are then matched at the boundaries of the spheres.

A more general approach is the projector augmented wave method (PAW) presented here, which offers APW as a special case [26], and the pseudopotential method as a well defined approximation [58]. The PAW method was first proposed by Blöchl in 1994 [25].

6.1 The Transformation Operator

The features of the wave functions, are very different in different regions of space. In the bonding region it is smooth, but near the nuclei it displays rapid oscillations, which are very demanding on the numerical representation of the wave functions. To address this problem, we seek a linear transformation $\hat{\mathcal{T}}$ which takes us from an auxiliary smooth wave function $|\tilde{\psi}_n\rangle$ to the true all electron Kohn-Sham single particle wave function $|\psi_n\rangle$

$$|\psi_n\rangle = \hat{\mathcal{T}}|\tilde{\psi}_n\rangle \tag{6.1}$$

where n is the quantum state label, containing a $\mathbf{k}$ index, a band index, and a spin index.

This transformation yields the transformed KS equations

$$\hat{\mathcal{T}}^{\dagger}\hat{H}\hat{\mathcal{T}}|\tilde{\psi}_n\rangle = \epsilon_n\hat{\mathcal{T}}^{\dagger}\hat{\mathcal{T}}|\tilde{\psi}_n\rangle \tag{6.2}$$

which needs to be solved instead of the usual KS equation. Now we need to define $\hat{\mathcal{T}}$ in a suitable way, such that the auxiliary wave functions obtained from solving (6.2) becomes smooth.

Since the true wave functions are already smooth at a certain minimum distance from the core, $\hat{\mathcal{T}}$ should only modify the wave function close to the nuclei. We thus define

$$\hat{\mathcal{T}} = 1 + \sum_a \hat{\mathcal{T}}^a \tag{6.3}$$

where a is an atom index, and the atom-centered transformation, $\hat{\mathcal{T}}^a$, has no effect outside a certain atom-specific augmentation region $|\mathbf{r} - \mathbf{R}^a| < r_c^a$. The cut-off radii, r_c^a should be chosen such that there is no overlap of the augmentation spheres.

Inside the augmentation spheres, we expand the true wave function in the partial waves ϕ_i^a, and for each of these partial waves, we define a corresponding auxiliary smooth partial wave $\tilde{\phi}_i^a$, and require that

$$|\phi_i^a\rangle = (1 + \hat{\mathcal{T}}^a)|\tilde{\phi}_i^a\rangle \quad \Leftrightarrow \quad \hat{\mathcal{T}}^a|\tilde{\phi}_i^a\rangle = |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \tag{6.4}$$

for all i, a. This completely defines $\hat{\mathcal{T}}$, given ϕ and $\tilde{\phi}$.

Since $\hat{\mathcal{T}}^a$ should do nothing outside the augmentation sphere, we see from (6.4) that we must require the partial wave and its smooth counterpart to be identical outside the augmentation sphere

$$\forall a, \quad \phi_i^a(\mathbf{r}) = \tilde{\phi}_i^a(\mathbf{r}), \text{ for } r > r_c^a$$

where $\phi_i^a(\mathbf{r}) = \langle\mathbf{r}|\phi_i^a\rangle$ and likewise for $\tilde{\phi}_i^a$.

If the smooth partial waves form a complete set inside the augmentation sphere, we can formally expand the smooth all electron wave functions as

$$|\tilde{\psi}_n\rangle = \sum_i P_{ni}^a|\tilde{\phi}_i^a\rangle, \text{ for } |\mathbf{r} - \mathbf{R}^a| < r_c^a \tag{6.5}$$

where P_{ni}^a are some, for now, undetermined expansion coefficients.

Since $|\phi_i^a\rangle = \hat{\mathcal{T}}|\tilde{\phi}_i^a\rangle$ we see that the expansion

$$|\psi_n\rangle = \hat{\mathcal{T}}|\tilde{\psi}_n\rangle = \sum_i P_{ni}^a|\phi_i^a\rangle, \text{ for } |\mathbf{r} - \mathbf{R}^a| < r_c^a \tag{6.6}$$

has identical expansion coefficients, P_{ni}^a.

As we require $\hat{\mathcal{T}}$ to be linear, the coefficients P_{ni}^a must be linear functionals of $|\tilde{\psi}_n\rangle$, i.e.

$$P_{ni}^a = \langle\tilde{p}_i^a|\tilde{\psi}_n\rangle = \int d\mathbf{r}\,\tilde{p}_i^{a*}(\mathbf{r} - \mathbf{R}^a)\tilde{\psi}_n(\mathbf{r}) \tag{6.7}$$

where $|\tilde{p}_i^a\rangle$ are some fixed functions termed smooth projector functions.

As there is no overlap between the augmentation spheres, we expect the one center expansion of the smooth all electron wave function, $|\tilde{\psi}_n^a\rangle = \sum_i|\tilde{\phi}_i^a\rangle\langle\tilde{p}_i^a|\tilde{\psi}_n\rangle$ to reduce to $|\tilde{\psi}_n\rangle$ itself inside the augmentation sphere defined by a. Thus, the smooth projector functions must satisfy

$$\sum_i|\tilde{\phi}_i^a\rangle\langle\tilde{p}_i^a| = 1 \tag{6.8}$$

inside each augmentation sphere. This also implies that

$$\langle\tilde{p}_{i_1}^a|\tilde{\phi}_{i_2}^a\rangle = \delta_{i_1,i_2} \text{ , for } |\mathbf{r} - \mathbf{R}^a| < r_c^a \tag{6.9}$$

i.e. the projector functions should be orthonormal to the smooth partial waves inside the augmentation sphere. There are no restrictions on $\tilde{p}_i^a$ outside the augmentation spheres, so for convenience we might as well define them as local functions, i.e. $\tilde{p}_i^a(\mathbf{r}) = 0$ for $r > r_c^a$.

Note that the completeness relation (6.8) is equivalent to the requirement that $\tilde{p}_i^a$ should produce the correct expansion coefficients of (6.5)-(6.6), while (6.9) is merely an implication of this restriction. Translating (6.8) to an explicit restriction on the projector functions is a rather involved procedure, but according to Blöchl, [25], the most general form of the projector functions is:

$$\langle \tilde{p}_i^a | = \sum_j (\{\langle f_k^a | \tilde{\phi}_l^a \rangle\})_{ij}^{-1} \langle f_j^a | \tag{6.10}$$

where $|f_j^a\rangle$ is any set of linearly independent functions. The projector functions will be localized if the functions $|f_j^a\rangle$ are localized.

Using the completeness relation (6.8), we see that

$$\hat{\mathcal{T}}^a = \sum_i \hat{\mathcal{T}}^a |\tilde{\phi}_i^a\rangle\langle\tilde{p}_i^a| = \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle\tilde{p}_i^a|$$

where the first equality is true in all of space, since (6.8) holds inside the augmentation spheres and outside $\hat{\mathcal{T}}^a$ is zero, so anything can be multiplied with it. The second equality is due to (6.4) (remember that $|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle = 0$ outside the augmentation sphere). Thus we conclude that

$$\hat{\mathcal{T}} = 1 + \sum_a \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle\tilde{p}_i^a| \tag{6.11}$$

To summarize, we obtain the all electron KS wave function $\psi_n(\mathbf{r}) = \langle\mathbf{r}|\psi_n\rangle$ from the transformation

$$\psi_n(\mathbf{r}) = \tilde{\psi}_n(\mathbf{r}) + \sum_a \sum_i \left(\phi_i^a(\mathbf{r}) - \tilde{\phi}_i^a(\mathbf{r})\right)\langle\tilde{p}_i^a|\tilde{\psi}_n\rangle \tag{6.12}$$

where the smooth (and thereby numerically convenient) auxiliary wave function $\tilde{\psi}_n(\mathbf{r})$ is obtained by solving the eigenvalue equation (6.2).

The transformation (6.12) is expressed in terms of the three components: a) the partial waves $\phi_i^a(\mathbf{r})$, b) the smooth partial waves $\tilde{\phi}_i^a(\mathbf{r})$, and c) the smooth projector functions $\tilde{p}_i^a(\mathbf{r})$.

The restriction on the choice of these sets of functions are: a) Since the partial- and smooth partial wave functions are used to expand the all electron wave functions, i.e. are used as atom-specific basis sets, these must be complete (inside the augmentation spheres). b) the smooth projector functions must satisfy (6.8), i.e. be constructed according to (6.10). All remaining degrees of freedom are used to make the expansions converge as fast as possible, and to make the functions termed 'smooth', as smooth as possible. For a specific choice of these sets of functions, see section 7.2. As the partial- and smooth partial waves are merely used as basis sets they can be chosen as real functions (any imaginary parts of the functions they expand, are then introduced through the complex expansion coefficients P_{ni}^a). In the remainder of this document ϕ and $\tilde{\phi}$ will be assumed real.

Note that the sets of functions needed to define the transformation are system independent, and as such they can conveniently be pre-calculated and tabulated for each element of the periodic table.

For future convenience, we also define the one center expansions

$$\psi_n^a(\mathbf{r}) = \sum_i \phi_i^a(\mathbf{r})\langle\tilde{p}_i^a|\tilde{\psi}_n\rangle \tag{6.13a}$$

$$\tilde{\psi}_n^a(\mathbf{r}) = \sum_i \tilde{\phi}_i^a(\mathbf{r})\langle\tilde{p}_i^a|\tilde{\psi}_n\rangle \tag{6.13b}$$

In terms of these, the all electron KS wave function is

$$\psi_n(\mathbf{r}) = \tilde{\psi}_n(\mathbf{r}) + \sum_a \left(\psi_n^a(\mathbf{r} - \mathbf{R}^a) - \tilde{\psi}_n^a(\mathbf{r} - \mathbf{R}^a)\right) \tag{6.14}$$

So what have we achieved by this transformation? The trouble of the original KS wave functions, was that they displayed rapid oscillations in some parts of space, and smooth behavior in other parts of space. By the decomposition (6.12) we have separated the original wave functions into auxiliary wave functions which are smooth everywhere and a contribution which contains rapid oscillations, but only contributes in certain, small, areas of space. This decomposition is shown on the front page for the hydrogen molecule. Having separated the different types of waves, these can be treated individually. The localized atom centered parts, are indicated by a superscript a, and can efficiently be represented on atom centered radial grids. Smooth functions are indicated by a tilde ˜. The delocalized parts (no superscript a) are all smooth, and can thus be represented on coarse Fourier- or real space grids.

6.2   The Frozen Core Approximation

In the frozen core approximation, it is assumed that the core states are naturally localized within the augmentation spheres, and that the core states of the isolated atoms are not changed by the formation of molecules or solids. Thus the core KS states are identical to the atomic core states:

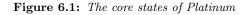$$|\psi_n^c\rangle = |\phi_\alpha^{a,\mathrm{core}}\rangle$$

where the index n on the left hand site refers to both a specific atom, a, and an atomic state, α.

In this approximation only valence states are included in the expansions of $|\psi_n\rangle$, (6.6), and $|\tilde{\psi}_n\rangle$, (6.5).

Figure 6.1, shows the atomic states of Platinum in its ground state, obtained with an atomic DFT program at an LDA level, using spherical averaging, i.e. a spin-compensated calculation, assuming the degenerate occupation 9/10 of all 5d states, and both of the 6s states half filled. It is seen that at the typical length of atomic interaction (the indicated cut-off $r_c = 2.5$ Bohr is approximately half the inter-atomic distance in bulk Pt), only the 5d and 6s states are non-zero.

Figure 6.1: *The core states of Platinum*

6.3   Expectation Values

The expectation value of an operator $\widehat{O}$ is, within the frozen core approximation, given by

$$\langle\widehat{O}\rangle = \sum_n^{\mathrm{val}} f_n\langle\psi_n|\widehat{O}|\psi_n\rangle + \sum_a^{\mathrm{core}}\sum_\alpha \langle\phi_\alpha^{a,\mathrm{core}}|\widehat{O}|\phi_\alpha^{a,\mathrm{core}}\rangle \tag{6.15}$$

using that $\langle\psi_n|\widehat{O}|\psi_n\rangle = \langle\tilde{\psi}_n|\hat{\mathcal{T}}^\dagger\widehat{O}\hat{\mathcal{T}}|\tilde{\psi}_n\rangle$, and skipping the state index for notational convenience, we see that

$$
\begin{aligned}
\langle\psi|\widehat{O}|\psi\rangle &= \langle\tilde{\psi} + \sum_a(\psi^a - \tilde{\psi}^a)|\widehat{O}|\tilde{\psi} + \sum_a(\psi^a - \tilde{\psi}^a)\rangle \\
&= \langle\tilde{\psi}|\widehat{O}|\tilde{\psi}\rangle + \sum_{aa'}\langle\psi^a - \tilde{\psi}^a|\widehat{O}|\psi^{a'} - \tilde{\psi}^{a'}\rangle + \sum_a\left(\langle\tilde{\psi}|\widehat{O}|\psi^a - \tilde{\psi}^a\rangle + \langle\psi^a - \tilde{\psi}^a|\widehat{O}|\tilde{\psi}\rangle\right) \\
&= \langle\tilde{\psi}|\widehat{O}|\tilde{\psi}\rangle + \sum_a\left(\langle\psi^a|\widehat{O}|\psi^a\rangle - \langle\tilde{\psi}^a|\widehat{O}|\tilde{\psi}^a\rangle\right) \\
&\quad + \sum_a\left(\langle\psi^a - \tilde{\psi}^a|\widehat{O}|\tilde{\psi} - \tilde{\psi}^a\rangle + \langle\tilde{\psi} - \tilde{\psi}^a|\widehat{O}|\psi^a - \tilde{\psi}^a\rangle\right) \\
&\quad + \sum_{a\neq a'}\langle\psi^a - \tilde{\psi}^a|\widehat{O}|\psi^{a'} - \tilde{\psi}^{a'}\rangle
\end{aligned}
\tag{6.16}
$$

For local operators[1] the last two lines does not contribute. The first line, because $|\psi^a - \tilde{\psi}^a\rangle$ is only non-zero inside the spheres, while $|\tilde{\psi} - \tilde{\psi}^a\rangle$ is only non-zero outside the spheres. The second line simply because $|\psi^a - \tilde{\psi}^a\rangle$ is zero outside the spheres, so two such states centered on different nuclei have no overlap (provided that the augmentation spheres do not overlap).

Reintroducing the partial waves in the one-center expansions, we see that

$$\sum_n^{\text{val}} f_n \langle \psi_n^a | \widehat{O} | \psi_n^a \rangle = \sum_n^{\text{val}} f_n \sum_{i_1 i_2} \langle \phi_{i_1}^a P_{ni_1}^a | \widehat{O} | \phi_{i_2}^a P_{ni_2}^a \rangle = \sum_{i_1 i_2} \langle \phi_{i_1}^a | \widehat{O} | \phi_{i_2}^a \rangle \sum_n^{\text{val}} f_n P_{ni_1}^{a*} P_{ni_2}^a \qquad (6.17)$$

and likewise for the smooth waves.

Introducing the Hermitian one-center density matrix

$$D_{i_1 i_2}^a = \sum_n f_n P_{ni_1}^{a*} P_{ni_2}^a = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_{i_1}^a \rangle \langle \tilde{p}_{i_2}^a | \tilde{\psi}_n \rangle \qquad (6.18)$$

We conclude that for any local operator $\widehat{O}$, the expectation value is

$$\langle \widehat{O} \rangle = \sum_n^{\text{val}} f_n \langle \tilde{\psi}_n | \widehat{O} | \tilde{\psi}_n \rangle + \sum_a \sum_{i_1 i_2} \left(\langle \phi_{i_1}^a | \widehat{O} | \phi_{i_2}^a \rangle - \langle \tilde{\phi}_{i_1}^a | \widehat{O} | \tilde{\phi}_{i_2}^a \rangle \right) D_{i_1 i_2}^a + \sum_a \sum_\alpha^{\text{core}} \langle \phi_\alpha^{a,\text{core}} | \widehat{O} | \phi_\alpha^{a,\text{core}} \rangle$$

$$(6.19)$$

6.4 Densities

The electron density is obviously a very important quantity in DFT, as all observables in principle are calculated as functionals of the density. In reality the kinetic energy is calculated as a functional of the orbitals, and some specific exchange-correlation functionals also rely on KS-orbitals rather then the density for their evaluation, but these are still *implicit* functionals of the density.

To obtain the electron density we need to determine the expectation value of the real-space projection operator $|\mathbf{r}\rangle\langle\mathbf{r}|$

$$n(\mathbf{r}) = \sum_n f_n \langle \psi_n | \mathbf{r} \rangle \langle \mathbf{r} | \psi_n \rangle = \sum_n f_n |\psi_n(\mathbf{r})|^2 \qquad (6.20)$$

where f_n are the occupation numbers.

As the real-space projection operator is obviously a local operator, we can use the results (6.19) of the previous section, and immediately arrive at

$$n(\mathbf{r}) = \sum_n^{\text{val}} f_n |\tilde{\psi}_n|^2 + \sum_a \sum_{i_1 i_2} \left(\phi_{i_1}^a \phi_{i_2}^a - \tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a \right) D_{i_1 i_2}^a + \sum_a \sum_\alpha^{\text{core}} |\phi_\alpha^{a,\text{core}}|^2 \qquad (6.21)$$

To ensure that (6.21) reproduce the correct density even though some of the core states are not strictly localized within the augmentation spheres, a smooth core density, $\tilde{n}_c(\mathbf{r})$, is usually constructed, which is identical to the core density outside the augmentation sphere, and a smooth continuation inside. Thus the density is typically evaluated as

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_a (n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r})) \qquad (6.22)$$

where

$$\tilde{n}(\mathbf{r}) = \sum_n^{\text{val}} f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \tilde{n}_c(\mathbf{r}) \qquad (6.23a)$$

$$n^a(\mathbf{r}) = \sum_{i_1 i_2} D_{i_1 i_2}^a \phi_{i_1}^a(\mathbf{r}) \phi_{i_2}^a(\mathbf{r}) + n_c^a(\mathbf{r}) \qquad (6.23b)$$

$$\tilde{n}^a(\mathbf{r}) = \sum_{i_1 i_2} D_{i_1 i_2}^a \tilde{\phi}_{i_1}^a(\mathbf{r}) \tilde{\phi}_{i_2}^a(\mathbf{r}) + \tilde{n}_c^a(\mathbf{r}) \qquad (6.23c)$$

---

[1]Local operator $\widehat{O}$: An operator which does not correlate separate parts of space, i.e. $\langle \mathbf{r} | \widehat{O} | \mathbf{r}' \rangle = 0$ if $\mathbf{r} \neq \mathbf{r}'$.

6.5   Total Energies

The total energy of the electronic system is given by eq. (3.25):

$$E[n] = T_s[n] + U_H[n] + V_{ext}[n] + E_{xc}[n] \tag{6.24}$$

In this section, the usual energy expression above, is sought re-expressed in terms of the PAW quantities: the smooth waves and the auxiliary partial waves.

For the local and semi-local functionals, we can utilize (6.19), while the nonlocal parts needs more careful consideration.

6.5.1   The Semi-local Contributions

The kinetic energy functional $T_s = \sum_n f_n \langle \psi_n| - \frac{1}{2}\nabla^2|\psi_n\rangle$ is obviously a (semi-) local functional, so we can apply (6.19) and immediately arrive at:

$$
\begin{aligned}
T_s[\{\psi_n\}] &= \sum_n f_n \langle \psi_n| - \tfrac{1}{2}\nabla^2|\psi_n\rangle \\
&= \sum_n^{\text{val}} f_n \langle \tilde{\psi}_n| - \tfrac{1}{2}\nabla^2|\tilde{\psi}_n\rangle + \sum_a \Delta T_s^a[\{D_{i_1 i_2}^a\}]
\end{aligned} \tag{6.25}
$$

where

$$\Delta T_s^a[\{D_{i_1 i_2}^a\}] = \sum_{i_1 i_2} D_{i_1 i_2}^a \left(\langle \phi_{i_1}^a| - \tfrac{1}{2}\nabla^2|\phi_{i_2}^a\rangle - \langle \tilde{\phi}_{i_1}^a| - \tfrac{1}{2}\nabla^2|\tilde{\phi}_{i_2}^a\rangle \right) + \sum_a \sum_\alpha^{\text{core}} \langle \phi_\alpha^{a,\text{core}}| - \tfrac{1}{2}\nabla^2|\phi_\alpha^{a,\text{core}}\rangle \tag{6.26}$$

For LDA and GGA type exchange-correlation functionals, E_{xc} is likewise, per definition, a semi-local functional, such that it can be expressed as

$$E_{xc}[n] = E_{xc}[\tilde{n}] + \sum_a \left(E_{xc}[n^a] - E_{xc}[\tilde{n}^a] \right) \tag{6.27}$$

By virtue of (6.23b)-(6.23c) we can consider the atomic corrections as functionals of the density matrix defined in (6.18), i.e.

$$E_{xc}[n] = E_{xc}[\tilde{n}] + \sum_a \Delta E_{xc}^a[\{D_{i_1 i_2}^a\}] \tag{6.28}$$

where

$$\Delta E_{xc}^a[\{D_{i_1 i_2}^a\}] = E_{xc}[n^a] - E_{xc}[\tilde{n}^a] \tag{6.29}$$

The case of nonlocal exact-exchange will be discussed in section 6.7.

6.5.2   The Nonlocal Contributions

The Hartree term is both nonlinear and nonlocal, so more care needs to be taken when introducing the PAW transformation for this expression.

In the following we will assume that there is no 'true' external field, such that $V_{\text{ext}}[n]$ is only due to the static nuclei, i.e. it is a sum of the classical interaction of the electron density with the static ionic potential, and the electrostatic energy of the nuclei.[2]

We define the total classical electrostatic energy functional as

$$E_C[n] = U_H[n] + V_{\text{ext}}[n] = \frac{1}{2}((n)) + (n|\sum_a Z^a) + \tfrac{1}{2}\sum_{a \neq a'}(Z^a|Z^{a'}) \tag{6.30}$$

---

[2]The inclusion of an actual external potential is straight forward, and is shown in section G.

where the notation (f|g) indicates the Coulomb integral

$$(f|g) = \iint d\mathbf{r}d\mathbf{r}' \frac{f^*(\mathbf{r})g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{6.31}$$

and I have introduced the short hand notation $((f)) = (f|f)$. In (6.30), $Z^a(\mathbf{r})$ is the charge density of the nucleus at atomic site a, which in the classical point approximation is given by

$$Z^a(\mathbf{r}) = -\mathcal{Z}^a \delta(\mathbf{r} - \mathbf{R}^a) \tag{6.32}$$

with $\mathcal{Z}^a$ being the atomic number of the nuclei. As the Hartree energy of a density with non-zero total charge is numerically inconvenient, we introduce the charge neutral total density

$$\rho(\mathbf{r}) = n(\mathbf{r}) + \sum_a Z^a(\mathbf{r}) \quad (= n_{\text{electrons}} + n_{\text{nuclei}}) \tag{6.33}$$

In terms of this, the coulombic energy of the system can be expressed by

$$E_C[n] = U'_H[\rho] = \frac{1}{2}((n + \sum_a Z^a))' \tag{6.34}$$

where the prime indicates that one should remember the self-interaction error of the nuclei introduced in the Hartree energy of the total density. This correction is obviously ill defined, and different schemes exist for making this correction. As it turns out, this correction is handled very naturally in the PAW formalism.

For now, we will focus on the term $((\rho)) = ((n + \sum_a Z^a))$. If one where to directly include the expansion of $n(\mathbf{r})$ according to (6.22), one would get:

$$((n + \sum_a Z^a)) = ((\tilde{n} + \sum_a n^a - \tilde{n}^a + Z^a))$$
$$= ((\tilde{n})) + \sum_{aa'}(n^a - \tilde{n}^a + Z^a | n^{a'} - \tilde{n}^{a'} + Z^{a'}) + 2\sum_a (\tilde{n} | n^a - \tilde{n}^a + Z^a)$$

where in the last expression, the first term is the Hartree energy of the smooth electron density, which is numerically problematic because of the nonzero total charge (see e.g. section 8.3.1). The second term contains a double summation over all nuclei, which would scale badly with system size, and the last term involves integrations of densities represented on incompatible grids (remember that the one-center densities are represented on radial grids to capture the oscillatory behavior near the nuclei)[3]. This is clearly not a feasible procedure. To correct these problem we add and subtract some atom centered compensation charges $\tilde{Z}^a$:

$$((n + \sum_a \tilde{Z}^a + \sum_a \left[Z^a - \tilde{Z}^a \right])) = ((\tilde{n} + \sum_a \tilde{Z}^a)) + \sum_{aa'}(n^a - \tilde{n}^a + Z^a - \tilde{Z}^a | n^{a'} - \tilde{n}^{a'} + Z^{a'} - \tilde{Z}^a)$$
$$+ 2\sum_a (\tilde{n} + \sum_{a'} \tilde{Z}^{a'} | n^a - \tilde{n}^a + Z^a - \tilde{Z}^a)$$

If we define $\tilde{Z}^a(\mathbf{r})$ in such a way that $n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) + Z^a(\mathbf{r}) - \tilde{Z}^a(\mathbf{r})$ has no multipole moments, i.e.

$$\int d\mathbf{r} r^l Y_L(\widehat{\mathbf{r} - \mathbf{R}^a})(n^a - \tilde{n}^a + Z^a - \tilde{Z}^a) = 0 \tag{6.35}$$

for all a, the potentials of these densities are zero outside their respective augmentation spheres ($L = (l, m)$ is a collective angular- and magnetic quantum number). Exploiting this feature, the Coulomb integral reduce to

$$((n + \sum_a Z^a)) = ((\tilde{n} + \sum_a \tilde{Z}^a)) + \sum_a((n^a - \tilde{n}^a + Z^a - \tilde{Z}^a)) + 2\sum_a (\tilde{n}^a + \tilde{Z}^a | n^a - \tilde{n}^a + Z^a - \tilde{Z}^a)$$
$$= ((\tilde{n} + \sum_a \tilde{Z}^a)) + \sum_a \left(((n^a + Z^a)) - ((\tilde{n}^a + \tilde{Z}^a)) \right)$$

---

[3]One could separate the terms in other ways, but it is impossible to separate the smooth and the localized terms completely.

where it has been used that inside the augmentation spheres $\tilde{n} = \tilde{n}^a$. In this expression, we have circumvented all of the previous problems. None of the terms correlates functions on different grids, there is only a single summation over the atomic sites, and furthermore the only thing that has to be evaluated in the full space is the Hartree energy of $\tilde{n}(\mathbf{r}) + \sum_a \tilde{Z}^a(\mathbf{r})$ which is charge neutral (see eq. (6.42)).

Inserting the final expression in (6.30), we see that

$$
\begin{aligned}
E_C[n] &= \frac{1}{2}((\tilde{n} + \textstyle\sum_a \tilde{Z}^a)) + \frac{1}{2}\sum_a \left(((n^a + Z^a))' - ((\tilde{n}^a + \tilde{Z}^a)) \right) \\
&= U_H[\tilde{\rho}] + \frac{1}{2}\sum_a \left(((n^a)) + 2(n^a | Z^a) - ((\tilde{n}^a + \tilde{Z}^a)) \right)
\end{aligned}
\tag{6.36}
$$

where we have introduced the smooth total density

$$
\tilde{\rho}(\mathbf{r}) = \tilde{n} + \sum_a \tilde{Z}^a(\mathbf{r})
\tag{6.37}
$$

Note that the problem with the self interaction error of the nuclei could easily be resolved once it was moved to the atom centered part, as handling charged densities is not a problem on radial grids.

To obtain an explicit expression for the compensation charges, we make a multipole expansion of $\tilde{Z}^a(\mathbf{r})$

$$
\tilde{Z}^a = \sum_L Q_L^a \, \tilde{g}_L^a(\mathbf{r})
\tag{6.38}
$$

where $\tilde{g}_L^a(\mathbf{r})$ is any smooth function localized within $|\mathbf{r} - \mathbf{R}^a| < r_c^a$, satisfying

$$
\int d\mathbf{r} r^l Y_L(\widehat{\mathbf{r} - \mathbf{R}^a}) \tilde{g}_{L'}^a(\mathbf{r}) = \delta_{LL'}
\tag{6.39}
$$

Plugging the expansion (6.38) into equations (6.35), we see that the expansion coefficients Q_L^a from must be chosen according to

$$
Q_L^a = \int d\mathbf{r} r^l Y_L(\hat{\mathbf{r}})(n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) + Z^a(\mathbf{r})) = \Delta^a \delta_{l,0} + \sum_{i_1 i_2} \Delta_{L i_1 i_2}^a D_{i_1 i_2}^a
\tag{6.40}
$$

where

$$
\Delta^a = \int d\mathbf{r} Y_{00}(\hat{\mathbf{r}})[n_c^a(r) - \tilde{n}_c^a(r) - \mathcal{Z}^a \delta(\mathbf{r})]
\tag{6.41a}
$$

$$
\Delta_{L i_1 i_2}^a = \int d\mathbf{r} r^l Y_L(\hat{\mathbf{r}})[\phi_{i_1}^a(\mathbf{r})\phi_{i_2}^a(\mathbf{r}) - \tilde{\phi}_{i_1}^a(\mathbf{r})\tilde{\phi}_{i_2}^a(\mathbf{r})]
\tag{6.41b}
$$

and it has been used that the core densities are spherical (we consider only closed shell frozen cores). This completely defines the compensation charges $\tilde{Z}^a(\mathbf{r})$.

Note that the special case $l = 0$ of (6.35), implies that

$$
\int d\mathbf{r} \left[n^a - \tilde{n}^a + Z^a - \tilde{Z}^a \right] = 0
$$

$$
\Downarrow
$$

$$
\int d\mathbf{r} \left[\tilde{n}(\mathbf{r}) + \sum_a \tilde{Z}^a(\mathbf{r}) \right] = \int d\mathbf{r} \left[n(\mathbf{r}) + \sum_a Z^a(\mathbf{r}) \right]
$$

$$
\Updownarrow
$$

$$
\int d\mathbf{r} \, \tilde{\rho}(\mathbf{r}) = \int d\mathbf{r} \, \rho(\mathbf{r}) = 0
\tag{6.42}
$$

i.e. that the smooth total density has zero total charge, making the evaluation of the Hartree energy numerically convenient.

In summary, we conclude that the classical coulomb interaction energy which in the KS formalism was given by $E_C[n] = U'_H[\rho]$, in the PAW formalism becomes a pure Hartree energy (no self-interaction correction) of the smooth total density $\tilde{\rho}$ plus some one-center corrections

$$E_C[n] = U_H[\tilde{\rho}] + \sum_a \Delta E_C^a[\{D_{i_1 i_2}^a\}] \tag{6.43}$$

where the corrections

$$\Delta E_C^a[\{D_{i_1 i_2}^a\}] = \tfrac{1}{2}((n^a)) + (n^a|Z^a) - \tfrac{1}{2}((\tilde{n}^a)) - (\tilde{n}^a|\tilde{Z}^a) - \tfrac{1}{2}((\tilde{Z}^a))$$

$$= \tfrac{1}{2}\left[((n_c^a)) - ((\tilde{n}_c^a))\right] - \mathcal{Z}^a \int d\mathbf{r} \frac{n_c^a(r)}{r} - \sum_L Q_L^a(\tilde{n}_c^a|\tilde{g}_L^a)$$

$$+ \sum_{i_1 i_2} D_{i_1 i_2}^{a*} \left[(\phi_{i_1}^a \phi_{i_2}^a | n_c^a) - (\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{n}_c^a) - \mathcal{Z}^a \int d\mathbf{r} \frac{\phi_{i_1}^a(\mathbf{r})\phi_{i_2}^a(\mathbf{r})}{r} - \sum_L Q_L^a(\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{g}_L^a) \right]$$

$$+ \frac{1}{2} \sum_{i_1 i_2 i_3 i_4} D_{i_1 i_2}^{a*} \left[(\phi_{i_1}^a \phi_{i_2}^a | \phi_{i_3}^a \phi_{i_4}^a) - (\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{\phi}_{i_3}^a \tilde{\phi}_{i_4}^a) \right] D_{i_3 i_4}^a - \frac{1}{2} \sum_{LL'} Q_L^a Q_{L'}^a (\tilde{g}_L^a | \tilde{g}_{L'}^a)$$

are simple products of system independent tensors with the one-center density matrix $D_{i_1 i_2}^a$. Note that Q_L^a by virtue of (6.40) is also a functional of the density matrix.

6.5.3 Summary

Summing up all the energy contributions, we see that the Kohn-Sham total energy

$$E[n] = T_s[\{\psi_n\}] + U'_H[\rho] + E_{xc}[n]$$

can be separated into a part calculated on smooth functions, $\tilde{E}$, and some atomic corrections, ΔE^a, involving quantities localized around the nuclei only.

$$E = \tilde{E} + \sum_a \Delta E^a \tag{6.44}$$

where the smooth part

$$\tilde{E} = T_s[\{\tilde{\psi}_n\}] + U_H[\tilde{\rho}] + E_{xc}[\tilde{n}] \tag{6.45}$$

is the usual energy functional, but evaluated on the smooth functions $\tilde{n}$ and $\tilde{\rho}$ instead of n and ρ, and with the soft compensation charges $\tilde{Z}^a$ instead of the nuclei charges $Z^a(\mathbf{r})$. The corrections

$$\Delta E^a = \Delta T_s^a + \Delta E_C^a + \Delta E_{xc}^a \tag{6.46}$$

can be expanded in powers of the density matrix according to

$$\Delta E^a = A^a + \sum_{i_1 i_2} B_{i_1 i_2}^a D_{i_1 i_2}^a + \sum_{i_1 i_2 i_3 i_4} D_{i_1 i_2}^{a*} C_{i_1 i_2 i_3 i_4}^a D_{i_3 i_4}^a + \Delta E_{xc}^a(\{D_{i_1 i_2}^a\}) \tag{6.47}$$

where A^a, $B_{i_1 i_2}^a$, and $C_{i_1 i_2 i_3 i_4}^a$ are system independent tensors that can be pre-calculated and stored for each specie in the periodic table of elements. Expanded in powers of Δ^a and $\Delta_{L i_1 i_2}^a$ from the expansion coefficients of $\tilde{Z}^a$, the tensors A, B, and C are

$$A^a = F^a + \Delta^a K_{00}^a + (\Delta^a)^2 N_{00,00}^a \tag{6.48a}$$

$$B_{i_1 i_2}^a = I_{i_1 i_2}^a + \Delta^a M_{i_1 i_2, 00}^a + \sum_L \Delta_{L i_1 i_2}^a \left(K_L^a + 2\Delta^a N_{00,00}^a \right) \tag{6.48b}$$

$$C_{i_1 i_2 i_3 i_4}^a = J_{i_1 i_2 i_3 i_4}^a + \frac{1}{2} \sum_L \left(M_{i_1 i_2 L}^a \Delta_{L i_3 i_4}^a + M_{i_3 i_4 L}^a \Delta_{L i_1 i_2}^a \right) + \sum_{LL'} \Delta_{L i_1 i_2}^a N_{LL'}^a \Delta_{L' i_3 i_4}^a \tag{6.48c}$$

where the six tensors F, K, N, I, M and J are given by

$$F^a = \sum_{\alpha}^{\text{core}} \langle \phi_\alpha^{a,\text{core}} | -\tfrac{1}{2}\nabla^2 | \phi_\alpha^{a,\text{core}} \rangle + \tfrac{1}{2}\left[((n_c^a)) - ((\tilde{n}_c^a))\right] - \mathcal{Z}^a \int d\mathbf{r}\, \frac{n_c^a(r)}{r}$$

$$I_{i_1 i_2}^a = \langle \phi_{i_1}^a | -\tfrac{1}{2}\nabla^2 | \phi_{i_2}^a \rangle - \langle \tilde{\phi}_{i_1}^a | -\tfrac{1}{2}\nabla^2 | \tilde{\phi}_{i_2}^a \rangle + (\phi_{i_1}^a \phi_{i_2}^a | n_c^a) - (\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{n}_c^a) - \mathcal{Z}^a \int d\mathbf{r}\, \frac{\phi_{i_1}^a(\mathbf{r})\phi_{i_2}^a(\mathbf{r})}{r}$$

$$K_L^a = -(\tilde{n}_c^a | \tilde{g}_L^a)$$

$$N_{LL'}^a = -\frac{1}{2}(\tilde{g}_L^a | \tilde{g}_{L'}^a)$$

$$M_{i_1 i_2 L}^a = -(\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{g}_L^a)$$

$$J_{i_1 i_2 i_3 i_4}^a = \frac{1}{2}\left[(\phi_{i_1}^a \phi_{i_2}^a | \phi_{i_3}^a \phi_{i_4}^a) - (\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{\phi}_{i_3}^a \tilde{\phi}_{i_4}^a)\right]$$

Note that all integrals can be limited to the inside of the augmentation sphere. For example $(\phi_{i_1}^a \phi_{i_2}^a | n_c^a)$ has contributions outside the augmentation sphere, but these are exactly canceled by the contributions outside the spheres of $(\tilde{\phi}_{i_1}^a \tilde{\phi}_{i_2}^a | \tilde{n}_c^a)$, in which region the two expressions are identical.

The $C_{i_1 i_2 i_3 i_4}^a$ tensor has been written in a symmetric form, such that it is invariant under the following symmetry operations:

$$i_1 \leftrightarrow i_2 \qquad\qquad i_3 \leftrightarrow i_4 \qquad\qquad i_1 i_2 \leftrightarrow i_3 i_4 \qquad\qquad (6.50)$$

To arrive at the symmetric form, it has been used that

$$\sum_{i_1 i_2 i_3 i_4 L} D_{i_1 i_2}^{a*} M_{i_1 i_2 L}^a \Delta_{L i_3 i_4}^a D_{i_3 i_4}^a = \frac{1}{2}\sum_{i_1 i_2 i_3 i_4 L}\left(M_{i_1 i_2 L}^a \Delta_{L i_3 i_4}^a + M_{i_3 i_4 L}^a \Delta_{L i_1 i_2}^a\right) D_{i_3 i_4}^a$$

due to the symmetry of M and Δ, and that the density matrix is hermitian.

Both the Hamiltonian and the forces can be derived from the total energy functional (6.44). The Hamiltonian will be derived in the following section. For a derivation of the force in PAW, see appendix F.

6.6 The Transformed Kohn-Sham Equation

The variational quantity in the PAW formalism is the smooth wave function $\tilde{\psi}_n$. From this, all other quantities, such as the density matrix, the soft compensation charges, the transformation operator, etc. are determined by various projections of $\tilde{\psi}_n$ onto the projector functions, and expansions in our chosen basis functions, the partial and smooth partial waves. To obtain the smooth wave functions, we need to solve the eigenvalue equation

$$\widehat{\tilde{H}}\tilde{\psi}_n(\mathbf{r}) = \epsilon_n \hat{S}\tilde{\psi}_n(\mathbf{r}) \qquad\qquad (6.51)$$

where the overlap operator $\hat{S} = \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}}$ and $\widehat{\tilde{H}} = \hat{\mathcal{T}}^\dagger \widehat{H}\hat{\mathcal{T}}$ is the transformed Hamiltonian.

6.6.1 Orthogonality

In the original form, the eigen states of the KS equation where orthogonal, i.e. $\langle \psi_n | \psi_m \rangle = \delta_{nm}$ while in the transformed version

$$\langle \tilde{\psi}_n | \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}} | \tilde{\psi}_m \rangle = \delta_{nm} \qquad\qquad (6.52)$$

i.e. the smooth wave function are only orthogonal with respect to the weight $\hat{S}$.

The explicit form of the overlap operator is

$$\hat{S} = \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}}$$

$$= \left(1 + \sum_a \hat{\mathcal{T}}^a\right)^\dagger \left(1 + \sum_a \hat{\mathcal{T}}^a\right)$$

$$= 1 + \sum_a \left(\hat{\mathcal{T}}^{a\dagger} + \hat{\mathcal{T}}^a + \hat{\mathcal{T}}^{a\dagger}\hat{\mathcal{T}}^a\right)$$

$$= 1 + \sum_a \left[\sum_i |\tilde{p}_i^a\rangle(\langle\phi_i^a| - \langle\tilde{\phi}_i^a|)\sum_j |\tilde{\phi}_j^a\rangle\langle\tilde{p}_j^a| + \sum_j |\tilde{\phi}_j^a\rangle\langle\tilde{p}_j^a|\sum_i(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle)\langle\tilde{p}_i^a| \right.$$
$$\left. + \sum_i |\tilde{p}_i^a\rangle(\langle\phi_i^a| - \langle\tilde{\phi}_i^a|)\sum_j(|\phi_j^a\rangle - |\tilde{\phi}_j^a\rangle)\langle\tilde{p}_j^a|\right] \tag{6.53}$$

$$= 1 + \sum_a \sum_{ij} |\tilde{p}_i^a\rangle(\langle\phi_i^a|\phi_j^a\rangle - \langle\tilde{\phi}_i^a|\tilde{\phi}_j^a\rangle)\langle\tilde{p}_j^a|$$

$$= 1 + \sum_a \sum_{ij} |\tilde{p}_i^a\rangle\sqrt{4\pi}\Delta_{00,ij}^a\langle\tilde{p}_j^a|$$

The orthogonality condition (6.52) must be kept in mind when applying numerical schemes for solving (6.51). For example plane waves are no longer orthogonal, in the sense that $\langle\mathbf{G}|\hat{S}|\mathbf{G}'\rangle \neq \delta_{\mathbf{G},\mathbf{G}'}$.

6.6.2 The Hamiltonian

To determine the transformed Hamiltonian, one could apply the transformation $\widehat{\tilde{H}} = \hat{\mathcal{T}}^\dagger\widehat{H}\hat{\mathcal{T}}$ directly, which would be straight forward for the local parts of $\widehat{H}$, but to take advantage of the trick used to determine the total energy of the nonlocal term ($E_C[n]$), we make use of the relation

$$\frac{\delta E}{\delta\tilde{\psi}_n^*(\mathbf{r})} = f_n\widehat{\tilde{H}}\tilde{\psi}_n(\mathbf{r}) \tag{6.54}$$

Using this, we get

$$\frac{\delta E}{\delta\tilde{\psi}_n^*(\mathbf{r})} = \frac{\delta}{\delta\tilde{\psi}_n^*(\mathbf{r})}\left[T_s[\{\tilde{\psi}_n\}] + E_{xc}[\tilde{n}] + U_H[\tilde{\rho}] + \Delta E^a[\{D_{i_1i_2}^a\}]\right]$$

$$= \frac{\delta T_s[\{\tilde{\psi}_n\}]}{\delta\tilde{\psi}_n^*(\mathbf{r})}$$

$$+ \int d\mathbf{r}'\left[\frac{\delta E_{xc}[\tilde{n}]}{\delta\tilde{n}(\mathbf{r}')} + \frac{\delta U_H[\tilde{\rho}]}{\delta\tilde{n}(\mathbf{r}')}\right]\frac{\delta\tilde{n}(\mathbf{r}')}{\delta\tilde{\psi}_n^*(\mathbf{r})}$$

$$+ \sum_a \sum_{i_1i_2}\left[\int d\mathbf{r}'\frac{\delta U_H[\tilde{n} + \sum_a \tilde{Z}^a]}{\delta\tilde{Z}^a(\mathbf{r}')}\frac{\delta\tilde{Z}^a(\mathbf{r}')}{\delta D_{i_1i_2}^a} + \frac{\delta\Delta E^a}{\delta D_{i_1i_2}^a}\right]\frac{\delta D_{i_1i_2}^a}{\delta\tilde{\psi}_n^*(\mathbf{r})}$$

$$= f_n(-\tfrac{1}{2}\nabla^2)\psi_n(\mathbf{r})$$

$$+ \int d\mathbf{r}'\left[v_{xc}[\tilde{n}](\mathbf{r}') + u_H[\tilde{\rho}](\mathbf{r}')\right]f_n\delta(\mathbf{r} - \mathbf{r}')\tilde{\psi}_n(\mathbf{r}')$$

$$+ \sum_a \sum_{i_1i_2}\left[\int d\mathbf{r}'u_H[\tilde{n} + \sum_a \tilde{Z}^a](\mathbf{r}')\sum_L \Delta_{Li_1i_2}^a\tilde{g}_L^a(\mathbf{r}') + \frac{\delta\Delta E^a}{\delta D_{i_1i_2}^a}\right]f_n\tilde{p}_{i_1}^a(\mathbf{r})P_{ni_2}^a$$

where $v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$ is the usual local (LDA) or semilocal (GGA) exchange correlation potential, and $u_H[n](\mathbf{r}) = \frac{\delta U_H[n]}{\delta n(\mathbf{r})} = \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the usual Hartree potential.

From these results, we can write down the transformed Hamiltonian as

$$\widehat{\tilde{H}} = -\tfrac{1}{2}\nabla^2 + u_H[\tilde{\rho}] + v_{xc}[\tilde{n}] + \sum_a \sum_{i_1i_2} |\tilde{p}_{i_1}^a\rangle\Delta H_{i_1i_2}^a\langle\tilde{p}_{i_2}^a| \tag{6.55}$$

where the nonlocal part of the Hamiltonian is given in terms of the tensor

$$
\begin{aligned}
\Delta H_{i_1 i_2}^a &= \sum_L \Delta_{L i_1 i_2}^a \int d\mathbf{r} u_H[\tilde{\rho}](\mathbf{r}) \tilde{g}_L^a(\mathbf{r}) + \frac{\delta \Delta E^a}{\delta D_{i_1 i_2}^a} \\
&= \sum_L \Delta_{L i_1 i_2}^a \int d\mathbf{r} u_H[\tilde{\rho}](\mathbf{r}) \tilde{g}_L^a(\mathbf{r}) + B_{i_1 i_2}^a + 2 \sum_{i_3 i_4} C_{i_1 i_2 i_3 i_4}^a D_{i_3 i_4}^a + \frac{\delta \Delta E_{xc}}{\delta D_{i_1 i_2}^a}
\end{aligned}
\tag{6.56}
$$

Note that to justify taking the derivative with respect to D only, and not its complex conjugate, the symmetry properties (6.50) has been used to get $D_{i_1 i_2}^{a*} C_{i_1 i_2 i_3 i_4}^a D_{i_3 i_4}^a = D_{i_1 i_2}^a C_{i_1 i_2 i_3 i_4}^a D_{i_3 i_4}^a$.

6.7 Exact Exchange in PAW

In this section, an expression will be derived for the exact exchange total energy and non-local potential in the PAW formalism.

For exchange, the spin label can no longer be ignored, so in this section spin has been included as prescribed in section 2.4.

6.7.1 Exact Exchange Energy

The exact exchange energy is given by:

$$
\begin{aligned}
E_{\text{xx}} &= -\frac{1}{2} \sum_{nn'}^{\text{occ}} \delta_{\sigma_n, \sigma_{n'}} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_n(\mathbf{r}) \psi_{n'}^*(\mathbf{r}) \psi_n^*(\mathbf{r}') \psi_{n'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&= -\frac{1}{2} \sum_{nn'} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} \int d\mathbf{r} d\mathbf{r}' \frac{n_{nn'}^*(\mathbf{r}) n_{nn'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&= -\frac{1}{2} \sum_{nn'} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'}))
\end{aligned}
\tag{6.57}
$$

where

$$
n_{nn'}(\mathbf{r}) = \psi_n^*(\mathbf{r}) \psi_{n'}(\mathbf{r})
\tag{6.58}
$$

Note that these exchange 'densities' doesn't correspond to any physical quantity, and that they are complex in general.

Remembering that for the valence states

$$
\psi_n = \tilde{\psi}_n + \sum_a \left(\psi_n^a - \tilde{\psi}_n^a \right)
$$

while for the core states

$$
\psi_n^c = \phi_\alpha^{a,\text{core}}
$$

the double summation over all occupied states in (6.57) is going to involve terms which are products of valence states only, some which are products of only core states, and some with mixed products, i.e.

$$
\begin{aligned}
E_{\text{xx}} &= -\frac{1}{2} \sum_{nn'}^{\text{occ}} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) \\
&= -\frac{1}{2} \sum_n^{\text{val}} \sum_{n'}^{\text{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) - \sum_n^{\text{val}} \sum_{n'}^{\text{core}} f_n \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) - \frac{1}{2} \sum_n^{\text{core}} \sum_{n'}^{\text{core}} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) \\
&= -\frac{1}{2} \sum_n^{\text{val}} \sum_{n'}^{\text{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) - \frac{1}{2} \sum_n^{\text{val}} \sum_{n'}^{\text{core}} f_n ((n_{nn'})) - \frac{1}{4} \sum_n^{\text{core}} \sum_{n'}^{\text{core}} ((n_{nn'}))
\end{aligned}
\tag{6.59}
$$

Here it has been assumed that the core states form closed shells.

In the following, the three contributions will be treated individually.

The Valence-Valence Interaction

In this section we treat the valence-valence contribution

$$E_{\text{xx}}^{\text{v-v}} = -\frac{1}{2} \sum_{nn'}^{\text{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} ((n_{nn'})) \tag{6.60}$$

to the exchange energy only.

When both n and n' are valence states, the exchange density reduce to

$$
\begin{aligned}
n_{nn'} &= \left(\tilde{\psi}_n + \sum_a \left(\psi_n^a - \tilde{\psi}_n^a \right) \right)^* \left(\tilde{\psi}_{n'} + \sum_a \left(\psi_{n'}^a - \tilde{\psi}_{n'}^a \right) \right) \\
&= \tilde{\psi}_n^* \tilde{\psi}_{n'} + \sum_a \left(\psi_n^a - \tilde{\psi}_n^a \right)^* \sum_a \left(\psi_{n'}^a - \tilde{\psi}_{n'}^a \right) + \tilde{\psi}_n^* \sum_a \left(\psi_{n'}^a - \tilde{\psi}_{n'}^a \right) + \tilde{\psi}_{n'} \sum_a \left(\psi_n^a - \tilde{\psi}_n^a \right)^* \\
&= \tilde{\psi}_n^* \tilde{\psi}_{n'} + \sum_a \left(\psi_n^{a*} \psi_{n'}^a - \tilde{\psi}_n^{a*} \tilde{\psi}_{n'}^a \right) \\
&= \tilde{n}_{nn'} + \sum_a \left(n_{nn'}^a - \tilde{n}_{nn'}^a \right)
\end{aligned}
$$

where $\tilde{n}_{nn'} = \tilde{\psi}_n^* \tilde{\psi}_{n'}$, $n_{nn'}^a = \psi_n^{a*} \psi_{n'}^a$, and $\tilde{n}_{nn'}^a = \tilde{\psi}_n^{a*} \tilde{\psi}_{n'}^a$.

To avoid interactions between one-center exchange densities $(n_{nn'}^a - \tilde{n}_{nn'}^a)$ centered on different atoms, in the expression (6.60), we add and subtract the atom-centered compensation charge $\tilde{Z}_{nn'}^a(\mathbf{r})$

$$n_{nn'} = \tilde{n}_{nn'} + \sum_a \tilde{Z}_{nn'}^a + \sum_a \left(n_{nn'}^a - \tilde{n}_{nn'}^a - \tilde{Z}_{nn'}^a \right) \tag{6.61}$$

where the compensation charges are expansions of the form

$$\tilde{Z}_{nn'}^a(\mathbf{r}) = \sum_L Q_{Lnn'}^a \tilde{g}_L^a(\mathbf{r})$$

The expansion functions, $\tilde{g}_L^a$, are the same as in (6.38), and the expansion coefficients of the compensation charges, $Q_{Lnn'}^a$, are chosen such that $n_{nn'}^a - \tilde{n}_{nn'}^a - \tilde{Z}_{nn'}^a$ in (6.61) has no multipole moments, i.e.

$$\int d\mathbf{r} r^l \left[n_{nn'}^a(\mathbf{r}) - \tilde{n}_{nn'}^a(\mathbf{r}) - \tilde{Z}_{nn'}^a(\mathbf{r}) \right] Y_L(\hat{\mathbf{r}}) = 0 \tag{6.62}$$

for all L. Inserting the expansions of the densities

$$n_{nn'}^a(\mathbf{r}) = \sum_{i_1 i_2}^{\text{val}} \phi_{i_1}^a(\mathbf{r}) \phi_{i_2}^a(\mathbf{r}) P_{ni_1}^{a*} P_{n'i_2}^a \quad \text{and} \quad \tilde{n}_{nn'}^a(\mathbf{r}) = \sum_{i_1 i_2}^{\text{val}} \tilde{\phi}_{i_1}^a(\mathbf{r}) \tilde{\phi}_{i_2}^a(\mathbf{r}) P_{ni_1}^{a*} P_{n'i_2}^a \tag{6.63}$$

we see that

$$\int d\mathbf{r} Y_L(\hat{\mathbf{r}}) r^l \left[\sum_{i_1 i_2}^{\text{val}} \left(\phi_{i_1}^a(\mathbf{r}) \phi_{i_2}^a(\mathbf{r}) - \tilde{\phi}_{i_1}^a(\mathbf{r}) \tilde{\phi}_{i_2}^a(\mathbf{r}) \right) P_{ni_1}^{a*} P_{n'i_2}^a - \sum_{L'} Q_{L'nn'}^a \tilde{g}_{L'}^a(\mathbf{r}) \right] = 0$$

I.e. the expansion coefficients of the compensation charges must be chosen as

$$Q_{Lnn'}^a = \sum_{i_1 i_2}^{\text{val}} \Delta_{Li_1 i_2}^a P_{ni_1}^{a*} P_{n'i_2}^a \tag{6.64}$$

where the system independent tensors $\Delta_{Li_1 i_2}^a$ are the same as those of equation (6.41b).

Inserting the exchange density (6.61) in the energy expression (6.60), we get (dropping the state labels for brevity)

$$
\begin{aligned}
((n)) &= ((\tilde{n} + \sum_a \tilde{Z}^a + \sum_a (n^a - \tilde{n}^a - \tilde{Z}^a)) \\
&= ((\tilde{n} + \sum_a \tilde{Z}^a)) + 2\operatorname{Re}(\tilde{n} + \sum_a \tilde{Z}^a | \sum_a n^a - \tilde{n}^a - \tilde{Z}^a) + ((\sum_a n^a - \tilde{n}^a - \tilde{Z}^a))
\end{aligned}
\tag{6.65}
$$

using that per construction, the potential of $n_{nn'}^a(\mathbf{r}') - \tilde{n}_{nn'}^a(\mathbf{r}') - \tilde{Z}_{nn'}^a(\mathbf{r}')$ is zero outside the augmentation sphere (as the density is localized within these spheres, and has no multipole moments), and that inside any such $\tilde{n}_{nn'} = \tilde{n}_{nn'}^a$, this can be reduced to:

$$
\begin{aligned}
((n)) &= ((\tilde{n} + \sum_a \tilde{Z}^a)) + 2\operatorname{Re}\sum_a (\tilde{n}^a + \tilde{Z}^a | n^a - \tilde{n}^a - \tilde{Z}^a)_a + \sum_a ((n^a - \tilde{n}^a - \tilde{Z}^a))_a \\
&= ((\tilde{n} + \sum_a \tilde{Z}^a)) + \operatorname{Re}\sum_a (n^a + \tilde{n}^a + \tilde{Z}^a | n^a - \tilde{n}^a - \tilde{Z}^a) \\
&= ((\tilde{n} + \sum_a \tilde{Z}^a)) + \sum_a \left\{ ((n^a)) - ((\tilde{n}^a + \tilde{Z}^a)) \right\}
\end{aligned}
\tag{6.66}
$$

Note that the special case $l = 0$ of (6.62), implies that

$$
\int d\mathbf{r} \left[n_{nn'}^a - \tilde{n}_{nn'}^a - \tilde{Z}_{nn'}^a \right] = 0
$$
$$
\Downarrow
$$
$$
\int d\mathbf{r} \left[\tilde{n}_{nn'} + \sum_a \tilde{Z}_{nn'} \right] = \int d\mathbf{r}\, n_{nn'} = \delta_{nn'}
\tag{6.67}
$$

as the true exchange densities, $n_{nn'}$, formed by the full all-electron KS wave functions, are orthonormal. This implies that that the argument of the first Coulomb integral in eq. (6.66) has a nonzero total charge $(= 1)$, for $n = n'$. This causes some problems for the numerical procedures for evaluating such integrals, see section 8.3.1 for a discussion, and suggested solutions to this problem.

Inspired by (6.66), we now decompose the valence-valence contribution to the exchange energy, in a soft exchange contribution and an atomic correction

$$
E_{\mathrm{xx}}^{\mathrm{v\text{-}v}} = \tilde{E}_{\mathrm{xx}} + \sum_a \Delta E_{\mathrm{xx}}^{a,\mathrm{v\text{-}v}}
\tag{6.68}
$$

where the soft contribution $\tilde{E}_{\mathrm{xx}}$ is

$$
\tilde{E}_{\mathrm{xx}} \equiv -\frac{1}{2} \sum_{nn'}^{\mathrm{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} ((\tilde{n}_{nn'} + \sum_a \tilde{Z}_{nn'}^a))
\tag{6.69}
$$

and the PAW atomic correction, $\Delta E_{\mathrm{xx}}^{a,\mathrm{v\text{-}v}}$ is

$$
\Delta E_{\mathrm{xx}}^{a,\mathrm{v\text{-}v}} = -\frac{1}{2} \sum_{nn'}^{\mathrm{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} \left\{ ((n_{nn'}^a)) - ((\tilde{n}_{nn'}^a + \tilde{Z}_{nn'}^a)) \right\}
\tag{6.70}
$$

Inserting the relations (6.63) and (6.64) and preceding in much the same way as for the Hartree energy, one eventually end up with the expression

$$
\begin{aligned}
\Delta E_{\mathrm{xx}}^{a,\mathrm{v\text{-}v}} &= -\sum_{nn'}^{\mathrm{val}} \sum_{i_1 i_2 i_3 i_4}^{\mathrm{val}} f_n f_{n'} \delta_{\sigma_n, \sigma_{n'}} P_{ni_1}^{a*} P_{n'i_2}^a P_{ni_3}^a P_{n'i_4}^{a*} C_{i_1 i_2 i_3 i_4}^a \\
&= -\sum_\sigma \sum_{i_1 i_2 i_3 i_4}^{\mathrm{val}} D_{i_1 i_2}^{a*}(\sigma) C_{i_1 i_3 i_2 i_4}^a D_{i_3 i_4}^a(\sigma)
\end{aligned}
\tag{6.71}
$$

where the system independent tensor C is identical to the tensor $C^a_{i_1 i_2 i_3 i_4}$ used to evaluate the total energy, eq. (6.48c), and a spin specific density matrix has been introduced by

$$D^a_{i_1 i_2}(\sigma) = \sum_n f_n \delta_{\sigma_n, \sigma} \langle \tilde{\psi}_n | \tilde{p}^a_{i_1} \rangle \langle \tilde{p}^a_{i_2} | \tilde{\psi}_n \rangle \tag{6.72}$$

Note that the order of the two indices i_2 and i_3 of C in eq. (6.71) are exchanged, as compared to the equivalent expression for the Hartree energy.

The Valence-Core Interaction

Taking n to be a valence state and n' a core state, the exchange density becomes:

$$n_{nn'} = \left(\tilde{\psi}_n + \sum_a (\psi^a_n - \tilde{\psi}^a_n) \right)^* \psi^c_{n'} = \psi^{a*}_n \phi^{a,\text{core}}_\alpha = \sum_i \phi^a_i P^{a*}_{ni} \phi^{a,\text{core}}_\alpha \tag{6.73}$$

where it has been used that the core states $\phi^{a,\text{core}}_\alpha$ are localized within the augmentation spheres, and that inside any such, the smooth all-electron wave function $\tilde{\psi}_n$ is identical to its one-center expansion, $\tilde{\psi}^{a*}_n$. The index $n' = \{a, \alpha\}$ on the core states is a joint index referring to both a specific atom, a, and an atomic core state, α.

From this we see that:

$$
\begin{aligned}
E^{\text{v-c}}_{\text{xx}} &= -\frac{1}{2} \sum_n^{\text{val}} \sum_{n'}^{\text{core}} f_n (n_{nn'} | n_{nn'}) \\
&= -\frac{1}{2} \sum_n^{\text{val}} \sum_a \sum_\alpha^{\text{core}} \sum_{i_1 i_2}^{\text{val}} f_n (\phi^a_{i_1} P^{a*}_{ni_1} \phi^{a,\text{core}}_\alpha | \phi^a_{i_2} P^{a*}_{ni_2} \phi^{a,\text{core}}_\alpha) \\
&= -\sum_a \sum_{i_1 i_2}^{\text{val}} D^a_{i_1 i_2} X^a_{i_1 i_2}
\end{aligned}
\tag{6.74}
$$

where $D^a_{i_1 i_2}$ is the hermitian density matrix of equation (6.18) and the system independent hermitian tensor $X^a_{i_1 i_2}$ is given by:

$$X^a_{i_1 i_2} = \frac{1}{2} \sum_\alpha^{\text{core}} \iint d\mathbf{r} d\mathbf{r}' \phi^a_{i_1}(\mathbf{r}) \phi^{a,\text{core}}_\alpha(\mathbf{r}) \frac{\phi^a_{i_2}(\mathbf{r}') \phi^{a,\text{core}}_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{6.75}$$

The Core-Core Interaction

The core-core contribution to the exact exchange energy is simply given by:

$$E^{\text{c-c}}_{\text{xx}} = -\frac{1}{4} \sum_{nn'}^{\text{core}} ((\psi^{c*}_n \psi^c_{n'})) = -\frac{1}{4} \sum_a \sum_{\alpha, \alpha'}^{\text{core}} ((\phi^{a,\text{core}}_\alpha \phi^{a,\text{core}}_{\alpha'})) \tag{6.76}$$

Where we have again used the assumption that the core states of different atoms do not overlap. That the core-core contribution to the exchange energy only includes exchange between orbitals on the same atom implies that the $E^{\text{c-c}}_{\text{xx}}$ energy contribution only appears as a reference energy, and is as such canceled when calculating energy differences. If total energies are deemed interesting, one can precalculate and tabulate the exchange energy of the core states for each type of atom, and add this reference energy to the total (exchange) energy at the end of calculations.

Summary

Summarizing, the exact exchange energy is in the PAW formalism given by

$$E_{\text{xx}} = \tilde{E}_{\text{xx}} + \sum_a \Delta E^a_{xx}$$

where $\Delta E_{xx}^a = \Delta E_{xx}^{a,\text{v-v}} + E_{xx}^{a,\text{v-c}} + E_{xx}^{a,\text{c-c}}$ and

$$\tilde{E}_{xx} = -\frac{1}{2}\sum_{nn'}^{\text{val}} f_n f_{n'} \delta_{\sigma_n,\sigma_{n'}} ((\tilde{\psi}_n^* \tilde{\psi}_{n'} + \sum_a \tilde{Z}_{nn'}^a)) \qquad \text{(Soft valence-valence interaction)}$$

$$\Delta E_{xx}^{a,\text{v-v}} = -\sum_\sigma \sum_{i_1 i_2 i_3 i_4}^{\text{val}} D_{i_1 i_3}^{a*}(\sigma) C_{i_1 i_2 i_3 i_4}^a D_{i_2 i_4}^a(\sigma) \qquad \text{(Atomic valence-valence correction)}$$

$$E_{xx}^{a,\text{v-c}} = -\sum_{i_1 i_2}^{\text{val}} D_{i_1 i_2}^a X_{i_1 i_2}^a \qquad \text{(Atomic valence-core interaction)}$$

$$E_{xx}^{a,\text{c-c}} = -\frac{1}{4}\sum_{\alpha_1 \alpha_2}^{\text{core}} ((\phi_{\alpha_1}^{a,\text{core}} \phi_{\alpha_2}^{a,\text{core}})) \qquad \text{(Atomic core-core interaction)}$$

6.7.2   The Exact Exchange Potential

To determine the expression for the non-local potential of exact exchange in the PAW formalism, while conserving the tricks used to transform the total energy, we use the same procedure as for determining the transformed Hamiltonian of the KS problem, i.e. using

$$f_n \hat{v}_{xx} \tilde{\psi}_n(\mathbf{r}) = \frac{\delta E_{xx}}{\delta \tilde{\psi}_n^*(\mathbf{r})}$$

where

$$E_{xx} = -\frac{1}{2}\sum_{nn'}^{\text{val}} f_n f_{n'} \delta_{\sigma_n,\sigma_{n'}} ((\tilde{n}_{nn'} + \sum_a \tilde{Z}_{nn'}^a))$$

$$+ \sum_a \left[-\sum_\sigma \sum_{i_1 i_2 i_3 i_4}^{\text{val}} D_{i_1 i_2}^{a*}(\sigma) C_{i_1 i_3 i_2 i_4}^a D_{i_3 i_4}^a(\sigma) - \sum_{i_1 i_2}^{\text{val}} D_{i_1 i_2}^a X_{i_1 i_2}^a + E_{xx}^{a,\text{c-c}} \right]$$

with the smooth compensation charges $\tilde{Z}_{nn'}^a(\mathbf{r})$ and the exchange densities $\tilde{n}_{nn'}(\mathbf{r})$ given by

$$\tilde{Z}_{nn'}^a(\mathbf{r}) = \sum_L \sum_{i_1 i_2}^{\text{val}} \Delta_{L i_1 i_2}^a P_{n i_1}^{a*} P_{n' i_2}^a \tilde{g}_L^a(\mathbf{r})$$

$$\tilde{n}_{nn'}(\mathbf{r}) = \tilde{\psi}_n^*(\mathbf{r}) \tilde{\psi}_{n'}(\mathbf{r})$$

The potential corresponding to this energy is found from

$$f_n \hat{v}_{xx} \tilde{\psi}_n(\mathbf{r}) = \frac{\delta \tilde{E}_{xx}}{\delta \tilde{\psi}_n^*(\mathbf{r})} + \sum_a \frac{\delta \Delta E_{xx}^a}{\delta \tilde{\psi}_n^*(\mathbf{r})}$$

$$= \sum_{pq} \int d\mathbf{r}' \left[\frac{\delta \tilde{E}_{xx}}{\delta \tilde{n}_{pq}(\mathbf{r}')} \frac{\delta \tilde{n}_{pq}(\mathbf{r}')}{\delta \tilde{\psi}_n^*(\mathbf{r})} + \frac{\delta \tilde{E}_{xx}}{\delta \tilde{n}_{pq}^*(\mathbf{r}')} \frac{\delta \tilde{n}_{pq}^*(\mathbf{r}')}{\delta \tilde{\psi}_n^*(\mathbf{r})} + \sum_a \frac{\delta \tilde{E}_{xx}}{\delta \tilde{Z}_{pq}^a(\mathbf{r}')} \frac{\delta \tilde{Z}_{pq}^a(\mathbf{r}')}{\delta \tilde{\psi}_n^*(\mathbf{r})} + \frac{\delta \tilde{E}_{xx}}{\delta \tilde{Z}_{pq}^{a*}(\mathbf{r}')} \frac{\delta \tilde{Z}_{pq}^{a*}(\mathbf{r}')}{\delta \tilde{\psi}_n^*(\mathbf{r})} \right]$$

$$+ \sum_a \sum_{i_1 i_2} \sum_\sigma \left[\frac{\delta \Delta E_{xx}^a}{D_{i_1 i_2}^a(\sigma)} \frac{D_{i_1 i_2}^a(\sigma)}{\delta \tilde{\psi}_n^*(\mathbf{r})} + \frac{\delta \Delta E_{xx}^a}{D_{i_1 i_2}^{a*}(\sigma)} \frac{D_{i_1 i_2}^{a*}(\sigma)}{\delta \tilde{\psi}_n^*(\mathbf{r})} \right]$$

$$= \sum_{pq} \int d\mathbf{r}' \left[f_p f_q \delta_{\sigma_p,\sigma_q} \tilde{v}_{pq}(\mathbf{r}') \delta_{pn} \delta(\mathbf{r} - \mathbf{r}') \tilde{\psi}_q(\mathbf{r}') \right.$$

$$\left. + \sum_a f_p f_q \delta_{\sigma_p,\sigma_q} \tilde{v}_{pq}(\mathbf{r}') \sum_L \tilde{g}_L^a(\mathbf{r}') \sum_{i_1 i_2} \delta_{pn} \Delta_{L i_1 i_2}^a \tilde{p}_{i_1}^a(\mathbf{r}) P_{q i_2}^a \right]$$

$$+ \sum_a \sum_{i_1 i_2} \left[-X_{i_1 i_2}^a - \sum_{i_3 i_4} \left(D_{i_3 i_4}^{a*} C_{i_3 i_1 i_4 i_2}^a + C_{i_1 i_3 i_2 i_4}^a D_{i_3 i_4}^a \right) \right] \tilde{p}_{i_1}^a(\mathbf{r}) P_{n i_2}^a$$

where

$$\tilde{v}_{nn'}(\mathbf{r}) = -\int d\mathbf{r}' \frac{(\tilde{n}_{nn'}(\mathbf{r}') + \sum_a \tilde{Z}^a_{nn'}(\mathbf{r}'))^*}{|\mathbf{r} - \mathbf{r}'|} \tag{6.77}$$

From this, we see that the exchange potential is a nonlocal operator of the form

$$\hat{v}_{xx}|\tilde{\psi}_n\rangle = \sum_{n'} f_{n'}\delta_{\sigma_n,\sigma_{n'}} \left[\tilde{v}_{nn'} + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle v^a_{nn',i_1 i_2} \langle \tilde{p}^a_{i_2}| \right] |\tilde{\psi}_{n'}\rangle$$
$$- \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle \left[X^a_{i_1 i_2} + 2 \sum_{i_3 i_4} C^a_{i_1 i_3 i_2 i_4} D^a_{i_3 i_4} \right] \langle \tilde{p}^a_{i_2}|\tilde{\psi}_n\rangle \tag{6.78}$$

where the tensor

$$v^a_{nn',i_1 i_2} = \sum_L \Delta^a_{Li_1 i_2} \int d\mathbf{r} \tilde{g}^a_L(\mathbf{r})\tilde{v}_{nn'}(\mathbf{r}) \tag{6.79}$$

To get the factor of two in front of C the symmetry properties (6.50) has been used.

6.8   Summary

A hybrid HF-KS calculation in the PAW formalism, including a fraction λ of exact exchange, is performed by redefining the tensors A, B, and C according to

$$A^a \rightarrow A^a + \lambda E^{a,\text{c-c}}_{\text{xx}}$$
$$B^a_{i_1 i_2} \rightarrow B^a_{i_1 i_2} - \lambda X^a_{i_1 i_2}$$
$$C^a_{i_1 i_2 i_3 i_4} \rightarrow C^a_{i_1 i_2 i_3 i_4} - \lambda C^a_{i_1 i_3 i_2 i_4}$$

and multiplying all terms of A, B, and C involving the local exchange potential by a factor $1 - \lambda$. The PAW HF-KS equation to be solved is

$$\hat{\overline{\overline{H}}}|\tilde{\psi}_n\rangle = \epsilon_n \hat{S}|\tilde{\psi}_n\rangle \tag{6.80}$$

with $\hat{S}$ given by (6.53), and $\hat{\overline{\overline{H}}}$ by

$$\hat{\overline{\overline{H}}}|\tilde{\psi}_n\rangle = \left[-\tfrac{1}{2}\nabla^2 + u_H[\tilde{\rho}](\mathbf{r}) + (1-\lambda)v_x[\tilde{n}](\mathbf{r}) + v_c[\tilde{n}](\mathbf{r}) \right]|\tilde{\psi}_n\rangle + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle \Delta H^a_{i_1 i_2} \langle \tilde{p}^a_{i_2}|\tilde{\psi}_n\rangle$$
$$+ \lambda \sum_{n'} f_{n'}\delta_{\sigma_n,\sigma_{n'}} \left[\tilde{v}_{nn'}(\mathbf{r}) + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle v^a_{nn',i_1 i_2} \langle \tilde{p}^a_{i_2}| \right] |\tilde{\psi}_{n'}\rangle \tag{6.81}$$

where

$$\Delta H^a_{i_1 i_2} = \sum_L \Delta^a_{Li_1 i_2} \int d\mathbf{r} u_H[\tilde{\rho}](\mathbf{r})\tilde{g}^a_L(\mathbf{r}) + B^a_{i_1 i_2} + 2\sum_{i_3 i_4} C^a_{i_1 i_2 i_3 i_4} D^a_{i_3 i_4} + (1-\lambda)\frac{\delta\Delta E_x}{\delta D^a_{i_1 i_2}} + \frac{\delta\Delta E_c}{\delta D^a_{i_1 i_2}} \tag{6.82}$$

with $\tilde{v}_{nn'}$ given by (6.77) and $v^a_{nn',i_1 i_2}$ by (6.79).

The total energy can then be evaluated by

$$E = T_s[\{\tilde{\psi}_n\}] + U_H[\tilde{\rho}] + \lambda E_{\text{xx}}[\{\tilde{n}_{nn'} + \sum_a \tilde{Z}^a_{nn'}\}] + (1-\lambda)E_x[\tilde{n}] + E_c[\tilde{n}] + \sum_a \Delta E^a \tag{6.83}$$

with

$$E_{\text{xx}} = 1/2 \sum_{nn'} \delta_{\sigma_n,\sigma_{n'}} \int d\mathbf{r}\tilde{v}_{nn'}(\mathbf{r})(\tilde{n}_{nn'}(\mathbf{r}) + \sum_a \tilde{Z}^a_{nn'}(\mathbf{r}))$$

and ΔE^a given by

$$\Delta E^a = A^a + \sum_{i_1 i_2} B^a_{i_1 i_2} D^a_{i_1 i_2} + \sum_{i_1 i_2 i_3 i_4} D^{a*}_{i_1 i_2} C^a_{i_1 i_2 i_3 i_4} D^a_{i_3 i_4} + (1 - \lambda)\Delta E^a_x(\{D^a_{i_1 i_2}\}) + \Delta E^a_c(\{D^a_{i_1 i_2}\})$$

(6.84)

with the redefined tensors A, B, and C.

Having solved the eigenvalue problem (6.80), the eigenvalues are known. This can be used to determine, for example, the kinetic energy of the pseudo wave functions, $T_s[\tilde{n}]$, without doing the explicit (and computationally costly) computation. This can be seen by operating with $\sum_n f_n \langle \tilde{\psi}_n |$ on eq. (6.81) to get:

$$T_s[\{\tilde{\psi}_n\}] = \sum_n f_n \epsilon_n - \int d\mathbf{r}[\tilde{n}(\mathbf{r}) - \tilde{n}_c(\mathbf{r})]\left[u_H[\tilde{\rho}](\mathbf{r}) + v_{xc}[\tilde{n}](\mathbf{r})\right] - \sum_a \sum_{i_1 i_2} \Delta H^a_{i_1 i_2} D^a_{i_1 i_2} \quad (6.85)$$

When including Fock exchange, one needs to add the additional term

$$\sum_{nn'} f_n \left[f_{n'} \delta_{\sigma_n, \sigma_{n'}} \int d\mathbf{r}\tilde{v}_{nn'}(\mathbf{r})\tilde{n}_{nn'}(\mathbf{r}) - \sum_a \sum_{i_1 i_2} P^a_{n i_1} P^a_{n' i_2} v^a_{nn', i_1 i_2} \right] \quad (6.86)$$

to the right hand side.

Chapter 7

Implementing PAW

For an implementation of PAW, one must specify a large number of data for each chemical element. This constitutes a data set which uniquely determines how the on-site PAW transformation works, at the site of the specific atom. For the generation of such data sets, one needs an atomic DFT program, with which basis sets can be generated. How to perform DFT calculations efficiently on an isolated atom will be discussed in the first section of this chapter, and the actual choice of data set parameters will be discussed in the second. The atomic DFT program plays the additional role of a small test program, against which implementations in the full PAW program can be tested.

7.1 Atoms

If we consider the Kohn-Sham equation for an isolated atom, (described by a non spin-dependent Hamiltonian), it is well known that the eigenstates can be represented by the product

$$\phi_{i\sigma_i}(\mathbf{r}\sigma) = R_j(r)Y_L(\hat{\mathbf{r}})\chi_{\sigma_i}(\sigma) \tag{7.1}$$

where R_j are real radial function, and Y_L are the (complex valued) spherical harmonics. $i = (n, l, m)$, $j = (n, l)$, and $L = (l, m)$.

Assuming identical filling of all atomic orbitals, i.e. $f_{i\sigma} = f_j$, the density becomes

$$n(\mathbf{r}) = \sum_i \sum_{\sigma_i} f_j |\phi_{i\sigma_i}(\mathbf{r}\sigma)|^2 = \sum_j 2\frac{2l+1}{4\pi} f_j |R_j(r)|^2 \tag{7.2}$$

where the first factor of 2 comes from the sum over spin, and the second factor from the sum over the magnetic quantum number using that

$$\sum_m |Y_{lm}|^2 = \frac{2l+1}{4\pi} \tag{7.3}$$

The identical filling of degenerate states is exact for closed shell systems, and corresponds to a spherical averaging of the density for open shell systems.

Determining potentials in a spherical coordinate system is usually done by exploiting the expansion of the Coulomb kernel

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_L \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_L^*(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}}') \tag{7.4}$$

with $r_< = \min(r, r')$ and $r_> = \max(r, r')$. Using this it is seen that for any density with a known

angular dependence, e.g. the density $R(r)Y_L(\hat{\mathbf{r}})$, the potential can be determined by

$$
\begin{aligned}
v[R(r)Y_L(\hat{\mathbf{r}})](\mathbf{r}) &= \int d\mathbf{r}' \frac{R(r')Y_L(\hat{\mathbf{r}}')}{|\mathbf{r}-\mathbf{r}'|} \\
&= \frac{4\pi}{2l+1} Y_L(\hat{\mathbf{r}}) \int_0^\infty r'^2 dr' R(r') \frac{r_<^l}{r_>^{l+1}} \\
&= \frac{4\pi}{2l+1} Y_L(\hat{\mathbf{r}}) \left[\int_0^r dr' R(r')r' \left(\frac{r'}{r}\right)^{l+1} + \int_r^\infty dr' R(r')r' \left(\frac{r}{r'}\right)^l \right]
\end{aligned}
\tag{7.5}
$$

if the angular dependence is not a spherical harmonic, one can always do a multipole expansion as described in section D.2, and use the above expression on the individual terms.

In the case of a radial density $n(\mathbf{r}) = n(r)$, the Hartree potential becomes

$$
u_H(r) = \frac{4\pi}{r} \int_0^r dr' n(r')r'^2 + 4\pi \int_r^\infty dr' n(r')r'
\tag{7.6}
$$

A purely radial dependent density also implies that the xc-potential is a radial function. Using this, the entire KS equation can be reduced to a 1D problem in r, while the angular part is treated analytically.

7.1.1 The Radial Kohn-Sham Equation

For a spherical KS potential, and using that Y_L are eigenstates of the Laplacian, as described in appendix D.3, the KS equation can be reduced to the simpler one-dimensional second order eigenvalue problem

$$
\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{l(l+1)}{2r^2} + v_s(r) \right] R_j(r) = \epsilon_j R_j(r)
\tag{7.7}
$$

If we introduce the radial wave function $u_j(r)$ defined by

$$
rR_j(r) = u_j(r)
\tag{7.8}
$$

the KS equation can be written as

$$
u_j''(r) + \left(2\epsilon_j - 2v_s(r) - \frac{l(l+1)}{r^2} \right) u_j(r) = 0
\tag{7.9}
$$

which is easily integrated using standard techniques. See e.g. [1, chapter 6].

7.1.2 Exact Exchange

The exact exchange energy for the radial problem is

$$
\begin{aligned}
E_x &= -\frac{1}{2} \sum_{i_1 i_2} f_{i_1} f_{i_2} \delta_{\sigma_{i_1},\sigma_{i_2}} \iint d\mathbf{r}d\mathbf{r}' \frac{R_{j_1}(r)Y_{L_1}^*(\hat{\mathbf{r}})R_{j_2}(r)Y_{L_2}(\hat{\mathbf{r}})R_{j_2}(r')Y_{L_2}^*(\hat{\mathbf{r}}')R_{j_1}(r')Y_{L_1}(\hat{\mathbf{r}}')}{|\mathbf{r}-\mathbf{r}'|} \\
&= -\frac{1}{4} \sum_{i_1 i_2} f_{j_1} f_{j_2} \sum_L \frac{4\pi}{2l+1} |G_{L_1 L_2}^L|^2 \iint drdr' \frac{r_<^l}{r_>^{l+1}} u_{j_1}(r)u_{j_2}(r)u_{j_2}(r')u_{j_1}(r') \\
&= -\frac{1}{4} \sum_{j_1 j_2} f_{j_1} f_{j_2} \sum_l \frac{4\pi}{2l+1} \left(\sum_{\substack{m \\ m_1 m_2}} |G_{L_1 L_2}^L|^2 \right) \iint drdr' \frac{r_<^l}{r_>^{l+1}} u_{j_1}(r)u_{j_2}(r)u_{j_2}(r')u_{j_1}(r')
\end{aligned}
\tag{7.10}
$$

where $G_{L_1 L_2}^L = \int d\hat{\mathbf{r}} Y_L(\hat{\mathbf{r}})Y_{L_1}(\hat{\mathbf{r}})Y_{L_2}^*(\hat{\mathbf{r}})$ are the Gaunt coefficients [65].

The Fock exchange potential

$$\hat{v}_x^{\text{NL}}\phi_{i_1}(\mathbf{r}) = -\sum_{i_2} f_{i_2}\delta_{\sigma_{i_1},\sigma_{i_2}}\phi_{i_2}(\mathbf{r})\int d\mathbf{r}'\frac{\phi_{i_2}(\mathbf{r}')\phi_{i_1}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

is reduced to

$$\hat{v}_x^{\text{NL}}R_{j_1}(r)Y_{L_1}(\hat{\mathbf{r}}) = -\tfrac{1}{2}\sum_{i_2}f_{j_2}R_{j_2}(r)Y_{L_2}(\hat{\mathbf{r}})\int d\mathbf{r}'\frac{R_{j_2}(r')Y_{L_2}^*(\hat{\mathbf{r}}')R_{j_1}(r')Y_{L_1}(\hat{\mathbf{r}}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= -\tfrac{1}{2}\sum_{j_2}f_{j_2}\frac{u_{j_2}(r)}{r}\sum_l\frac{4\pi}{2l+1}\left(\sum_{mm_2}G_{L_1L_2}^L Y_L(\hat{\mathbf{r}})Y_{L_2}(\hat{\mathbf{r}})\right)\int dr'\frac{r_<^l}{r_>^{l+1}}u_{j_2}(r')u_{j_1}(r')$$

$$= \frac{Y_{L_1}(\hat{\mathbf{r}})}{2r(2l_1+1)}\sum_{j_2}f_{j_2}u_{j_2}(r)\sum_l\frac{4\pi}{2l+1}\left(\sum_{\substack{m\\m_1m_2}}|G_{L_1L_2}^L|^2\right)\int dr'\frac{r_<^l}{r_>^{l+1}}u_{j_2}(r')u_{j_1}(r')$$

$$(7.11)$$

From which the radial potential

$$w_{j_1j_2}(r) = \frac{-1}{2(2l_1+1)(2l_2+1)}\sum_l\frac{4\pi}{2l+1}\left(\sum_{\substack{m\\m_1m_2}}|G_{L_1L_2}^L|^2\right)\int dr'\frac{r_<^l}{r_>^{l+1}}u_{j_2}(r')u_{j_1}(r') \qquad (7.12)$$

can be defined, in terms of which the radial non-local exchange operator can be written as

$$\hat{v}_x^{\text{NL}}u_{j_1}(r) = \sum_{j_2}f_{j_2}(2l_2+1)u_{j_2}(r)w_{j_1j_2}(r) \qquad (7.13)$$

This is the potential that should be included in the radial KS equation. In terms of this, the exchange energy becomes

$$E_x = \frac{1}{2}\sum_{j_1}f_{j_1}(2l_1+1)\int dr u_{j_1}(r)\hat{v}_x u_{j_1}(r) = \frac{1}{2}\sum_{j_1j_2}f_{j_1}f_{j_2}(2l_1+1)(2l_2+1)\int dr u_{j_1}(r)w_{j_1j_2}(r)u_{j_2}(r)$$

$$(7.14)$$

7.2 The Atomic Data Set of PAW

The very large degree of freedom when choosing the functions defining the PAW transformation means that the choice varies a great deal between different implementations. In any actual implementation expansions are obviously finite, and many numerical considerations must be made when choosing these basis sets, to ensure fast and reliable convergence. This section provides an overview of the information needed for uniquely defining the PAW transformation, and the level of freedom when choosing the parameters.

The Partial Waves

The basis functions, ϕ_i^a, for the expansion of $|\psi_n\rangle$ should be chosen to ensure a fast convergence to the KS wave function. For this reason we choose the partial waves as the eigenstates of the Schrödinger equation for the isolated spin-saturated atoms. Thus the index i is a combination of main-, angular-, and magnetic quantum number, (n, l, m). And the explicit form is

$$\phi_i^a(\mathbf{r}) = \phi_{nl}^a(r)Y_{lm}(\hat{\mathbf{r}})$$

where $\phi_{nl}^a(r)$ are the solutions of the radial KS Schrödinger equation (7.7), and Y_{lm} are the spherical harmonics. For convenience we choose $\phi_i^a(\mathbf{r})$ to be real, i.e. we use the real spherical harmonics of

appendix D.3. This choice of partial waves implies that the smooth partial waves and the smooth projector functions can also be chosen real, and as products of some radial functions and the same real spherical harmonic.

Note that including unbound states of the radial KS equation in the partial waves is not a problem, as the diverging tail is exactly canceled by the smooth partial waves. In practice we only integrate the KS equation outward from the origin to the cutoff radius for unbound states, thus making the energies free parameters. In principle the same could be done for the bound states, but in GPAW, the energies of bound states are fixed by making the inward integration for these states and doing the usual matching (see e.g. [1, chapter 6]), i.e. the energies are chosen as the eigenenergies of the system.

The Smooth Partial Waves

The smooth partial waves $\tilde{\psi}_i^a(\mathbf{r})$ are per construction identical to the partial waves outside the augmentation sphere. Inside the spheres, we can choose them as any smooth continuation. Presently GPAW uses simple 6'th order polynomials of even powers only (as odd powers in r results in a kink in the functions at the origin, i.e. that the first derivatives are not defined at this point), where the coefficients are used to match the partial waves smoothly at $r = r_c$. Other codes uses Bessel functions [58] or Gaussians.

The Smooth Projector Functions

The smooth projector functions are a bit more tricky. Making them orthonormal to $\tilde{\phi}_i^a(\mathbf{r})$ is a simple task of applying the usual Gram-Smith procedure. This is the only formal requirement, but in any actual implementation all expansions are necessarily finite, and we therefore want them to converge as fast as possible, so only a few terms needs to be evaluated.

A popular choice is to determine the smooth projector functions according to

$$|\tilde{p}_i^a\rangle = \left(-\tfrac{1}{2}\nabla^2 + \tilde{v}_s - \epsilon_i\right)|\tilde{\phi}_i^a\rangle \tag{7.15}$$

or equivalently

$$\tilde{p}_j^a(r) = \left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{l(l+1)}{2r^2} + \tilde{v}_s(r) - \epsilon_j\right]\tilde{\phi}_j^a(r) \tag{7.16}$$

where $\tilde{v}_s(r)$ is the smooth KS potential $u_H[\tilde{\rho}](r) + v_{xc}[\tilde{n}](r)$. And then enforce the complementary orthogonality condition $\langle\tilde{p}_j^a|\tilde{\phi}_{j'}^a\rangle = \delta_{j,j'}$ inside the augmentation sphere, by a standard Gram-Schmidt procedure [32]. Using this procedure ensures that the reference atom is described correctly despite the finite number of projectors.

The Smooth Compensation Charge Expansion Functions

The smooth compensation charges $\tilde{g}_L^a(\mathbf{r})$, are products of spherical harmonics, and radial functions $\tilde{g}_l^a(r)$ satisfying that

$$\int d\mathbf{r}\, r^l Y_L(\hat{\mathbf{r}})\tilde{g}_{L'}^a(\mathbf{r}) = \delta_{LL'} \tag{7.17}$$

In GPAW the radial functions are chosen as generalized Gaussian according to (here shown for $\mathbf{R}^a = 0$):

$$\tilde{g}_L^a(\mathbf{r}) = \tilde{g}_l^a(r)Y_L(\hat{\mathbf{r}}) \quad , \quad \tilde{g}_l^a(r) = \frac{1}{\sqrt{4\pi}}\frac{l!}{(2l+1)!}(4\alpha^a)^{l+3/2}r^l e^{-\alpha^a r^2} \tag{7.18}$$

where the atom-dependent decay factor α is chosen such that the charges are localized within the augmentation sphere.

With this choice of compensation charges, the tensors $N_{L_1 L_2}^a$ and the potential part of the $M_{i_1 i_2 L}^a$ tensors can be evaluated analytically, see [61].

The Core- and Smooth Core Densities

The core density follows directly from the all electron partial waves by

$$n_c(r) = \sum_i^{\text{core}} |\phi_i(\mathbf{r})|^2 = \sum_j^{\text{core}} 2(2l+1)|\phi_j(r)|^2/4\pi \tag{7.19}$$

The smooth core densities $\tilde{n}_c^a(\mathbf{r})$ are like the smooth partial waves expanded in a few (two or three) Bessel functions, Gaussians, polynomials or otherwise, fitted such that it matches the true core density smoothly at the cut-off radius.

The Localized Potential

An additional freedom in PAW is that for any operator $\widehat{L}$, localized within the augmentation spheres, we can exploit the identity (6.8)

$$\sum_i |\tilde{\phi}_i^a\rangle\langle\tilde{p}_i^a| = 1 \tag{7.20}$$

valid within the spheres, to get

$$\widehat{L} = \sum_a \sum_{i_1 i_2} |\tilde{p}_{i_1}^a\rangle\langle\tilde{\phi}_{i_1}^a|\widehat{L}|\tilde{\phi}_{i_2}^a\rangle\langle\tilde{p}_{i_2}^a|$$

so for any potential $\bar{v}(\mathbf{r}) = \sum_a \bar{v}^a(\mathbf{r}-\mathbf{R}^a)$ localized within the augmentation spheres (i.e. $\bar{v}^a(\mathbf{r}) = 0$ for $r > r_c^a$) we get the identity

$$0 = \int d\mathbf{r}\,\tilde{n}(\mathbf{r})\sum_a \bar{v}^a(\mathbf{r}) - \sum_a \int d\mathbf{r}\,\tilde{n}^a\bar{v}^a(\mathbf{r})$$

This expression can be used as an 'intelligent zero'. Using this, we can make the replacement of the smooth potential $\tilde{v}_s(\mathbf{r}) = u_H[\tilde{\rho}](\mathbf{r}) + v_{xc}[\tilde{n}](\mathbf{r}) \rightarrow \tilde{v}_s(\mathbf{r}) = u_H[\tilde{\rho}](\mathbf{r}) + v_{xc}[\tilde{n}](\mathbf{r}) + \bar{v}(\mathbf{r})$ if we also subtract $\int d\mathbf{r}\,\tilde{n}_c^a\bar{v}^a(\mathbf{r})$ from F^a and $\int d\mathbf{r}\,\tilde{\phi}_{i_1}^a\tilde{\phi}_{i_2}^a\bar{v}^a(\mathbf{r})$ from $I_{i_1 i_2}^a$. The advantage of doing this is that the Hartree potential and the xc-potential might not be optimally smooth close to the nuclei, but if we define the localized potential properly, the sum of the three potentials might still be smooth. Thus one can initially evaluate $u_H[\tilde{\rho}](\mathbf{r})$ and $v_{xc}[\tilde{n}](\mathbf{r})$ on an extra fine grid, add $\bar{v}(\mathbf{r})$ and then restrict the total potential to the coarse grid again before solving the KS equation.

The typical way of constructing the localized potentials $\bar{v}^a$ is by expanding it in some basis, and then choosing the coefficients such that the potential $u_H[\tilde{\rho}](\mathbf{r}) + v_{xc}[\tilde{n}](\mathbf{r}) + \bar{v}(\mathbf{r})$ is optimally smooth at the core for the reference system.

Inclusion of $\bar{v}^a(\mathbf{r})$ changes the forces on each atom in a trivial fashion.

Exact Exchange Components

The additional information required of a data set if exact exchange calculations are required are: 1) The core-core exchange energy contribution $E_{xx}^{a,\text{c-c}}$, which is calculated using the methods of section 7.1.2, restricting the state summations to the core orbitals only. 2) The matrix $X_{i_1 i_2}^a$ used to determine the valence-core contribution to the exchange energy. This can be determined by

$$\begin{aligned} X_{i_1 i_2}^a &= \sum_{i_c}^{\text{core}} \int\int \frac{\phi_{i_1}^a(\mathbf{r}')\phi_{i_c}^a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\phi_{i_2}^a(\mathbf{r})\phi_{i_c}^a(\mathbf{r})d\mathbf{r} \\ &= \sum_{i_c}^{\text{core}}\sum_L G_{L_1 L_c}^L G_{L_2 L_c}^L \frac{4\pi}{2l+1}\iint drdr'\frac{r_<^l}{r_>^{l+1}}u_{j_1}^a(r)u_{j_c}^a(r)u_{j_c}^a(r')u_{j_2}^a(r') \\ &= \sum_{j_c}^{\text{core}}\sum_l \frac{4\pi}{2l+1}\left(\sum_{mm_c}G_{L_1 L_c}^L G_{L_2 L_c}^L\right)\iint drdr'\frac{r_<^l}{r_>^{l+1}}u_{j_1}^a(r)u_{j_c}^a(r)u_{j_c}^a(r')u_{j_2}^a(r') \end{aligned} \tag{7.21}$$

The core-core exchange energy is only needed for total energy calculations; in energy differences it will disappear.

Summary

When constructing a data set for a specific atom, one must specify the following quantities, all defined within the augmentation spheres only:

1. ϕ_i^a from radial KS equation

2. $\tilde{\phi}_i^a$ by appropriate smooth continuation of ϕ_i^a

3. $\tilde{p}_i^a$ from equation (7.15)

4. $\tilde{g}_L^a$ localized within $r < r_c$, and satisfying $\int d\mathbf{r} r^{l'} \tilde{g}_L^a(\mathbf{r}) Y_{L'}(\widehat{\mathbf{r} - \mathbf{R}^a}) = \delta_{LL'}$

5. n_c^a follows from ϕ_i^a by (7.19)

6. $\tilde{n}_c^a$ by appropriate smooth continuation of n_c^a

7. $\bar{v}^a$ localized within $r < r_c^a$, otherwise freely chosen to make $\tilde{v}_s$ optimally smooth for the reference system

8. $X_{i_1 i_2}^a$ determined by (7.21)

The adjustable parameters besides the shape of $\tilde{\phi}^a$, $\tilde{g}_L^a$, $\bar{v}^a$, and $\tilde{n}_c^a$ are

1. Cut-off radii r_c^a

2. Frozen core states

3. Number of basis set functions (range of index i on ϕ_i^a, $\tilde{\phi}_i^a$, and $\tilde{p}_i^a$)

4. Energies of unbound partial waves

Choosing these parameters in such a way that the basis is sufficient for the description of all possible environments for the specific chemical element, while still ensuring a smooth pseudo wave function is a delicate procedure, although the optimal parameter choice is more stable than for e.g. norm conserving or ultra soft pseudopotentials.

Once the quantities above have been constructed, all other ingredients of the PAW transformation follows, such as Δ^a, $\Delta_{Lii'}^a$, A^a, $B_{i_1 i_2}^a$, and $C_{i_1 i_2 i_3 i_4}^a$, the first two are needed for the construction of the compensation charges and the overlap operator, and the last three for determining the Hamiltonian, and for evaluating the total energy.

Chapter 8

Numerical Results

The main analytic result of my work was the derivation of how to do hybrid HF-KS DFT calculations in the PAW formalism. Actually the expressions derived for the exact exchange energy functional and the non-local Fock operator are more general in the sense that they form the main ingredients of most exact exchange methods; the hybrid HF-KS method is simply the simplest to implement (and most widely used). This chapter focuses on the numerical results of the current implementation, sections 8.1 and 8.2, and on different numeric schemes for solving specific problems arising when trying to implement the method, section 8.3.

The tests of section 8.1 and 8.2 focus on total energy calculation using the EXX functional, which is the exchange-correlation functional, where correlation is neglected, and exchange is treated exactly. As the code currently doesn't support a self-consistent solution of the KS equation using the EXX functional, these are only calculated non-self-consistently, i.e. the EXX energy expression is evaluated using the orbitals obtained from doing a self-consistent calculation with some other functional (PBE in my case). This type of functional evaluation corresponds to a first order perturbation correction of the self-consistent xc-functional towards the EXX-functional, and should therefore produce sensible results.

8.1 Isolated Atoms

I have implemented the non-self-consistent evaluation of exact exchange in both the atomic all-electron calculator and the full PAW calculator of GPAW. The implementations follow the procedures described in section 6.7 for PAW, and section 7.1.2 for the atomic calculations.

A comparison of the two methods for 16 light atoms is shown in table 8.1. In both methods, the exchange energies are calculated on self-consistent PBE orbitals. The grid spacing of the PAW calculator is 0.16 Å, and the unit cell is a cube of side length 12.8 Å. Compensation charges are of s, p, and d type only. The atomic calculator treats the angular parts of the wave functions analytically, and the radial part is distributed on a radial grid, which extends to infinity, and has a very fine grid spacing near the nucleus. As the all-electron calculator can only treat spin compensated atoms, both calculations have been made spin unpolarized.

Note that in the PAW calculator, the core states are treated within the frozen core approximation (section 6.2). The different types of exchange interactions are therefor treated differently. The core-core energy is simply imported from the atomic calculator, which is why it is not shown on the table, the valence-core interaction is included by the multiplication of the density matrix with the X^a matrix (see section 6.7). The valence-valence interaction determined by making the exchange integral on a compensated exchange density $\tilde{n}_{n'n}(\mathbf{r}) + \sum_a \tilde{Z}^a_{n'n}(\mathbf{r})$, and adding some on-site correction $\Delta E^{a,\text{v-v}}_x$. In the atomic calculator, there is no difference in the treatment of the valence and core states, the division is merely to ease comparison of the methods.

The table shows excellent agreement between the two methods, with a maximum error of 0.4 eV for fluorine. This discrepancy is acceptable for total energy calculations, which are much harder

	Atomic calculator			PAW			
Sym.	All	val-val	val-core	All	val-val	val-core	$\Delta E_x^{a,\text{v-v}}$
H	3.9	3.9	-	3.9	3.9	-	-0.0
He	27.6	27.6	-	27.7	27.7	-	0.8
Li	46.5	1.6	0.5	46.5	1.6	0.5	0.0
Be	72.4	9.5	1.7	72.4	9.5	1.7	0.0
C	126.5	27.4	4.3	126.6	27.4	4.4	0.1
N	162.7	44.8	6.2	162.7	44.8	6.2	0.0
O	207.1	70.2	8.4	207.3	70.2	8.6	-0.4
F	261.7	105.3	11.0	262.1	105.4	11.3	-1.1
Ne	328.0	151.9	14.0	328.6	152.3	14.1	9.3
Na	378.9	1.5	0.7	378.9	1.5	0.7	0.0
Mg	434.8	7.8	2.3	434.8	7.8	2.3	0.0
Al	488.6	12.1	4.2	488.5	12.1	4.1	0.0
Si	545.5	19.1	6.6	545.4	19.1	6.5	0.1
P	606.5	29.7	9.7	606.5	29.7	9.7	0.1
S	672.6	44.9	13.5	672.6	44.8	13.5	0.2
Cl	744.5	65.3	17.8	744.4	65.3	17.7	0.4

Table 8.1: *Exact exchange energies of isolated atoms in eV calculated non-self-consistently using PBE orbitals. Contributions to the exchange energies are separated into valence-valence (val-val), valence-core (val-core), and core-core (included in 'all') contributions. The last column shows the on-site PAW corrections to the valence-valence part $\Delta E_x^{a,v\text{-}v}$ explicitly.*

to converge than energy differences. It is also seen that the PAW correction $\Delta E_x^{a,\text{v-v}}$ can be of considerable size; 9.3 eV for neon. This does not mean that it is necessarily important in bonding, i.e. it might remain unchanged despite the formation of bonds.
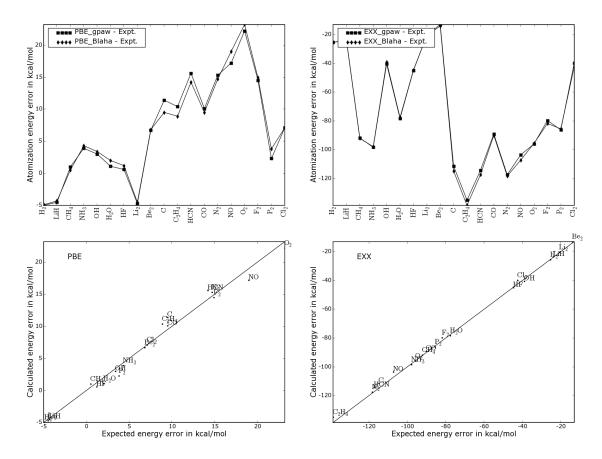
8.2   Molecules

In the article [28] by Blaha, Kurth, and Perdew, they report the atomization energy of 20 small molecules evaluated self-consistently using PBE xc-functional, and for a range of other functionals, including EXX, evaluated non-self-consistently with the PBE orbitals. This database serves as a benchmark for my implementation of exact exchange.

The atomization energies from [28] and those calculated in GPAW are compared in table 8.2. The test results have also been compiled graphically on figures 8.1 and 8.2. All values are in kcal/mol[1]. The GPAW calculations have been done with a $14 \times 12 \times 12$ Å unit cell, a grid spacing of 0.175 Å, and compensation charges have been included up to d type harmonics.

These calculations were all done with the setup files used in GPAW in February 2006. Redoing the calculations with the current setup files (calculated in May 2006), the mean absolute error of the PBE calculation (compared to Blaha) increased to 1.4 kcal/mol, and EXX increased to 3.0 kcal/mol, i.e. both increased by approximately a factor of two compared to the old setup files. This demonstrates that the remaining discrepancy is well within the uncertainty caused by the setup files. Figure 8.2 shows that the errors of the PBE calculations and the EXX calculations are highly correlated, indicating that the error might be dominated by errors in the kinetic- or Hartree energy terms.

It is important to take notice of the last column of table 8.2 showing the valence-valence contribution to the exchange energy only. Remember that the purpose of going throug all the added comlexity of the PAW method is that other pseudopotential methods doesn't have access to the core orbitals, making the valence-core part of exact exchange inaccessible. The table shows

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[1]Conversions factors are: 1 eV = 23.06 kcal/mol and 1 kcal/mol = 43.36 meV

Figure 8.1: *Comparison of results from Blaha* et al. *[28] and GPAW result for self-consistent PBE atomization energies (left) and perturbative (using PBE orbitals) EXX atomization energies (right). All values are relative to experimental data and measured in kcal/mol.*
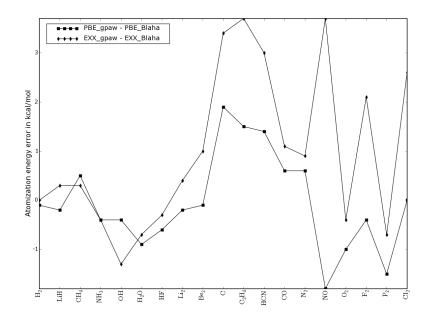

Figure 8.2: *Direct comparison of the Blaha and GPAW atomization energies.*

	Self-consistent PBE		Perturbative EXX		
Mol.	BLAHA	GPAW	BLAHA	GPAW	v-v only
H_2	104.6	104.5	84.0	84.0	84.0
LiH	53.5	53.3	33.9	34.2	30.4
CH_4	419.8	420.3	327.2	327.5	331.1
NH_3	301.7	301.3	199.5	199.1	203.4
OH	109.8	109.4	67.3	66.0	67.5
H_2O	234.2	233.3	154.6	153.9	156.4
HF	142.0	141.4	96.1	95.8	96.8
Li_2	19.9	19.7	3.5	3.9	-1.0
Be_2	9.8	9.7	-11.0	-10.0	-6.9
C_2H_2	414.9	416.8	290.6	294.0	293.7
C_2H_4	571.5	573.0	423.9	427.6	433.0
HCN	326.1	327.5	194.5	197.5	195.0
CO	268.8	269.4	169.2	170.3	165.9
N_2	243.2	243.8	110.2	111.1	107.0
NO	171.9	170.1	45.6	49.3	50.3
O_2	143.7	142.7	24.9	24.5	25.8
F_2	53.4	53.0	-43.3	-41.2	-40.8
P_2	121.1	119.6	31.8	31.1	16.5
Cl_2	65.1	65.1	15.5	18.1	19.5
MAE	-	0.7	-	1.4	3.6

Table 8.2: *Comparison of results from Blaha* et al. *[28] and GPAW result for self-consistent PBE atomization energies (left) and perturbative (using PBE orbitals) EXX atomization energies (right). All values are in kcal/mol. MAE is the mean absolute error of the GPAW results compared to Blaha.*

that this part is important for the correct description of exact exchange. For P_2, the valence-valence exchange energy difference is off by almost 14 kcal/mol compared to the total exchange difference. This is the justification for all the work done in section 6.

In reference [36], by Paier, Hirschl, Marsman, and Kresse, they have performed calculations on the G2-1 data set, and found that introducing 25% exact exchange in the PBE functional (i.e. using the PBE0 functional), reduces the mean absoloute error compared to experimental atomization energies from 8.4 to 3.7 kcal/mol.[2] These results are all determined with self-consistent calculations, and full geometry optimization. To see if any improvement over PBE can be achieved by evaluating exact exchange non-self-consistently, I have tabulated the data shown in table 8.3. These have been calculated with the new setup files of slightly reduced quality.

The table clearly shows that including 100% exact exchange, and neglecting correlation (the EXX functional) is a very bad idea, and also that PBE0 evaluated non self-consistently on average doesn't make any improvement on the PBE results (on the contrary the MAE is increased from 8.2 to 8.5 kcal/mol).

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[2]These values have also been compared to calculations done in GAUSSIAN. The two programs agree within 0.5 kcal/mol on average, and has a max deviation of 1.5 kcal/mol.

Mol	Expt	LDA	PBE*	revPBE	RPBE	PBE0	EXX
H_2	109.5	113.2	104.6	105.5	105.5	105.1	84.0
LiH	57.8	62.1	54.8	54.4	54.7	53.5	34.7
CH_4	419.3	462.9	420.6	412.2	411.3	411.3	325.2
NH_3	297.4	338.1	302.7	294.8	294.0	289.3	198.6
H_2O	232.2	265.0	232.8	226.1	225.2	219.7	150.4
HF	140.8	159.6	139.6	135.7	135.0	130.7	91.1
Li_2	24.4	24.1	20.4	19.7	20.7	19.1	3.9
LiF	138.9	152.9	136.2	130.6	130.8	122.4	77.5
Be_2	3.0	13.6	10.6	8.7	8.7	4.9	-12.9
C_2H_2	405.4	462.2	417.2	404.0	402.5	395.3	287.9
C_2H_4	562.6	634.1	573.4	557.9	556.2	551.7	418.9
HCN	311.9	362.8	328.4	317.0	315.7	303.1	191.8
CO	259.3	297.9	268.1	258.4	257.1	246.0	164.2
N_2	228.5	268.5	244.8	235.0	234.0	218.1	108.5
O_2	120.5	173.4	142.5	133.3	132.0	114.7	19.6
F_2	38.5	77.8	53.1	46.1	45.2	28.4	-46.5
P_2	117.3	146.0	123.3	117.2	116.4	107.5	30.7
Cl_2	58.0	85.4	67.5	62.1	61.4	55.9	11.8
MAE	-	31.9	8.2	5.0	5.1	8.5	77.0

Table 8.3: *Atomization energies in kcal/mol for a self number of functionals. * indicates that the PBE functional has been evaluated self-consistently; all other functionals are evaluated using PBE densities. The unit cell is a cube of side length 21.8 Å, grid-spacing is 0.16 Å, max angular momentum of compensation charges is lmax = 2.*

8.3   Miscellaneous

In addition to the implementation of the non-self-consistent evaluation of exact exchange, I have done the following work:

Parallel implementation
 To support calculations on large systems, I have designed the code to work in parallel computations. I have some test results, but they are not interesting, as they just show that the parallel calculations gives the same results as serial calculations.

Wannier functions
 The computational time of exact exchange evaluation scales quadratically with the number of bands, which makes it the limiting factor for most systems. To avoid this, I have made a version of the code, which makes the rotation of the KS functions into the localized Wannier function, as described in appendix B. The locality of the Wannier functions can then be used to skip evaluation of exchange terms, for which the overlap is known to be (practical) zero. The transformation to Wannier functions and subsequent evaluation of the exchange integrals works without complaint, giving almost exact identical results to the KS orbital based code, but I have not yet implemented the part to exploit the locality of the basis. The problems are that a) the success of the localization procedure is hard to predict. The localization process does output a center and a measure of the spread of the resulting Wannier functions, but determining a safe cut-off distance from these is not trivial. b) the actual construction of the Wannier functions is quite time-consuming, defeating the entire purpose for all but the largest of systems.

Different Poisson solvers
 The Poisson solver in GPAW can not handle charged densities. This is usually not a problem when doing calculations on neutral systems, but when evaluating exact exchange in PAW, we need to determine the potential (6.77) of the exchange density $\tilde{n}_{n'n}(\mathbf{r}) + \sum_a \tilde{Z}^a_{n'n}(\mathbf{r})$, which has unit total charge for the diagonal $n = n'$ terms, regardless of the total charge of the considered system. The different methods I implemented to handle this problem are discussed and tested in section 8.3.1.

Spherical harmonics
 One could suspect that the product $\phi_n(\mathbf{r})\phi_{n'}(\mathbf{r})$ has more angular features than $n(\mathbf{r}) = \sum_n |\phi_n(\mathbf{r})|^2$, thus making higher order components of the exchange compensation charges $\tilde{Z}_{nn'}$ required than for the standard compensation charges $\tilde{Z}$. Going to higher orders was not possible in GPAW as the first few spherical harmonics where simply hard-coded into the program. Spherical harmonics has many potential uses in the code, for example for making multipole expansions of the density, such that the BC's of the real-space Poisson solver can be correctly determined (in stead of the Dirichlet conditions currently enforced). Spherical harmonics are also needed to make higher order Gaussian neutralization of charged densities, as will be described in section 8.3.1.

 All in all, I decided to write some code for automatically generating arbitrary spherical harmonics. The recurrence relations needed for generating spherical harmonics in polar coordinates are quite standard, but when they are needed in Cartesian form, this requires a subsequent translation of the coordinates. To avoid this, I rewrote the standard recurrence relations to generate the harmonics in Cartesian form directly. The equations and tests of the program can be found in appendix D.3.

Time Scalings

An important aspect of exact exchange, and one of the things that prevents its widespread use, is the computational cost of the evaluation. The double sum over states, and the solution of a

Poisson equation implies that calculating the exchange potential scales like

$$(n_{\text{bands}} N_k)^2 N_{\text{grid-points}} \ln N_{\text{grid-points}}$$

assuming an FFT Poisson solver.

In my non-self-consistent evaluations, the exact exchange part only takes up to 10% of the total time. According to J. Paier, who implemented a self-consistent evaluation in VASP, including exact exchange in a DFT calculation takes between 50 and 100 times more time than standard GGA evaluations. This obviously depends on the size of the system, being worse for larger systems.

8.3.1 The Poisson Equation

In general, the potential $v(\mathbf{r})$ associated with the density $n(\mathbf{r})$, is defined by:

$$v(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{8.1}$$

which is the solution of the Poisson equation

$$\nabla^2 v(\mathbf{r}) = -4\pi n(\mathbf{r}) \tag{8.2}$$

The divergence as $\mathbf{r} \to \mathbf{r}'$ of the integrand in (8.1) makes it hard to handle numerically, so solving (8.2) is usually preferable. This can either be done directly in real space, or it can be done in reciprocal space.

Reciprocal Space

The Fourier transform of (8.2) is (my convention for the Fourier transform is summarized in appendix C)

$$-k^2 v(\mathbf{k}) = -4\pi n(\mathbf{k}) \tag{8.3}$$

thus the potential can be determined from

$$v(\mathbf{k}) = 4\pi n(\mathbf{k})/k^2 \tag{8.4}$$

If one works in real space, the procedure requires a Fourier transform of the density, a division, and an inverse Fourier transform of the potential back to real space. With the Fast Fourier Transform (FFT) the Fourier transformation is only an order $N \log N$ operation, so this is much faster than making the integration for each grid point, which costs N^2 flops (N for the integration times N grid-points).

For the evaluation of energies, we often encounter the Coulomb integrals

$$(n_1 | n_2) = \iint d\mathbf{r} d\mathbf{r}' \, \frac{n_1^*(\mathbf{r}) n_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r} \, n_1^*(\mathbf{r}) v_2(\mathbf{r}) \tag{8.5}$$

where v_2 is the potential of n_2.

Inserting the Fourier transform of $n_1(\mathbf{r})$ and $v_2(\mathbf{r})$ in this expression, we get the particularly simple expression:

$$\begin{aligned}
(n_1 | n_2) &= \int d\mathbf{r} \, n_1^*(\mathbf{r}) v_2(\mathbf{r}) \\
&= \int d\mathbf{r} \int \frac{d\mathbf{k}}{(2\pi)^3} n_1^*(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} \int \frac{d\mathbf{k}'}{(2\pi)^3} \frac{4\pi n(\mathbf{k}')}{\mathbf{k}'^2} e^{i\mathbf{k}'\cdot\mathbf{r}} \\
&= 4\pi \iint \frac{d\mathbf{k} d\mathbf{k}'}{(2\pi)^6} \frac{n_1^*(\mathbf{k}) n_2(\mathbf{k}')}{\mathbf{k}'^2} \int d\mathbf{r} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \\
&= 4\pi \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{n_1^*(\mathbf{k}) n_2(\mathbf{k})}{\mathbf{k}^2}
\end{aligned} \tag{8.6}$$

Or in the discrete case[3]

$$(n_1|n_2) = \frac{4\pi}{V} \sum_{\mathbf{k}} \frac{n_{1,\mathbf{k}}^* n_{2,\mathbf{k}}}{k^2} \tag{8.7}$$

So we do not have to transform back to real space, and the double integration of (8.5) is replaced by a single integration.

There are two problems with solving the Poisson equation in reciprocal space: a) The enforcement of periodic boundary conditions, which is a problem if the original density was isolated in space, in which case the FFT produce erroneous interactions with the periodically repeated images of the original densities. b) The division by k^2, which is a problem if the density has a non-zero total charge, since $n(\mathbf{k} = \mathbf{0}) = \int d\mathbf{r} n(\mathbf{r})$.

The following two sections describes two different techniques for solving these problems, which have both been implemented and tested for performance.

The Tuckerman Trick

The first technique is due to Tuckerman [62], and is designed for the reciprocal space approach to the Poisson equation.

Consider for simplicity a cubic unit cell of side length L. Figure 8.3 shows a sketch of the system in 1D, including the artificially repeated images of the density. If we know that the density
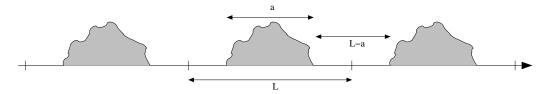

Figure 8.3: *1D sketch of the Tuckerman problem.*

is localized within a sphere of diameter a, we can write the potential as

$$v_T(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}') \phi(|\mathbf{r} - \mathbf{r}'|) \tag{8.8}$$

where $\phi(\mathbf{r})$ is a truncated Coulomb kernel

$$\phi(r) = \begin{cases} 1/r & , r < r_c \\ 0 & , r \geq r_c \end{cases} \tag{8.9}$$

with a cut-off radius r_c satisfying $a < r_c < L - a$, see figure 8.3. From this, it follows that $a < L/2$, i.e. the unit cell must be at least twice as big as the extent of the density. Making a Fourier transform of this potential we get

$$\int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot \mathbf{r}} v_T(\mathbf{k}) = \int d\mathbf{r}' \int \frac{d\mathbf{k}'}{(2\pi)^3} e^{i\mathbf{k}' \cdot \mathbf{r}'} n(\mathbf{k}) \phi(|\mathbf{r} - \mathbf{r}'|)$$
$$= \int \frac{d\mathbf{k}'}{(2\pi)^3} e^{i\mathbf{k}' \cdot \mathbf{r}} n(\mathbf{k}') \int d\mathbf{r}'' \, e^{i\mathbf{k}' \cdot \mathbf{r}''} \phi(r'') \tag{8.10}$$

where $\mathbf{r}'' = \mathbf{r}' - \mathbf{r}$. From this we see that the potential in reciprocal space is

$$v_T(\mathbf{k}) = 2\pi n(\mathbf{k}) \int_0^{r_c} r d\mathbf{r} \int_0^\pi \sin\theta d\theta e^{ikr\cos\theta}$$
$$= 4\pi n(\mathbf{k}) \int_{r=0}^{r_c} d\mathbf{r} \cos(kr)/k \tag{8.11}$$
$$= \frac{4\pi n(\mathbf{k})}{k^2}(1 - \cos(kr_c))$$

---

[3]In a numerical Fourier transform, e.g. FFT, eq. (C.4) has a prefactor $1/N^3$ instead of $1/V$, thus (8.7) would read $(n_1|n_2) = \frac{4\pi V}{N^6} \sum_{\mathbf{k}} n_{1,\mathbf{k}}^* n_{2,\mathbf{k}}/k^2$

And the expression for the Coulomb integral becomes

$$(n_1|n_2) = 4\pi \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{n_1^*(\mathbf{k})n_2(\mathbf{k})}{\mathbf{k}^2}(1 - \cos(kr_c)) \tag{8.12}$$

The Tuckerman potential does not suffer from the divergence at $\mathbf{k} = 0$ as:

$$\lim_{\mathbf{k}\to 0} v_T(\mathbf{k}) = 2\pi r_c^2 \tag{8.13}$$

Thus both the problem with non charge-neutral densities, and with the artificial interactions with periodic images are avoided. The cure however is rather expensive, as the unit-cell must be twice as big as the extend of the density in all three dimensions.

Gaussian neutralization

Another way of coping with the non-zero total charge, is to just subtract a density of the same total charge as the original, but with a a well known potential, and then add this afterward. Take for example the Gaussian density distribution (of unit total charge) described by

$$n_g(\mathbf{r}) = \left(\frac{a}{\pi}\right)^{3/2} e^{-ar^2}, \qquad n_g(\mathbf{k}) = e^{-k^2/4a} \tag{8.14}$$

with the potential

$$v_g(\mathbf{r}) = \frac{\text{erf}(\sqrt{a}r)}{r}, \qquad v_g(\mathbf{k}) = \frac{4\pi}{k^2}e^{-k^2/4a} \tag{8.15}$$

To determine the potential of a density n with total charge Z, we can then calculate

$$v[n](\mathbf{r}) = v[n - Zn_g](\mathbf{r}) + Zv_g(\mathbf{r}) \tag{8.16}$$

where $v[n](\mathbf{r})$ is the potential of the density n.

To do a symmetric neutralization of both densities in a Coulomb integral, one could do

$$(n_1|n_2) = (n_1 - Z_1 n_g|n_2 - Z_2 n_g) + (Z_2^* n_1 + Z_1 n_2^* - Z_1^* Z_2 n_g|n_g) \tag{8.17}$$

This procedure solves the problem with non-zero total charge, but there can still be artificial interactions from higher order moments (than the monopole) with the periodic images. To take care of these, one could simply proceed with subtracting generalized gaussians of higher order:

$$v[n](\mathbf{r}) = v\left[n - \sum_L Q_L g_L(\mathbf{r})\right](\mathbf{r}) + \sum_L Q_L v_L(\mathbf{r}) \tag{8.18}$$

where Q_L are the multipole moments of n, g_L are generalized gaussians, and v_L are the potential of the gaussians (7.18), can be determined analytically in terms of Whittaker functions. These proved difficult to implement,as they satisfied quite complicated recursion relations.

This method is applicable to both real and reciprocal space solvers. Presently I only neutralize the monopole.

Real Space

In principle densities of non-zero total charge is not a problem when solving the Poisson equation by some real-space differential equation solver. The specific choice of solver used in GPAW however can not handle charged systems, so when using the real space solver, I neutralize the density using gaussians, as explained in the previous paragraph.

A different problem in real space is that if one applies Dirichlet BC's, the potential must be completely localized within the unit cell to be described properly. Alternatively, one could do a multipole expansion of the density, as described in appendix D.2, and then apply the correct BC's. In this case only the density itself should be completely contained within the unit cell, for the potential to be described correctly.

Periodic Systems

All the procedures described above for handling charged systems, involved isolated systems. Of course charged systems does not make sense if it is periodically repeated, as this would imply an infinite total charge. On the other hand, the densities of the exchange potential (6.77) has a non-zero charge for diagonal terms of the summation ($n = n'$) independently of the choice of BC's. How this should be handled is still an unsolved problem in my code. Many papers discuss the problem of charged systems in a periodic cell, but most seem to base their ideas on the periodic boundary conditions being artificial, i.e. that in reality the charged system is isolated and one should just correct the error of applying periodic BC's.

Test of Different Poisson Approaches

To test my different Coulomb energy calculators, I have applied them to the the electron density of the Hydrogen atom, i.e. the square of the $1s$ wave function

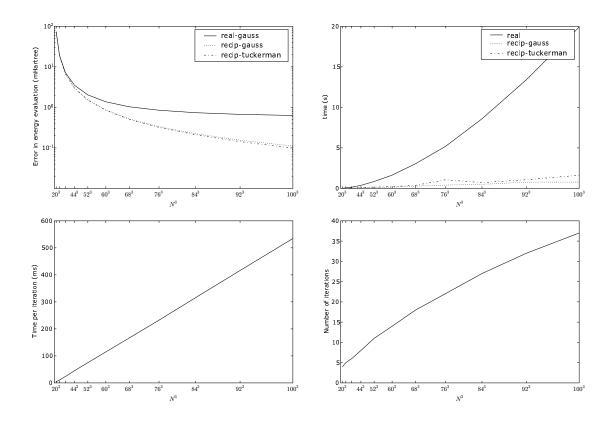$$n_{1s}(\mathbf{r}) = \frac{1}{\pi} e^{-2r} \tag{8.19}$$

for which the Hartree energy can be calculated analytically

$$U_H[n_{1s}] = \frac{1}{2}((n_{1s})) = \frac{5}{16} = 0.3125 \text{Ha} \tag{8.20}$$

or equivalently, the exact exchange energy -5/16 Ha (for one electron systems the potential and the energy of the Hartree and Exchange functionals are equal but of opposite sign). This model system has both a non-zero total charge, and a slowly decaying density. It also has a cusp at the origin, which makes it difficult to resolve using uniform grids. The results are shown in figure 8.4 The upper left figure shows the convergence of the Hartree energy with respect to the number of grid-points, using the three different methods: 1) Real space, neutralized with a Gaussian 2) Solved in reciprocal space with a Gaussian neutralization and 3) Integrated in reciprocal space using the Tuckerman trick. It is seen that all methods converge almost exponentially to within 3 mHartree at $44^3 = 85184$ grid-points. After that not much accuracy can be gained, especially not for the real-space solver.

The upper right figure compares the computational cost of the three methods. The real-space solver determines the potential by an iterative approach. It is seen that the real-space method scales quadratically with the total number of grid-points (the time per iteration (bottom left) increases linearly, and the number of iterations required for the Poisson solver to converge (bottom right) scales approximately linear with the number of grid-points). The two **k**-space methods scale almost linearly ($N \log N$) with the grid-points, the Gaussian neutralization being slightly faster than the Tuckerman procedure (presumably due to the evaluation of the cosine function in (8.11)). The size of the unit cell is 20 Bohr.

It seems that solving the Poisson equation in reciprocal space, using a gaussian neutralization is the best choice, so this is the method I use for all serial calculations. When running the code in parallel, I use the real-space solver, as this is the only one that works in parallel presently.

Figure 8.4: *Top: Convergence of the Hartree energy of Hydrogen (left) and time scaling (right) for 3 different poisson approaches.*
Bottom: Timings of the real-space poisson solver. Time per iteration of the solver (left), and number of iterations as a function of the number of grid-points (right). Unit cell size: 20 Bohr for all calculations.

Chapter 9

Conclusion

Several tests show that inclusion of exact exchange in density functional calculations improves atomization energies of molecules, the HOMO-LUMO band gaps of the Kohn-Sham orbitals, the cohesive energies of solids etc to a large degree, and so seems to be an important step towards reaching chemical accuracy in the predicted values of DFT. There are also theoretical arguments why exchange should be treated exactly, among other things, exact exchange removes the spurious self-interaction of the Hartree potential, and has the correct $1/r$ asymptotic behavior required for the existence of a Rydberg series. Unfortunately including non-local contributions in the exchange energy, is incompatible with local approximations of the correlation energy, as the supposed long range cancellation can not be achieved. This incompatibility is sought solved by a) including only a fraction of exact exchange, or b) screen the Coulomb kernel of exact exchange c) devise new (non-local) correlation functionals compatible with non-local exact exchange.

The subject of implementing exact exchange in PAW had, at the start of my project, not been studied in literature. There has however recently been published a paper by Paier *et al.* [36], on the subject. Although they use the formulation of PAW by Joubert and Kresse, [58], their final equations seems to be equivalent to mine. They have made a self-consistent implementation of the hybrid HF-KS method, and the results demonstrated in the paper shows promise for the application of the method. Specifically they show consistent results with existing all-electron implementations of exact exchange. They get an agreement in atomization energies of less than 1 kcal/mol of their plane wave based PAW program VASP compared to GAUSSIAN which is an all electron method using a localized basis set. That PAW calculations can compare this well with all electron methods is encouraging, as the computational speed-up of using PAW is very high.

I have made an implementation of exact exchange in the GPAW program, which currently supports non-self-consistent EXX evaluations for isolated systems. Testing the code shows that it performs well. I have made all the derivations necessary for a self-consistent implementation of e.g. hybrid HF-KS or a number of other exchange methods. The only part missing is the actual implementation.

Future work includes making the code work for periodic systems, finishing the implementation of the self-consistent hybrid HF-KS scheme, including other exact exchange methods like KLI, LHF, and OEP, which are all procedures for localizing the non-local HF potential (in the sense of making it multiplicative; the resulting potential is still non-local in the sense that it depends on the global structure of the density) and to introduce screened exchange, which is just a screening of the coulomb kernel of the exact exchange expression, making it more compatible with local correlation approximations.

One should note that the purpose of going through all the added complexity of the PAW method is that it is much faster than traditional all electron methods, and exact exchange is inaccessible in other pseudopotential methods, as it requires access to the core orbitals.

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Appendix A

Exact Exchange

The non-interacting system is described by the Hamiltonian

$$H_0 = \sum_\nu \epsilon_\nu c_\nu^\dagger c_\nu \tag{A.1}$$

where $c_\nu^\dagger$ and c_ν is the creation and annihilation operator respectively, indicating the creation/annihilation of a particle in the single particle state ν.

The eigenstates of the Hamiltonian is a Slater determinant denoted by $|n_1 n_2 n_3 \ldots\rangle$, where n_ν is the occupation of the single particle state ν. The occupations n_ν can take the values 0 or 1, and we keep the number of particles fixed, i.e. $\sum_\nu n_\nu = N$. $\sum_{\{n_\nu\}}$ Will be used to indicate the infinite sum over all possible slater determinants, i.e. all exited states of the N particle non-interacting system. I.e.

$$\sum_{\{n_\nu\}} = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \sum_{n_3=0}^1 \cdots$$

The Coulomb interaction is included as a perturbation to H_0

$$H = H_0 + V_{int} \tag{A.2}$$

where V_{int} in the first quantization is:

$$V_{int} = \frac{1}{2} \sum_{i \neq j} v(\mathbf{r}_i - \mathbf{r}_j) \tag{A.3}$$

and in second quantization:

$$V_{int} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta,\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma \tag{A.4}$$

where

$$v_{\alpha\beta,\gamma\delta} = \iint d\mathbf{r} d\mathbf{r}' \phi_\alpha^*(\mathbf{r}) \phi_\beta^*(\mathbf{r}') v(|\mathbf{r} - \mathbf{r}'|) \phi_\gamma(\mathbf{r}) \phi_\delta(\mathbf{r}') \tag{A.5}$$

and $v(|\mathbf{r} - \mathbf{r}'|) = 1/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb kernel.

To determine expectation values, we need the density matrix

$$\rho_0 = e^{-\beta H_0} \tag{A.6}$$

with $\beta = 1/k_B T$, and we need the partition function

$$
\begin{aligned}
Z_0 &= \mathrm{Tr}\,\rho_0 \\
&= \sum_{\{n_\nu\}} \langle n_1 n_2 \ldots | e^{-\beta \sum_\nu \epsilon_\nu c_\nu^\dagger c_\nu} | n_1 n_2 \ldots \rangle \\
&= \sum_{\{n_\nu\}} \prod_\nu e^{-\beta \epsilon_\nu n_\nu} \\
&= \prod_\nu \left(1 + e^{-\beta \epsilon_\nu} \right)
\end{aligned}
\tag{A.7}
$$

where n_ν is the occupation of state ν.
We can now determine

$$
\begin{aligned}
\langle V_{int} \rangle_0 &= \frac{1}{Z_0} \mathrm{Tr}[\rho_0 V_{int}] \\
&= \frac{1}{Z_0} \sum_{\{n_\nu\}} \langle n_1 n_2 \ldots | e^{-\beta \sum_\nu \epsilon_\nu c_\nu^\dagger c_\nu} \frac{1}{2} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta,\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma | n_1 n_2 \ldots \rangle \\
&= \frac{1}{2 Z_0} \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta,\gamma\delta} \sum_{\{n_\nu\}} \langle n_1 n_2 \ldots | c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma | n_1 n_2 \ldots \rangle \prod_\nu e^{-\beta \epsilon_\nu n_\nu}
\end{aligned}
\tag{A.8}
$$

using wicks theorem, we see that $\langle n_1 n_2 \ldots | c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma | n_1 n_2 \ldots \rangle = n_\alpha n_\beta (\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})$

$$
\begin{aligned}
\langle V_{int} \rangle_0 &= \frac{1}{2 Z_0} \sum_{\alpha\beta} \sum_{\{n_\nu\}} n_\alpha n_\beta \left[v_{\alpha\beta,\alpha\beta} - v_{\alpha\beta,\beta\alpha} \right] \prod_\nu e^{-\beta \epsilon_\nu n_\nu} \\
&= \frac{1}{2} \sum_{\alpha\beta} \left[v_{\alpha\beta,\alpha\beta} - v_{\alpha\beta,\beta\alpha} \right] e^{-\beta \epsilon_\alpha} e^{-\beta \epsilon_\beta} \frac{\prod_{\nu \neq \alpha,\beta} \left(1 + e^{-\beta \epsilon_\nu} \right)}{\prod_\nu \left(1 + e^{-\beta \epsilon_\nu} \right)} \\
&= \frac{1}{2} \sum_{\alpha\beta} \left[v_{\alpha\beta,\alpha\beta} - v_{\alpha\beta,\beta\alpha} \right] e^{-\beta \epsilon_\alpha} \underbrace{\frac{e^{-\beta \epsilon_\alpha}}{1 + e^{-\beta \epsilon_\alpha}}}_{f_\alpha} \underbrace{\frac{e^{-\beta \epsilon_\beta}}{1 + e^{-\beta \epsilon_\beta}}}_{f_\beta} \\
&= \frac{1}{2} \sum_{\alpha\beta} f_\alpha f_\beta \left[v_{\alpha\beta,\alpha\beta} - v_{\alpha\beta,\beta\alpha} \right]
\end{aligned}
\tag{A.9}
$$

where we have identified the Fermi distributions f. Inserting eq. (A.5) we see that:

$$
\begin{aligned}
\langle V_{int} \rangle_0 &= \frac{1}{2} \sum_{\alpha\beta} f_\alpha f_\beta \iint d\mathbf{r} d\mathbf{r}' \left[\frac{\phi_\alpha^*(\mathbf{r}) \phi_\beta^*(\mathbf{r}') \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\phi_\alpha^*(\mathbf{r}) \phi_\beta^*(\mathbf{r}') \phi_\beta(\mathbf{r}) \phi_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \\
&= \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\left[\sum_\alpha f_\alpha |\phi_\alpha(\mathbf{r})|^2 \right] \left[\sum_\beta f_\beta |\phi_\beta(\mathbf{r}')|^2 \right]}{|\mathbf{r} - \mathbf{r}'|} \\
&\quad - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{|\sum_\alpha f_\alpha \phi_\alpha^*(\mathbf{r}) \phi_\alpha(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \\
&= U_H + E_x
\end{aligned}
\tag{A.10}
$$

Appendix B

Wannier Functions and Exact Exchange

Although the Bloch representation is very advantageous for the actual calculations of the eigenstate of a single particle Hamiltonian, it is not necessarily well suited for other purposes, such as visualization, interpretation and tight-binding approximations, for which localized states are more convenient. Therefore a suitable (unitary) transformation of the Bloch states, subsequent to using these for solving the appropriate Schrödinger equation, is often applied.

For a crystal of N_k lattice point, or equivalently a Monkhorst-Pack sampling of the Brillouin zone with a total of N_k **k**-points, the Wannier transformation is defined by

$$w_{n\mathbf{R}} = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{\mathbf{k}nm} \psi_{m\mathbf{k}} \tag{B.1}$$

To get the inverse transformation, we multiply by $\sum_{\mathbf{R}} \exp(i\mathbf{k}'\cdot\mathbf{R})/\sqrt{N_k}$ on both sides

$$\frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}} e^{i\mathbf{k}'\cdot\mathbf{R}} w_{n\mathbf{R}} = \sum_{\mathbf{k}} \underbrace{\frac{1}{N_k} \sum_{\mathbf{R}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}}}_{\delta_{\mathbf{kk}'}} \sum_m U_{\mathbf{k}nm} \psi_{m\mathbf{k}} = \sum_m U_{\mathbf{k}'nm} \psi_{m\mathbf{k}'} \tag{B.2}$$

and multiplying by $\sum_n U_{\mathbf{k}'nl}^*$ we get

$$\sum_n U_{\mathbf{k}'nl}^* \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}} e^{i\mathbf{k}'\cdot\mathbf{R}} w_{n\mathbf{R}} = \sum_m \underbrace{\sum_n U_{\mathbf{k}'nl}^* U_{\mathbf{k}'nm}}_{\delta_{lm}} \psi_{m\mathbf{k}'} = \psi_{l\mathbf{k}'} \tag{B.3}$$

where it has been used that **U** is unitary, i.e. $\mathbf{U}\cdot\mathbf{U}^\dagger = \mathbf{1} \Rightarrow \sum_\delta U_{\alpha\delta} U_{\beta\delta}^* = \delta_{\alpha\beta}$.

From this, we get the inverse rotation

$$\psi_{n\mathbf{k}} = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{\mathbf{k}mn}^* w_{m\mathbf{R}} \tag{B.4}$$

The Wannier functions have a very useful translational symmetry. This is seen by using that $\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})\psi_{n\mathbf{k}}(\mathbf{r})$, to get

$$\begin{aligned}
w_{n\mathbf{R}}(\mathbf{r}) &= \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{\mathbf{k}nm} \psi_{m\mathbf{k}}(\mathbf{r}) \\
&= \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{\mathbf{k}nm} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{m\mathbf{k}}(\mathbf{r}-\mathbf{R}) \\
&= w_{n\mathbf{0}}(\mathbf{r}-\mathbf{R})
\end{aligned} \tag{B.5}$$

Exact Exchange

To determine the expression for exact exchange in terms of Wannier functions, the inverse transformation is applied to the standard expression

$$
\begin{aligned}
E_{xx} &= -\frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} \sum_{nm} f_n f_m ((\psi_{n\mathbf{k}}^* \psi_{m\mathbf{k}'})) \\
&= -\frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} \sum_{nm} f_n f_m (\psi_{n\mathbf{k}}^* \psi_{m\mathbf{k}'} | \psi_{n\mathbf{k}}^* \psi_{m\mathbf{k}'}) \\
&= -\frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} \sum_{nm} f_n f_m \left(\frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_\alpha} \sum_\alpha U_{\mathbf{k}\alpha n} w_{\alpha\mathbf{R}_\alpha}^* \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_\beta} e^{i\mathbf{k}'\cdot\mathbf{R}_\beta} \sum_\beta U_{\mathbf{k}'\beta m}^* w_{\beta\mathbf{R}_\beta} \right. \\
&\qquad\qquad\qquad \left. \left| \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_\gamma} e^{-i\mathbf{k}\cdot\mathbf{R}_\gamma} \sum_\gamma U_{\mathbf{k}\gamma n} w_{\gamma\mathbf{R}_\gamma}^* \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_\delta} e^{i\mathbf{k}'\cdot\mathbf{R}_\delta} \sum_\delta U_{\mathbf{k}'\delta m}^* w_{\delta\mathbf{R}_\delta} \right) \right. \\
&= -\frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} \sum_{\substack{\mathbf{R}_\alpha\mathbf{R}_\beta \\ \mathbf{R}_\gamma\mathbf{R}_\delta}} F_{\mathbf{R}_\alpha\mathbf{R}_\gamma}^{\alpha\gamma} F_{\mathbf{R}_\beta\mathbf{R}_\delta}^{*\,\beta\delta} (w_{\alpha\mathbf{R}_\alpha}^* w_{\beta\mathbf{R}_\beta} | w_{\gamma\mathbf{R}_\gamma}^* w_{\delta\mathbf{R}_\delta})
\end{aligned}
$$

$$\tag{B.6}$$

where

$$
F_{\mathbf{R}_\alpha\mathbf{R}_\gamma}^{\alpha\gamma} = \frac{1}{N_k} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}_\alpha - \mathbf{R}_\gamma)} \sum_n f_n U_{\mathbf{k}\alpha n}^* U_{\mathbf{k}\gamma n}
\tag{B.7}
$$

For extended systems with a band-gap, the occupation numbers are all unity below the Fermi level, so

$$
F_{\mathbf{R}_\alpha\mathbf{R}_\gamma}^{\alpha\gamma} = \frac{1}{N_k} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}_\alpha - \mathbf{R}_\gamma)} \sum_n U_{\mathbf{k}\alpha n}^* U_{\mathbf{k}\gamma n} = \delta_{\alpha\gamma} \frac{1}{N_k} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}_\alpha - \mathbf{R}_\gamma)} = \delta_{\alpha\gamma} \delta_{\mathbf{R}_\alpha\mathbf{R}_\gamma}
\tag{B.8}
$$

such that

$$
\begin{aligned}
E_{xx} &= -\frac{1}{2} \sum_{\alpha\beta} \sum_{\mathbf{R}_\alpha\mathbf{R}_\beta} (w_{\alpha\mathbf{R}_\alpha}^* w_{\beta\mathbf{R}_\beta} | w_{\alpha\mathbf{R}_\alpha}^* w_{\beta\mathbf{R}_\beta}) \\
&= -\frac{1}{2} \sum_{\alpha\beta} \sum_{\mathbf{R}\mathbf{R}'} ((w_{\alpha\mathbf{R}}^* w_{\beta\mathbf{R}'})) \\
&= -\frac{N_k}{2} \sum_{\alpha\beta} \sum_{\mathbf{R}} ((w_{\alpha\mathbf{0}}^* w_{\beta\mathbf{R}}))
\end{aligned}
\tag{B.9}
$$

where in the last line, the translational symmetry of the Wannier functions have been used to reduce the order of the summation.

Appendix C

Fourier Transform

To represent a state $|f\rangle$ as a function of position in real space, we project it onto the basis functions of real space $|\mathbf{r}\rangle$, to get $\langle \mathbf{r}|f\rangle = f(\mathbf{r})$. At times it is advantageous to represent states in reciprocal (or Fourier) space. This is the space spanned by the periodic eigenstates $|\mathbf{k}\rangle$ of the Laplace operator:

$$\langle \mathbf{r}|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{C.1}$$

Due to the periodicity of the complex exponential, the eigenstates $|\mathbf{k}\rangle$ are only distinct for $-\pi \leq \mathbf{k}\cdot\mathbf{r} < \pi$ (or a similar 2π interval).

C.1 Finite Volume - Discrete k

For a finite real space, the periodic boundary conditions required of the $\mathbf{k}$-states imply a discrete spectrum of eigenstates. In this case, we have the completeness relations

$$\int d\mathbf{r}|\mathbf{r}\rangle\langle \mathbf{r}| = 1 \tag{C.2a}$$

$$\frac{1}{V}\sum_{\mathbf{k}}|\mathbf{k}\rangle\langle \mathbf{k}| = 1 \tag{C.2b}$$

from which it is easily seen that

$$f(\mathbf{r}) = \langle \mathbf{r}|f\rangle = \frac{1}{V}\sum_{\mathbf{k}}\langle \mathbf{r}|\mathbf{k}\rangle\langle \mathbf{k}|f\rangle = \frac{1}{V}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}f_{\mathbf{k}} \tag{C.3}$$

and

$$f_{\mathbf{k}} = \langle \mathbf{k}|f\rangle = \int d\mathbf{r}\langle \mathbf{k}|\mathbf{r}\rangle\langle \mathbf{r}|f\rangle = \int d\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r}) \tag{C.4}$$

Note the useful relations to the Dirac delta functions

$$\langle \mathbf{r}|\mathbf{r}'\rangle = \frac{1}{V}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}') \quad \text{and} \quad \langle \mathbf{k}|\mathbf{k}'\rangle = \int d\mathbf{r}e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = V\delta_{\mathbf{k},\mathbf{k}'} \tag{C.5}$$

C.2 Infinite Volume - Continuous k

The continuous version of the Fourier transform is obtained by the substitution

$$\frac{1}{V}\sum_{\mathbf{k}} \rightarrow \int \frac{d\mathbf{k}}{(2\pi)^3} \tag{C.6}$$

such that the transformation rules (C.3)-(C.4) translates to

$$f(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3} f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{C.7}$$

and

$$f(\mathbf{k}) = \int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{C.8}$$

In the continuous case, the delta functions are given by

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}') \quad \text{and} \quad \langle \mathbf{k} | \mathbf{k}' \rangle = \int d\mathbf{r} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = (2\pi)^3 \delta(\mathbf{k} - \mathbf{k}') \tag{C.9}$$

Appendix D

Multipoles and Spherical Harmonics

D.1 Spherical polar coordinates

I choose the name convention for the curvilinear coordinates of the spherical coordinate system, in which ϕ is the azimuthal angle in the xy-plane from the x-axis with $0 \leq \phi < 2\pi$, θ is the polar angle from the z-axis with $0 \leq \theta \leq \pi$, and r is the distance (radius) from a point to the origin. This is the convention most commonly used among physicists, while mathematicians usually interchange the two angular coordinates.
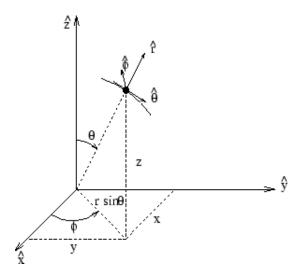

Figure D.1: *Spherical polar coordinates*

The spherical coordinates (r, θ, ϕ) are related to the Cartesian coordinates (x, y, z) by

$$
\begin{cases}
r & = \sqrt{x^2 + y^2 + z^2} \\
\theta & = \tan^{-1}(\sqrt{x^2 + y^2}/z) \\
\phi & = \tan^{-1}(y/x)
\end{cases}
\qquad
\begin{cases}
\hat{\mathbf{r}} & = \sin\theta\cos\phi\hat{\mathbf{x}} + \sin\theta\sin\phi\hat{\mathbf{y}} + \cos\theta\hat{\mathbf{z}} \\
\hat{\boldsymbol{\theta}} & = \cos\theta\cos\phi\hat{\mathbf{x}} + \cos\theta\sin\phi\hat{\mathbf{y}} - \sin\theta\hat{\mathbf{z}} \\
\hat{\boldsymbol{\phi}} & = -\sin\phi\hat{\mathbf{x}} + \cos\phi\hat{\mathbf{y}}
\end{cases}
\qquad \text{(D.1)}
$$

where the inverse tangent must be suitably defined to take the correct quadrant of (x, y) into account.

Inversely, the Cartesian coordinates are related to the spherical by

$$
\begin{cases}
x & = r\cos\phi\sin\theta \\
y & = r\sin\phi\sin\theta \\
z & = r\cos\theta
\end{cases}
\qquad
\begin{cases}
\hat{\mathbf{x}} & = \sin\theta\cos\phi\hat{\mathbf{r}} + \cos\theta\cos\phi\hat{\boldsymbol{\theta}} - \sin\phi\hat{\boldsymbol{\phi}} \\
\hat{\mathbf{y}} & = \sin\theta\sin\phi\hat{\mathbf{r}} + \cos\theta\sin\phi\hat{\boldsymbol{\theta}} + \cos\phi\hat{\boldsymbol{\phi}} \\
\hat{\mathbf{z}} & = \cos\theta\hat{\mathbf{r}} - \sin\theta\hat{\boldsymbol{\theta}}
\end{cases}
\tag{D.2}
$$

The relevant differential quantities are:

Line element:
$$d\mathbf{l} = dr\hat{\mathbf{r}} + rd\theta\hat{\boldsymbol{\theta}} + r\sin\theta d\phi\hat{\boldsymbol{\phi}} \tag{D.3a}$$

Volume element:
$$d\mathbf{r} = r^2\sin\theta dr d\theta d\phi \tag{D.3b}$$

Gradient:
$$\boldsymbol{\nabla}t = \frac{\partial t}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial t}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial t}{\partial\phi}\hat{\boldsymbol{\phi}} \tag{D.3c}$$

Divergence:
$$\boldsymbol{\nabla}\cdot\mathbf{v} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta v_\theta) + \frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial\phi} \tag{D.3d}$$

Curl:
$$\boldsymbol{\nabla}\times\mathbf{v} = \frac{1}{r\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta v_\phi) - \frac{\partial v_\theta}{\partial\phi}\right]\hat{\mathbf{r}}$$
$$+ \frac{1}{r}\left[\frac{1}{\sin\theta}\frac{\partial v_r}{\partial\phi} - \frac{\partial}{\partial r}(rv_\phi)\right]\hat{\boldsymbol{\theta}} + \frac{1}{r}\left[\frac{\partial}{\partial r}(rv_\theta) - \frac{\partial v_r}{\partial\theta}\right]\hat{\boldsymbol{\phi}} \tag{D.3e}$$

Laplacian:
$$\nabla^2 t = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial t}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial t}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 t}{\partial\phi^2} \tag{D.3f}$$

D.2 Multipole Expansion

The potential $v(\mathbf{r})$ of the density $n(\mathbf{r})$ is given by

$$v(\mathbf{r}) = \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{D.4}$$

if we know that the density is localized within a sphere of radius R of our chosen origin, see the figure on the right, the integrand of eq. (D.4) is only nonzero for $r' < R$. If we only wish to know the potential at positions outside of said sphere, $r > R$, we can use the expansion theorem for the Coulomb kernel [32] in spherical harmonics Y_L (see section D.3 for a definition):

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_L \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y_L^*(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}}') \tag{D.5}$$

where, since $r' < R < r$, we can identify $r_< = \min(r, r') = r'$ and $r_> = \max(r, r') = r$.
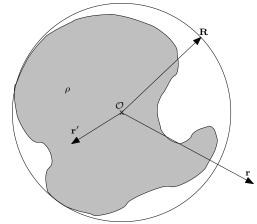
Inserting (D.5) in equation (D.4) we get the identity

$$v(\mathbf{r}) = \sum_L \frac{4\pi}{2l+1}\frac{Q_L}{r^{l+1}}Y_L^*(\mathbf{r}) \ , \text{ for } r > R \tag{D.6}$$

where the expansion coefficients Q_L are given by

$$Q_L = \int d\mathbf{r}\,r^l n(\mathbf{r})Y_L(\mathbf{r}) \tag{D.7}$$

The expansion (D.6) is called a multipole expansion, and the coefficients (D.7) the multipole moments. The set of moments Q_{lm} for fixed l are known as the monopole for $l = 0$, the dipole for $l = 1$, the quadrupole for $l = 2$, the octopole for $l = 3$ (as $2^3 = 8$), etc. Evidently the individual multipole components of the potential fall off as $1/r^{l+1}$ far from the density, so the dominant contributions should be the low order moments.

Generalized Gaussians

Consider the generalized Gaussian functions:

$$g_L(\mathbf{r}) = g_l(r)Y_L(\hat{\mathbf{r}}) \tag{D.8}$$

where $Y_L(\hat{\mathbf{r}})$ are the spherical harmonics, and $g_l(r)$ are given by:

$$g_l(r) = \frac{1}{\sqrt{4\pi}} \frac{l!}{(2l+1)!}(4\alpha)^{l+3/2}r^l e^{-\alpha r^2} \tag{D.9}$$

The spherical harmonics form a complete set of functions which are orthonormal with the weight $\sin\theta$. They can thus be used as an expansion basis for any radially independent function.

The gaussians $g_l(r)$ also form a complete set of functions. They are orthogonal with the weight r^2 and are normalized such that

$$\int r^2 d\mathbf{r} r^l g_l(r) = 1 \tag{D.10}$$

From which we conclude that the functions $g_L(\mathbf{r})$ form a complete basis set.

The multipole moments of $g_L(\mathbf{r})$ are $Q_{L'} = \delta_{L,L'}$, since

$$Q_{L'} = \int d\mathbf{r} r^{l'} g_L(\mathbf{r})Y_{L'}(\hat{\mathbf{r}}) = \int r^{l'+2}g_l(r)dr \int Y_L(\hat{\mathbf{r}})Y_{L'}(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \int r^{l+2}g_l(r)dr\delta_{L,L'} = \delta_{L,L'} \tag{D.11}$$

which makes them very useful for making expansions with specific multipole moments. The generalized Gaussians and various integrals of these, have been studied in detail in [61].

Note that using eq. (7.5), the potential of the gaussians can be evaluated analytically, giving $v_L(\mathbf{r}) = v_l(r)Y_L(\hat{\mathbf{r}})$, where the radial part is given by:

$$
\begin{aligned}
v_l(r) &= \frac{\sqrt{4\pi}l!(4a)^{l+3/2}}{(2l+1)(2l+1)!}\left[r^{-l-1}\int_0^r r'^{2l+2}e^{-ar'^2}dr' + r^l\int_r^\infty r'e^{-ar'^2}dr'\right] \\
&= \frac{2\sqrt{4\pi}\,l!\,(4a)^{l+1/2}}{(2l+1)(2l+1)!}r^l e^{ar^2}\left\{1 + \frac{2e^{ar^2/2}}{(2l+3)(ar^2)^{l/2+1/4}}\,\mathrm{M}_{\frac{2l+1}{4},\frac{2l+3}{4}}(ar^2)\right\} \\
&= \frac{8\sqrt{\pi a}\,l!}{(2l+1)(2l+1)!}(4ar)^l e^{ar^2}\left\{1 + \frac{2\sqrt{ar}}{(2l+3)}\,{}_1F_1(1, l+5/2; ar^2)\right\}
\end{aligned}
$$

where $\mathrm{M}_{k,m}(z)$ is the Whittaker function, and ${}_1F_1(k,m;z)$ is the confluent hypergeometric function of the first kind. The first few potentials are listed below.

$$
\begin{aligned}
v_0(r) &= \frac{4\sqrt{\pi}}{r^1}\left\{\sqrt{\pi}\operatorname{erf}(\sqrt{a}r)\right\} \\
v_1(r) &= \frac{4\sqrt{\pi}}{3r^2}\left\{\sqrt{\pi}\operatorname{erf}\left(\sqrt{a}r\right) - 2\sqrt{a}r e^{-ar^2}\right\} \\
v_2(r) &= \frac{4\sqrt{\pi}}{15r^3}\left\{3\sqrt{\pi}\operatorname{erf}\left(\sqrt{a}r\right) - \left(6 + 4(\sqrt{a}r)^2\right)\sqrt{a}r e^{-ar^2}\right\} \\
v_3(r) &= \frac{4\sqrt{\pi}}{105r^4}\left\{15\sqrt{\pi}\operatorname{erf}\left(\sqrt{a}r\right) - \left(30 + 20(\sqrt{a}r)^2 + 8(\sqrt{a}r)^4\right)\sqrt{a}r e^{-ar^2}\right\}
\end{aligned}
$$

D.3   Spherical Harmonics

Consider the orbital angular momentum operator

$$
\begin{aligned}
\hat{\mathbf{L}} &= \widehat{\mathbf{Q}} \times \widehat{\mathbf{P}} \\
&= r\hat{\mathbf{r}} \times -i\boldsymbol{\nabla} \\
&= -i\left[\hat{\boldsymbol{\phi}}\frac{\partial}{\partial\theta} - \hat{\boldsymbol{\theta}}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right]
\end{aligned} \tag{D.12}
$$

Let $Y(\theta, \phi)$ denote the set of common eigenstates for the two operators $\hat{L}^2$ and $\hat{L}_z$

$$\hat{L}^2 Y(\theta, \phi) = l(l+1)Y(\theta, \phi) \tag{D.13}$$

$$\hat{L}_z Y(\theta, \phi) = m Y(\theta, \phi) \tag{D.14}$$

This set of coupled differential equations has nontrivial bounded solutions that are 2π periodic in ϕ if and only if l is a nonnegative integer, and m is an integer in the range $|m| \le l$. The normalized eigenstates satisfying these conditions are known as the *spherical harmonics*

$$Y_l^m(\theta, \phi) = (-1)^{(m-|m|)/2} \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos\theta) e^{im\phi} \tag{D.15}$$

where $P_l^m(z)$ are the associated Legendre polynomials

$$P_l^m(z) = \frac{(-1)^m}{2^l l!}(1-z^2)^{m/2}\frac{d^{l+m}}{dz^{l+m}}(z^2-1)^l \tag{D.16}$$

The spherical harmonics of negative and positive m are related by a complex conjugation, through the relation

$$Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi) \tag{D.17}$$

and form a complete orthonormal set, satisfying

$$\int_0^\pi \int_0^{2\pi} \sin\theta d\theta d\phi Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \delta_{l,l'}\delta_{m,m'} \tag{D.18}$$

Note that as

$$\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{D.19}$$

we can express the Laplacian in terms of $\hat{L}^2$

$$\nabla^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{L}^2\right] \tag{D.20}$$

from which we conclude that

$$\nabla^2 Y_l^m(\theta, \phi) = -\frac{l(l+1)}{r^2}Y_l^m(\theta, \phi) \tag{D.21}$$

one can define a set of real spherical harmonics (RSH), y_l^m, by

$$y_l^0 = Y_l^0$$
$$y_l^m = \begin{cases} (Y_l^m + Y_l^{m*})/\sqrt{2} = \sqrt{2}\,\mathrm{Re}\,Y_l^m & , \; m > 0 \\ \left(Y_l^{|m|} + Y_l^{|m|*}\right)/i\sqrt{2} = \sqrt{2}\,\mathrm{Im}\,Y_l^{|m|} & , \; m < 0 \end{cases} \tag{D.22}$$

Which in explicit form is

$$y_l^m(\theta, \phi) = C_l^{|m|}P_l^{|m|}(\cos\theta)\Phi_m(\phi) \tag{D.23}$$

where

$$C_l^m = \begin{cases} \sqrt{\frac{2l+1}{4\pi}} & , \; m = 0 \\ \sqrt{\frac{2l+1}{2\pi}\frac{(l-m)!}{(l+m)!}} & , \; m > 0 \end{cases} \tag{D.24}$$

and

$$\Phi_m(\phi) = \begin{cases} \cos m\phi & , \; m \ge 0 \\ \sin|m|\phi & , \; m < 0 \end{cases} \tag{D.25}$$

The RSH satisfy the same equations as the ordinary spherical harmonics, except that it is no longer an eigenstate of $\hat{L}_z$.

When working in Cartesian coordinates, it is usually more convenient to work with the solid version of the RSH, here denoted by RSSH (real solid spherical harmonics). These are defined by $\bar{y}_l^m = r^l y_l^m$. The main reason for introducing the RSSH is that they are much more easily described in Cartesian coordinates, and the recursion formulas for generating them becomes much simpler, as will be shown shortly. The RSSH can be re-expressed as

$$
\begin{aligned}
\bar{y}_l^m(r, \theta, \phi) &= r^l C_l^{|m|} P_l^{|m|}(\cos\theta)\Phi_m(\phi) \\
&= C_l^{|m|} \frac{r^{l-|m|}}{\sin^{|m|}(\theta)} P_l^{|m|}(\cos\theta)\; r^{|m|} \sin^{|m|}(\theta)\Phi_m(\phi) \\
&= C_l^{|m|} \bar{P}_l^{|m|}(r, z)\bar{\Phi}_m(x, y) \\
&= \bar{y}_l^m(x, y, z)
\end{aligned}
\tag{D.26}
$$

where $\bar{P}_l^m(r, z) = r^{l-m}/\sin^m(\theta)P_l^m(\cos\theta)$ and $\bar{\Phi}_m(x, y) = \sin^m(\theta)\Phi_m(\phi)$. The advantage of this formulation is seen by using the recurrence formula

$$
\cos m\phi = \cos\phi\cos(m-1)\phi - \sin\phi\sin(m-1)\phi \tag{D.27}
$$
$$
\sin m\phi = \sin\phi\cos(m-1)\phi + \cos\phi\sin(m-1)\phi \tag{D.28}
$$

and the identities $x = r\sin\theta\cos\phi$ and $y = r\sin\theta\sin\phi$ to get

$$
\bar{\Phi}_0 = 1, \quad \bar{\Phi}_1 = x, \quad \bar{\Phi}_{-1} = y \tag{D.29}
$$
$$
m > 1: \quad \bar{\Phi}_m = x\bar{\Phi}_{|m|-1} - y\bar{\Phi}_{1-|m|} \tag{D.30}
$$
$$
m < -1: \quad \bar{\Phi}_m = y\bar{\Phi}_{|m|-1} + x\bar{\Phi}_{1-|m|} \tag{D.31}
$$

and using the recurrence relations of $P_l^m(\cos\theta)$ [35]

$$
P_0^0 = 1 \tag{D.32}
$$
$$
P_{m+1}^{m+1} = (2m+1)\sin\theta P_m^m \tag{D.33}
$$
$$
P_{m+1}^m = (2m+1)\cos\theta P_m^m \tag{D.34}
$$
$$
P_l^m = \frac{2l-1}{l-m}\cos\theta P_{l-1}^m - \frac{l+m-1}{l-m}P_{l-2}^m \tag{D.35}
$$

to get

$$
\bar{P}_0^0 = 1 \tag{D.36}
$$
$$
\bar{P}_{m+1}^{m+1} = (2m+1)\bar{P}_m^m \tag{D.37}
$$
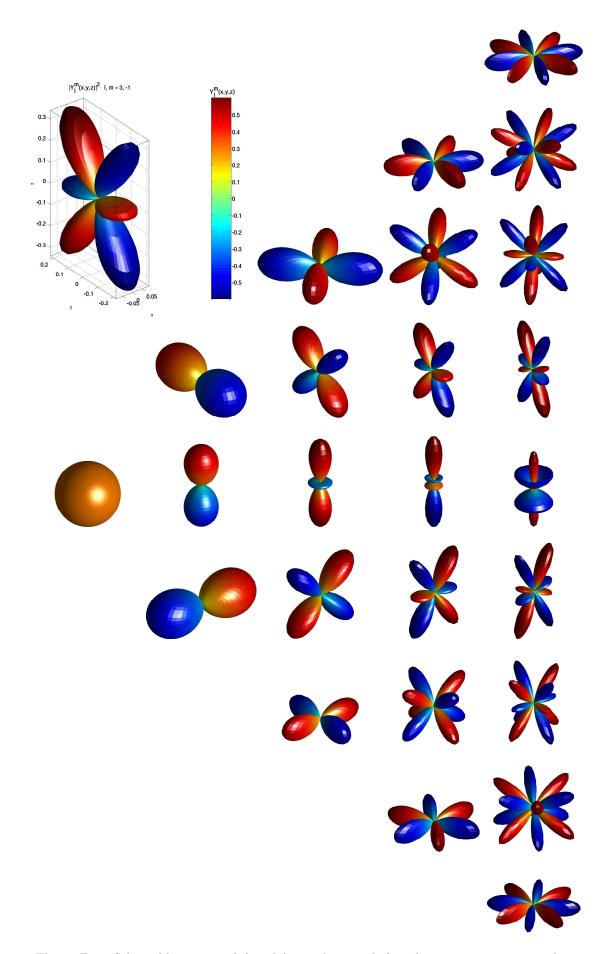$$
\bar{P}_{m+1}^m = (2m+1)z\bar{P}_m^m \tag{D.38}
$$
$$
\bar{P}_l^m = \frac{2l-1}{l-m}z\bar{P}_{l-1}^m - \frac{l+m-1}{l-m}r^2\bar{P}_{l-2}^m \tag{D.39}
$$

Note that $\bar{P}_l^m$ is a polynomial of order $l - m$ in z with only even (odd) powers of z if $l - m$ is even (odd). The collective power of z and r is $l - m$ in all terms of $\bar{P}_l^m$. The coordinate r only ever appears in even powers (so we never have to evaluate the square root $r = \sqrt{x^2 + y^2 + z^2}$).

The explicit form of the first 25 RSSH is shown in table D.1. A polar plot of the map of the unit sphere is shown in figure D.2 for the same 25 RSSH (or equivalently the real spherical harmonics, as these are identical on the unit sphere).

Note that $\bar{y}_l^m(x, y, z)$ is still an eigenstate of $\hat{L}^2$ with eigenvalue $l(l+1)$, but that $\nabla^2\bar{y}_l^m = 0$.

Figure D.2: *Spherical harmonics of, from left to right, s, p, d, f, and g type. m quantum numbers are increasing from the top and down.*

L	l	m	$\bar{y}_l^m = N \cdot f(x,y,z)$
0	0	0	$\sqrt{1/4\pi} \cdot 1$
1	1	-1	$\sqrt{3/4\pi} \cdot y$
2	1	0	$\sqrt{3/4\pi} \cdot z$
3	1	1	$\sqrt{3/4\pi} \cdot x$
4	2	-2	$\sqrt{15/4\pi} \cdot xy$
5	2	-1	$\sqrt{15/4\pi} \cdot yz$
6	2	0	$\sqrt{5/16\pi} \cdot (3z^2 - r^2)$
7	2	1	$\sqrt{15/4\pi} \cdot xz$
8	2	2	$\sqrt{15/16\pi} \cdot (x^2 - y^2)$
9	3	-3	$\sqrt{35/32\pi} \cdot (3x^2y - y^3)$
10	3	-2	$\sqrt{105/4\pi} \cdot xyz$
11	3	-1	$\sqrt{21/32\pi} \cdot (5yz^2 - yr^2)$
12	3	0	$\sqrt{7/16\pi} \cdot (5z^3 - 3zr^2)$
13	3	1	$\sqrt{21/32\pi} \cdot (5xz^2 - xr^2)$
14	3	2	$\sqrt{105/16\pi} \cdot (x^2z - y^2z)$
15	3	3	$\sqrt{35/32\pi} \cdot (x^3 - 3xy^2)$
16	4	-4	$\sqrt{315/16\pi} \cdot (x^3y - xy^3)$
17	4	-3	$\sqrt{315/32\pi} \cdot (3x^2yz - y^3z)$
18	4	-2	$\sqrt{45/16\pi} \cdot (7xyz^2 - xyr^2)$
19	4	-1	$\sqrt{45/32\pi} \cdot (7yz^3 - 3yzr^2)$
20	4	0	$\sqrt{9/256\pi} \cdot (35z^4 - 30z^2r^2)$
21	4	1	$\sqrt{45/32\pi} \cdot (7xz^3 - 3xzr^2)$
22	4	2	$\sqrt{45/64\pi} \cdot (7x^2z^2 - 7y^2z^2 - x^2r^2 + y^2r^2)$
23	4	3	$\sqrt{315/32\pi} \cdot (x^3z - 3xy^2z)$
24	4	4	$\sqrt{315/256\pi} \cdot (x^4 + y^4 - 6x^2y^2)$

Table D.1: *List of the first few real solid spherical harmonics in Cartesian form.*

Appendix E

Approximations of the Exchange-Correlation Functional

The value of the density is in functionals often given in terms of the Seitz radius r_s, or the Fermi wave length k_F. The Seitz radius, is the radius of the sphere, which for a homogeneous electron gas would contain exactly one electron

$$r_s^3 = 3/4\pi n$$

This gives a measure of the average distance between electrons.

The Fermi wave length is the energetically highest occupied plane wave in a homogeneous electron gas

$$k_F^3 = 3\pi^2 n$$

The gradient of the density is usually measured in terms of either of

$$s = \frac{|\nabla n|}{2k_F n}$$

$$t = \frac{|\nabla n|}{2k_s n\phi}$$

where $k_s = \sqrt{4k_F/\pi}$ and

$$\phi(\zeta) = \frac{1}{2}\left[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}\right] \tag{E.1}$$

ζ is the spin polarization defined as

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \tag{E.2}$$

From the explicit expression for exact exchange, the exact spin scaling relation $E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}E_x[2n_\uparrow] + \frac{1}{2}E_x[2n_\downarrow]$ can be derived, and from this, it follows that for the homogeneous electron gas

$$E_x[n_\uparrow, n_\downarrow] = E_x[n]\frac{1}{2}\left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3}\right] \tag{E.3}$$

where $E_x[n] = E_x[n/2, n/2]$ is the spin-compensated version of exchange. No exact spin scaling relation exist for correlation.

E.1   Local spin density approximation

In the local spin density approximation (LSD), the exchange-correlation is approximated by

$$E_{xc}[n_\uparrow, n_\downarrow] = \int d\mathbf{r} n(\mathbf{r}) e_{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \tag{E.4}$$

where e_x is the local exchange contribution of a homogeneous electron gas. For a spin saturated system, this would be (see e.g. the section on Thomas-Fermi theory 3.2.1)

$$e_x(n) = -\frac{3k_F}{4\pi} = -\frac{3}{4\pi}(3\pi^2 n)^{1/3} \tag{E.5}$$

this can be generalized to arbitrary spin polarization using the spin-scaling relation (E.3).

The correlation energy density is only known for the (spin saturated) homogeneous gas in the high-density (weak coupling) limit

$$e_c(n) = c_0 \ln r_s - c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots$$

with the constants $c_0 = (1 - \ln 2)/\pi^2 \approx 0.031091$ and $c_1 = 0.046644$, and in the low-density (strong coupling) limit

$$e_c(n) = -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \dots$$

where the two constants can be estimated by experimental techniques.

A parametrization, due to Perdew and Wang [18] which satisfy both limits is (other parameterizations are [15, 17, 16])

$$e_c(n) = -2c_0(1 + \alpha_1 r_s) \ln\left[1 + \frac{1}{2c_0(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)}\right] \tag{E.6}$$

where

$$\begin{aligned} \beta_1 &= \frac{1}{c_0} e^{-c_1/2c_0} \\ \beta_2 &= 2c_0\beta_1^2 \end{aligned} \tag{E.7}$$

and the remaining parameters α_1, β_3, and β_4 are fitted to results from quantum Monte-Carlo simulations of the homogeneous electron gas [17]

$$\alpha_1 = 0.21376 \qquad\qquad \beta_3 = 1.6382 \qquad\qquad \beta_4 = 0.49294$$

This parametrization was for $e_c(n) = e_c(n/2, n/2)$, i.e. the fully spin saturated case. For the fully spin polarized case, $e_c(n_\uparrow, n_\downarrow) = e_c(n, 0)$, the correlation energy density can be parametrized in the exact same way as in (E.6), but with the changed constants

$$\alpha_1 = 0.20548 \qquad\qquad \beta_3 = 3.3662 \qquad\qquad \beta_4 = 0.62517$$

Using these two extreme cases, the correlation energy can be generalized to arbitrary spin, using the Taylor expansion (due to [16])

$$e_c(n_\uparrow, n_\downarrow) = e_c(n) + \alpha_c(n)\frac{f(\zeta)}{f''(0)}(1 - \zeta^4) + [e_c(n, 0) - e_c(n)]f(\zeta)\zeta^4 \tag{E.8}$$

where

$$f(\zeta) = \frac{1}{2^{4/3} - 2}\left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2\right] \tag{E.9}$$

and $\alpha_c(n)$ can be parametrized in the same way as (E.6) with the modified parameters

$$\begin{aligned} c_0 &= 0.016887 \\ c_1 &= 0.035475 \\ \alpha_1 &= 0.11125 \\ \beta_3 &= 0.88026 \\ \beta_4 &= 0.49671 \end{aligned} \tag{E.10}$$

and β_1 and β_2 defined as before, (E.7).

E.2 PBE, revPBE, and RPBE

The Perdew-Burke-Ernzerhof functional (PBE) [19], the revision by Zhang and Yang revPBE [21] and by Hammer, Hansen and Nørskov RPBE [22] all use the correlation functional of PW91, in which the correlation energy functional is written as

$$E_c[n_\uparrow, n_\downarrow] = \int d\mathbf{r} n(\mathbf{r}) \left(e_c(r_s, \zeta) + H(r_s, \zeta, t) \right) \tag{E.11}$$

where $e_c(r_s, \zeta)$ is the local correlation functional of LSD, and

$$H(r_s, \zeta, t) = c_0 \phi^3 \ln \left\{ 1 + \frac{\beta_{MB}}{c_0} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\} \tag{E.12}$$

where

$$A = \frac{\beta_{MB}}{c_0} \frac{1}{e^{-e_c(r_s, \zeta)/c_0 \phi^3} - 1} \tag{E.13}$$

and $\beta_{MB} = 0.066725$. The exchange functional is written as

$$E_x[n] = \int d\mathbf{r} n(\mathbf{r}) e_x(n) F_x(s) \tag{E.14}$$

where the enhancement factor for PBE and revPBE is

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa} \tag{E.15}$$

where $\mu = \beta_{MB} \pi^2/3 \approx 0.21951$ and

$$\kappa \leq 0.804 \tag{E.16}$$

to satisfy the Lieb-Oxford bound. Choosing $\kappa = 0.804$ one arrives at the PBE functional, choosing $\kappa = 1.245$ we get the revPBE functional, and modifying the form of F_x to

$$F_x(s) = 1 + \kappa \left(1 - e^{\mu s^2/\kappa} \right) \tag{E.17}$$

and keeping κ at 0.804, one gets the RPBE functional.

The expression (E.14) is generalized to arbitrary spin in the same way as LSD, i.e. by multiplying with $\frac{1}{2} \left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} \right]$.

Appendix F

Forces in PAW

In the ground state, the forces on each nuclei can be calculated directly from

$$
\begin{aligned}
\mathbf{F}^a &= -\frac{dE}{d\mathbf{R}^a} \\
&= -\frac{\partial E}{\partial \mathbf{R}^a} - \sum_n \left\{ \frac{\partial E}{\partial |\tilde{\psi}_n\rangle} \frac{d|\tilde{\psi}_n\rangle}{d\mathbf{R}^a} + h.c. \right\} \\
&= -\frac{\partial E}{\partial \mathbf{R}^a} - \sum_n f_n \epsilon_n \left\{ \langle \tilde{\psi}_n | \hat{S} \frac{d|\tilde{\psi}_n\rangle}{d\mathbf{R}^a} + h.c. \right\} \\
&= -\frac{\partial E}{\partial \mathbf{R}^a} + \sum_n f_n \epsilon_n \langle \tilde{\psi}_n | \frac{d\hat{S}}{d\mathbf{R}^a} | \tilde{\psi}_n \rangle
\end{aligned}
\tag{F.1}
$$

where $h.c.$ denotes the hermitian conjugate. To get to the second line, the chain rule has been applied. The third line follows from the relation

$$
\frac{\partial E}{\partial \langle \tilde{\psi}_n |} = f_n \widehat{\tilde{H}} | \tilde{\psi}_n \rangle = f_n \epsilon_n \hat{S} | \tilde{\psi}_n \rangle
\tag{F.2}
$$

The last line of (F.1) is obtained from the following manipulation of the orthogonality condition (6.52)

$$
\begin{aligned}
\delta_{nm} &= \langle \tilde{\psi}_n | \hat{S} | \tilde{\psi}_m \rangle \\
\Rightarrow \quad 0 &= \frac{d}{d\mathbf{R}^a} \langle \tilde{\psi}_n | \hat{S} | \tilde{\psi}_m \rangle = \frac{d\langle \tilde{\psi}_n |}{d\mathbf{R}^a} \hat{S} | \tilde{\psi}_m \rangle + \langle \tilde{\psi}_n | \frac{d\hat{S}}{d\mathbf{R}^a} | \tilde{\psi}_m \rangle + \langle \tilde{\psi}_n | \hat{S} \frac{d|\tilde{\psi}_m\rangle}{d\mathbf{R}^a} \\
\Leftrightarrow \quad \frac{d\langle \tilde{\psi}_n |}{d\mathbf{R}^a} \hat{S} | \tilde{\psi}_m \rangle + h.c. &= -\langle \tilde{\psi}_n | \frac{d\hat{S}}{d\mathbf{R}^a} | \tilde{\psi}_m \rangle
\end{aligned}
\tag{F.3}
$$

From the expression for the overlap operator (6.53), it follows that

$$
\frac{d\hat{S}}{d\mathbf{R}^a} = \sum_{i_1 i_2} \Delta S^a_{i_1 i_2} \left(\frac{d|\tilde{p}^a_{i_1}\rangle}{d\mathbf{R}^a} \langle \tilde{p}^a_{i_2} | + h.c. \right)
\tag{F.4}
$$

which, when inserted in (F.1), gives the force expression

$$
\mathbf{F}^a = -\frac{\partial E}{\partial \mathbf{R}^a} + \sum_n f_n \epsilon_n \sum_{i_1 i_2} \Delta S^a_{i_1 i_2} \left(P^{a*}_{ni_1} \langle \frac{d\tilde{p}^a_{i_2}}{d\mathbf{R}^a} | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \frac{d\tilde{p}^a_{i_1}}{d\mathbf{R}^a} \rangle P^a_{ni_2} \right)
\tag{F.5}
$$

Forces without exact exchange

In the absence of exact exchange, it is clear that the dependence of the total energy on the nuclei coordinates follows from

$$
\begin{aligned}
\frac{\partial E}{\partial \mathbf{R}^a} &= \int d\mathbf{r}' \frac{\delta E}{\delta \tilde{n}(\mathbf{r}')} \frac{\partial \tilde{n}(\mathbf{r}')}{\partial \mathbf{R}^a} + \sum_{i_1 i_2} \frac{\partial E}{\partial D^a_{i_1 i_2}} \frac{\partial D^a_{i_1 i_2}}{\partial \mathbf{R}^a} + \int d\mathbf{r}' \sum_L \frac{\delta E}{\delta \tilde{g}^a_L(\mathbf{r}')} \frac{\partial \tilde{g}^a_L(\mathbf{r}')}{\partial \mathbf{R}^a} \\
&= \int d\mathbf{r}' \tilde{v}_{\text{eff}}(\mathbf{r}') \frac{\partial \tilde{n}^a_c(\mathbf{r}')}{\partial \mathbf{R}^a} + \sum_{i_1 i_2} \Delta H^a_{i_1 i_2} \frac{\partial D^a_{i_1 i_2}}{\partial \mathbf{R}^a} + \int d\mathbf{r}' \sum_L u_H(\mathbf{r}') Q_L \frac{\partial \tilde{g}^a_L(\mathbf{r}')}{\partial \mathbf{R}^a}
\end{aligned}
\tag{F.6}
$$

giving the force expression

$$
\begin{aligned}
\mathbf{F}^a = &- \int d\mathbf{r}' \left\{ \tilde{v}_{\text{eff}}(\mathbf{r}') \frac{\partial \tilde{n}^a_c(\mathbf{r}')}{\partial \mathbf{R}^a} + u_H(\mathbf{r}') \sum_L Q_L \frac{\partial \tilde{g}^a_L(\mathbf{r}')}{\partial \mathbf{R}^a} \right\} \\
&- \sum_n f_n \sum_{i_1 i_2} \left\{ \Delta H^a_{i_1 i_2} - \epsilon_n \Delta S^a_{i_1 i_2} \right\} \left(P^{a*}_{n i_1} \langle \frac{d\tilde{p}^a_{i_2}}{d\mathbf{R}^a} | \tilde{\psi}_n \rangle + \langle \tilde{\psi}_n | \frac{d\tilde{p}^a_{i_1}}{d\mathbf{R}^a} \rangle P^a_{n i_2} \right)
\end{aligned}
\tag{F.7}
$$

Forces with exact exchange

When including exact exchange, the atomic Hamiltonian, $\Delta H^a_{i_1 i_2}$ is redefined in accordance with the procedure described in section 6.8. In addition, we get the force contribution

$$
\mathbf{F}^a_{xx} = - \sum_{n_1 n_2} \int d\mathbf{r}' \frac{\delta \tilde{E}_{xx}}{\delta \tilde{Z}^a_{n_1 n_2}(\mathbf{r}')} \frac{\partial \tilde{Z}^a_{n_1 n_2}(\mathbf{r}')}{\partial \mathbf{R}^a}
\tag{F.8}
$$

The first partial derivative gives

$$
\frac{\delta \tilde{E}_{xx}}{\delta \tilde{Z}^a_{n_1 n_2}(\mathbf{r})} = f_{n_1} f_{n_2} \delta_{\sigma_{n_1} \sigma_{n_2}} \tilde{v}_{n_1 n_2}(\mathbf{r})
\tag{F.9}
$$

and the second gives

$$
\frac{\partial \tilde{Z}^a_{n_1 n_2}(\mathbf{r})}{\partial \mathbf{R}^a} = \sum_L \sum_{i_1 i_2} \Delta_{L i_1 i_2} \left(P^{a*}_{n_1 i_1} P^a_{n_2 i_2} \frac{\partial \tilde{g}^a_L(\mathbf{r})}{\partial \mathbf{R}^a} + \tilde{g}^a_L(\mathbf{r}) \frac{\partial P^{a*}_{n_1 i_1} P^a_{n_2 i_2}}{\partial \mathbf{R}^a} \right)
\tag{F.10}
$$

resulting in the force

$$
\begin{aligned}
\mathbf{F}^a_{xx} = &- \sum_{n_1 n_2} f_{n_1} f_{n_2} \delta_{\sigma_{n_1} \sigma_{n_2}} \left\{ \int d\mathbf{r}' \tilde{v}_{n_1 n_2}(\mathbf{r}') \sum_{i_1 i_2} P^{a*}_{n_1 i_1} P^a_{n_2 i_2} \sum_L \Delta_{L i_1 i_2} \frac{\partial \tilde{g}^a_L(\mathbf{r}')}{\partial \mathbf{R}^a} \right. \\
&\left. + \sum_{i_1 i_2} v^a_{n_1 n_2 i_1 i_2} \left(P^{a*}_{n_1 i_1} \langle \frac{d\tilde{p}^a_{i_2}}{d\mathbf{R}^a} | \tilde{\psi}_{n_2} \rangle + \langle \tilde{\psi}_{n_1} | \frac{d\tilde{p}^a_{i_1}}{d\mathbf{R}^a} \rangle P^a_{n_2 i_2} \right) \right\}
\end{aligned}
\tag{F.11}
$$

Note that these equations, (F.7) and (F.11), are only valid in the ground state. For a derivation of a force theorem in PAW, when one is not in the ground state, see [25].

Appendix G

The External Potential in PAW

The energy associated with the external potential $v_{\text{ext}}(\mathbf{r})$ is

$$E_{\text{ext}} = \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$$

$$= \int d\mathbf{r} \tilde{n}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + \sum_a \int d\mathbf{r} \left[n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) \right] v_{\text{ext}}(\mathbf{r})$$

I.e. we must add the pseudo energy contribution

$$\tilde{E}_{\text{ext}} = \int d\mathbf{r} \tilde{n}(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$$

and the atomic corrections:

$$\Delta E_{\text{ext}}^a = \int d\mathbf{r} \left[n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r}) \right] v_{\text{ext}}(\mathbf{r})$$

to the total energy.

In PAW, the Hamiltonian has the structure:

$$H = \frac{1}{f_n |\psi_n\rangle} \frac{\partial E}{\partial \langle \psi_n |} = \tilde{H} + \sum_a \sum_{i_1 i_2} |\tilde{p}_{i_1}^a\rangle \Delta H_{i_1 i_2}^a \langle \tilde{p}_{i_2}^a|$$

In our case, the extra contributions due to the external potential are:

$$\tilde{H}_{\text{ext}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r})$$

and

$$\Delta H_{i_1 i_2}^{a,\text{ext}} = \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \left\{ \phi_{i1}^a(\mathbf{r}) \phi_{i2}^a(\mathbf{r}) - \tilde{\phi}_{i1}^a(\mathbf{r}) \tilde{\phi}_{i2}^a(\mathbf{r}) \right\} \tag{G.1}$$

Thus we can write the atomic energy contribution as:

$$\Delta E_{\text{ext}}^a = \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \left[n_c^a(\mathbf{r}) - \tilde{n}_c^a(\mathbf{r}) + \sum_{i_1 i_2} D_{i_1 i_2}^a \left\{ \phi_{i1}^a(\mathbf{r}) \phi_{i2}^a(\mathbf{r}) - \tilde{\phi}_{i1}^a(\mathbf{r}) \tilde{\phi}_{i2}^a(\mathbf{r}) \right\} \right]$$

$$= \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \left[n_c^a(\mathbf{r}) - \tilde{n}_c^a(\mathbf{r}) \right] + \sum_{i_1 i_2} D_{i_1 i_2}^a \Delta H_{i_1 i_2}^{a,\text{ext}}$$

Computing all the elements of (G.1) can be time-consuming, as the external potential has to be expanded in som radial function at each nuclei. Making the assumption

$$v_{\text{ext}}(\mathbf{r}) \approx v_{\text{ext}}(\mathbf{R}^a) \text{ , for } |\mathbf{r} - \mathbf{R}^a| < r_c^a$$

We can reuse existing matrix elements from the expansion coefficients of the compensation charges, to get:

$$\Delta E_{\text{ext}}^a = v_{\text{ext}}(\mathbf{R}^a)(\sqrt{4\pi}Q_{00}^a + \mathcal{Z}^a)$$
$$\Delta H_{i_1 i_2}^{a,\text{ext}} = v_{\text{ext}}(\mathbf{R}^a)\sqrt{4\pi}\Delta_{00,i_1 i_2}^a$$