

**TOWARDS A NEW EXCHANGE-CORRELATION
DENSITY FUNCTIONAL FOR MORE ACCURATE BAND
GAP PREDICTIONS**

By:

IYOMO IREWOLE

Supervised By:

Dr Omololu AKIN-OJO



African University of Science and Technology

www.aust.edu.ng

P.M.B 681, Garki, Abuja F.C.T

Nigeria.

June, 2016

**TOWARDS A NEW EXCHANGE-CORRELATION DENSITY
FUNCTIONAL FOR MORE ACCURATE BAND GAP
PREDICTIONS**

A Thesis presented to the Department of

THEORETICAL AND APPLIED PHYSICS,
African University of Science and Technology, Abuja, Nigeria

in partial fulfillment of the requirements
for the degree of

MASTERS OF SCIENCE

By:

IYOMO IREWOLE
STUDENT ID: 40395

June, 2016

**TOWARDS A NEW EXCHANGE-CORRELATION DENSITY
FUNCTIONAL FOR MORE ACCURATE BAND GAP
PREDICTIONS**

By:
IYOMO IREWOLE
(40395)

A THESIS APPROVED BY THE DEPARTMENT OF THEORETICAL AND
APPLIED PHYSICS

RECOMMENDED:

.....
Supervisor: Dr Omololu AKIN-OJO

.....
Head, Department of Theoretical Physics

APPROVED:

.....
Chief Academic Officer (Prof. C. E. Chidume)

.....
Date

ABSTRACT

Density-Functional Theory (DFT) offers a simplification to electronic structure problems by using the electron density instead of the wave-function. Unlike the wave-function which is a function of $3N$ variables (excluding spin) for an N -electron system, the density depends only on three variables, irrespective of the number of electrons in the system. While DFT, in principle, gives an accurate description of ground state properties, practical applications of DFT are based on approximations to the so-called exchange-correlation (xc) potential. The exchange-correlation potential describes the effects of the Pauli exclusion principle and the electron-electron Coulomb repulsion beyond a purely electrostatic interaction of the electrons. A common description of exchange-correlation functional is the so-called local density approximation (LDA) which locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at that local density. While many ground state properties (such as lattice constants and bulk moduli) are well described in the LDA, the band gap is underestimated by as much as 50% in LDA compared to experiments.

In this thesis, we focus on the development of an exchange-correlation functional with adjustable parameters which can give more accurate band gap energies. This functional is based on the xc potential derived in 1988 from a tight-binding approximation by Hanke and Sham (HS)[\[1\]](#). Our contribution consists in expressing the HS potential in terms of the electron density and its gradient. This new expression for the xc functional was parameterized for the Si and Ge bulk systems and found to reduce the error in the LDA band gap prediction by an average of 22.3% for the systems (ZnO, MgO, ZnS, LiF, FeO and GaAs) that we tested it on.

ACKNOWLEDGMENTS

Thanks to everyone who have helped making this dream a reality!

To my supervisor, *Dr. Omololu Akin-Ojo*, I say a very big thank you! You have guided me in so many ways. Your teachings and supervision have always led me back on track whenever I have been lost or confused. Your inexhaustible enthusiasm has been a true source of inspiration for me; not only in my work, but also for life in general. If more people had your attitude to life, the world would be a far better place.

I am grateful to *Bruno Dandogbesi* and *Shaidu Yusuf* for the wonderful and remarkable ideas they shared with me and for providing me with some of the materials I needed to do this work. Keep up the good work, and good luck to you both.

A big “thank you” goes to my good friend Esther Idoko. The distraction you bring to the table during those intense study hours are probably what have kept me sane(?) in the course of this program.

Also, a special “thank you” to *Eremiokhale Elizabeth*. Your sacrifice is deeply appreciated! I could only imagine how I would have completed my program without a computer.

I say a big thank you to my friends and colleagues. *Ogenyi Sunday Joseph*: you have been more than an inspiration to me, my Ghanaian roommate *Yirijor John*: I would never have asked for a better roommate, my closest pal in class *Onwukwe Emmanuel Akwari*: I can only imagine what it would be like if I could work as hard as you do, my homeboy *Ahmad Muhammad*: the hilarious jokes you bring to class will always be remembered, my very good friend *Kakmeni Keou Nabil Stephane*: learning L^AT_EX with you was fun, my “mannest man” *Nwigbo Kenule T*: I will live

to admire your focus and passion for academics, and my best friend *Asare Joseph*: thank you for the happy times and the wonderful memories, I promise to cherish them always.

I must not forget few of my old and long-standing pals, especially *Amos Author Iji*, *Danjuma Isaac Dalyop*, *Delex Adewunmi Moses*, *Odunayo Felix Bamisi* and *Joel Reynolds*. You guys rock! I have never had any reason to regret the time we spend together and I truly appreciate all your support and encouragements both morally and financially.

Lastly, a huge “thank you” goes to my family for their continued love and emotional and financial support: My Dad, my one and only sister, *Lady T* (and husband *Pst Alex Ayodeji*), my brothers *Iyomo Kayode Williams* (and wife *Chinwe Calister*), *Iyomo Dare (Daresmho)* and *Iyomo Rotimi Williams (Angel de Rollisky)*; without whom my success and completion of M.Sc program would not have been possible. Above all, I thank the Almighty God.

DEDICATION

*To my late Mom.
Your graceful life and your blissful death
finally unlocked the hidden dimensions of my life.*

Contents

Abstract	i
Acknowledgments	ii
Dedication	iv
Contents	vi
1 Introduction	1
1.1 Successes and Failures of DFT	2
1.2 The Band Gap Problem	3
1.3 Atomic Units	4
2 Theoretical Background	6
2.1 Electronic Structure Problem	6
2.2 Wave-Function Based Methods	9
2.2.1 The Hartree-Fock Formalism	9
2.2.2 Correlated Methods Beyond Hartree-Fock	13
2.3 Density-Functional Theory	13
2.3.1 The Thomas-Fermi (TF) Model	14
2.3.2 The Hohenberg-Kohn (HK) Theorem	15
2.4 The Kohn-Sham (KS) Scheme	17
2.5 Interpretation of Kohn-Sham energies	20
2.6 Failure of DFT for Band Gap Energies	20

2.7	Past Work on Correcting DFT Band Gap Energies	22
3	Functional Development	25
3.1	Exchange-Correlation Functionals	25
3.1.1	The Local-Density Approximation (LDA)	26
3.1.2	The Generalized-Gradient Approximation (GGA)	27
3.1.3	Meta-GGA (mGGA)	28
3.1.4	Hybrid Schemes	29
3.2	A New Density Functional	30
3.2.1	$X\alpha$ -Method	30
3.2.2	The Corresponding xc Energy E_{xc}	32
4	Methods	35
4.1	Basis Sets	35
4.1.1	Plane Waves	36
4.1.2	Pseudo-potentials	37
4.2	Methodology	40
5	Results, Discussion and Conclusion	42
5.1	Results	42
5.2	Discussion	48
5.3	Conclusion and Perspective	48
A	Hanke-Sham (HS) xc Potential	49
A.1	Green's Function and Self-Energy Operator	49
A.2	A Tight-Binding (TB) Model for the Self-Energy (Σ_{xc})	51
A.3	A v_{xc} for Insulators and Semiconductors	54
	Bibliography	57

CHAPTER 1

Introduction

Density-Functional Theory (DFT) is one of the most popular and successful Quantum Mechanics (QM) approach for large systems. It is a widely used methods for “*ab initio*” calculations of the structure of atoms, molecules, crystals, surfaces and their interactions. It is nowadays routinely applied for calculating e.g., the binding energy of molecules in chemistry and the band structure of solids in physics. First application relevant for fields traditionally considered more distant from quantum mechanics, such as biology and mineralogy are beginning to appear. Superconductivity, atoms in the focus of strong laser pulses, relativistic effects in heavy elements and in atomic nuclei, classical liquids, and magnetic properties of alloys have been studied with DFT[2].

The Hamiltonian for a real material consisting of N electrons and M nuclei is given by

$$H = \sum_{\alpha=1}^M \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\alpha} \frac{Z_{\alpha}e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \sum_{\alpha<\beta} \frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_0|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \quad (1.1)$$

Here \mathbf{R}_{α} , Z_{α} , and M_{α} represent the position, nuclear charge, and mass of the α -th nucleus and \mathbf{r}_i is the position of electron i . The variables m and e are the mass and charge (magnitude) of the electron. If we invoke the Born-Oppenheimer approximation in which nuclei masses are set to infinity, we arrive at the ‘electronic’

Hamiltonian for a system with nuclei fixed at positions \mathbf{R}_α

$$H_{\text{el}} = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i,j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{R}_\alpha|} \quad (1.2)$$

This Hamiltonian is then used in the Schrödinger equation:

$$H_{\text{el}}\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \quad (1.3)$$

and solved for the wave-function $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ and energy E . Here $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ represents the position \mathbf{r}_i and spin σ_i of the i th electron. Solving Eq. (1.3) is a formidable task for $N > 2$; in fact, there is no analytical solution in this case. Computational methods can be used but become increasingly difficult as N increases.

DFT is an attempt to determine the ground state energy of the system without the use of the wave-function (which depends on $4N$ variables) but using the ground state density. The ground state density depends on only four variables, irrespective of the number of electrons in the system.

DFT owes this versatility to the generality of its fundamental concepts and the flexibility one has in implementing them. In spite of this flexibility and generality, DFT is based on quite a rigid conceptual framework. The conceptual roots of DFT was formed in the Thomas-Fermi (TF) model, and was put on a firm theoretical footing by the two theorems of Hohenberg and Kohn. In practice, much of the success of DFT can be traced to the similarity between the *electron density* in a molecule and the electron density in a hypothetical substance known as the *uniform electron gas (UEG)* or *jellium*[3, 4]. The idea—the local density approximation (LDA) (see §§3.1.1)—is attractively simple: if we know the properties of jellium, we can understand the electron cloud in a molecule by dividing it into tiny chunks of density and treating each as a piece of jellium. This model allows one to focus on the effects in solids that occur due to the quantum nature of electrons and their mutual repulsive interactions (due to like charge) without explicit introduction of the atomic lattice and structure making up a real material. At zero temperature, the properties of jellium depend solely upon the constant electronic density. This lends it to a treatment within DFT; the formalism itself provides the basis for the LDA to the exchange-correlation energy density functional.

1.1 Successes and Failures of DFT

Although DFT is exact in principle, in practice, approximations have to be made. Different approximations give different degrees of accuracy—different levels of suc-

cesses and failures. Simple DFT approximations have the following problems:

- inability to describe van der Waals interaction,
- neglect of so-called strong correlations,
- inclusion of self interaction (i.e., the electron interacts with itself) and
- the band gap problem in which simple DFT approximations yield band gaps which are smaller than the correct ones.

In this thesis, we focus on solving the last problem, namely the band gap problem.

Band gaps are predicted to be too small with LDA and GGA. The so-called “band gap problem” has been one of the major issues during the development of density functionals. For example, the properties of bulk silicon are shown in Table 1.1, according to the LDA calculations^{1,2}. The LDA gives the correct crystal symmetry, and one can see from the table that the lattice constant is well reproduced. The bulk modulus also comes out very well. But the electronic band gap, which may be defined either as the difference between electron removal and electron addition energy, or as the difference between Kohn-Sham eigenvalues for the highest occupied and lowest unoccupied orbitals, comes out much poorer. Hybrid functionals clearly improve the situation. A problem is the description of materials with strong electron correlations. For LDA and GGA many insulating transition metal oxides are described as metals. This changes again for the hybrid functionals which turns them into anti-ferromagnetic insulators, which is a dramatic improvement.

Property	LDA	Expt.
lattice constant a (Å)	5.42	5.42
bulk modulus B (Mbar)	0.96	0.99
band gap (eV)	0.52	1.17

Table 1.1: Ground state properties of Si in the LDA compared to experiment.

1.2 The Band Gap Problem

For an insulating solid, the fundamental gap is a useful property to predict. This fundamental gap is defined as the difference between the ionization potential I and

¹S. Baroni and R. Resta, Phys. Rev B **33**, 7017 (1986).

²M. Hybertson and S. Louie, Phys. Rev. B **34**, 5390 (1986).

the electron affinity A for an extended system, $E_g = I - A$. This gap is related to the difference between total energies of states differing by one electron. For an electron added to the system in the state c ($\epsilon_c = E_{N+1} - E_N$) and removed from the system in the state v ($\epsilon_v = E_N - E_{N-1}$), $E_g = \epsilon_c - \epsilon_v = E_{N+1} + E_{N-1} - 2E_N$.

The Kohn-Sham (KS) band gap in DFT, defined as the difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) KS energies is not equal to the fundamental band gap, even with the exact xc[11]. In exact DFT, the HOMO energy computed with the exact xc functional is equal to the negative ionization potential, i.e., $I = -\epsilon_{HOMO}$ but the LUMO energy is not equal to the electron affinity A , even when the exact functional is used. For this reason, gaps in DFT are strongly underestimated (up to 50%)[7, 8].

In this thesis, we attempt to solve this problem (the band gap problem) by using an exchange-correlation (xc) potential proposed by Hanke and Sham (HS)[1] that includes a correction term to the LDA xc potential to calculate the band gap of some insulators and semiconductors. We use a slightly modified form of the HS potential by expressing it in terms of the electron density and its gradient. This new functional is now employed with the $X\alpha$ -method, a scheme which we call AUST scheme, to do the calculations in this thesis. There is obviously an improvement of this scheme over the LDA as Table 1.2 below reveals. This is therefore an evidence that this missing term is responsible for a large part of the band gap problem, at least in common semiconductors and insulators.

	Si	Ge	ZnO	MgO	LiF	GaAs
Band gaps:						
LDA	0.47	0.00	0.75	4.70	8.94	0.30
AUST Scheme	1.69	0.74	3.34	5.63	9.89	1.53
Experiment	1.17	0.74	3.44	7.83	14.20	1.52

Table 1.2: Calculated and LDA band gaps compared with experiment. All energies are in eV.

1.3 Atomic Units

In this thesis we work in Hartree atomic units[9] in which e^2 has the dimension of energy-length. So most formulas will be quoted in atomic units, with no explicit dimensional quantities (such as the ones written so far). In Hartree atomic units,

lengths are expressed in units of the bohr,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \equiv 0.529 \text{ \AA} \equiv 1 \text{ bohr} \quad (1.4)$$

and energies in units of the hartree,

$$1 \text{ hartree} \equiv \frac{e^2}{4\pi\epsilon_0 a_0} \equiv 27.2 \text{ eV} \quad (1.5)$$

In Hartree atomic units, $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ where, m_e is the mass of the electron, e is the electron charge and ϵ_0 is the permittivity of free space. Confusingly (not in this thesis), one also sees energies quoted in Rydberg atomic units. In Rydberg atomic units, $\hbar = 1$, $e^2 = 2$, $m_e = 1/2$ and $4\pi\epsilon_0 = 1$.

Observe that the Hartree is the Coulomb repulsion between two electrons separated by one bohr;

$$\frac{e^2}{4\pi\epsilon_0 a_0} = 1 \text{ Hartree} \quad (1.6)$$

while the Rydberg is the electron energy of the hydrogen atom

$$\frac{1}{2} \frac{m_e e^4}{(4\pi\epsilon_0 \hbar)^2} = 1 \text{ Rydberg} \quad (1.7)$$

CHAPTER 2

Theoretical Background

This chapter introduces the theoretical framework of density functional theory (DFT). We start from the Schrödinger equation and rewrite the problem of electron interactions into its DFT equivalent. In the end, the ground state electronic energy of a system of interacting electrons is shown to be given by a minimization over electron densities of a total electronic energy functional. There are many excellent review articles and textbooks giving a comprehensive treatment of DFT, for example *Refs* [10]-[15].

2.1 Electronic Structure Problem

A major goal of most electronic structure problems is to solve the non-relativistic time independent many-body Schrödinger equation

$$\hat{H}\Psi(\{\mathbf{x}_i\}, \{\mathbf{R}_A\}) = E\Psi(\{\mathbf{x}_i\}, \{\mathbf{R}_A\}) \quad (2.1)$$

where for a system containing N electrons and M nuclei, $\Psi(\{\mathbf{x}_i\}, \{\mathbf{R}_A\})$ is the wavefunction written with space-spin coordinates ($\{\mathbf{x}_i\} = \{\mathbf{r}_i, \sigma_i\}$, $i = 1, \dots, N$) (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i = \uparrow$ or \downarrow) and nuclei spatial coordinates ($\{\mathbf{R}_A\}$, $A = 1, \dots, M$). The Hamiltonian \hat{H} , is a sum of all possible interactions between electrons and nuclei. In atomic units (energy in Hartree and length in Bohr), \hat{H} can be written

as:

$$\hat{H} = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{\hat{T}_e(\mathbf{r})} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{\hat{T}_n(\mathbf{R})} + \underbrace{\sum_{i=1, j>i}^N \frac{1}{r_{ij}}}_{\hat{W}_{ee}(\mathbf{r})} + \underbrace{\sum_{A=1, B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{\hat{W}_{nn}(\mathbf{R})} - \underbrace{\sum_{i, A=1}^{N, M} \frac{Z_A}{r_{iA}}}_{\hat{V}_{ne}(\mathbf{r}, \mathbf{R})} \quad (2.2)$$

i and j run over the N electrons, whereas A and B run over the M nuclei. \hat{T}_e and \hat{T}_n are respectively the kinetic energy operators of the electrons and the nuclei. \hat{W}_{ee} is the potential operator describing the electrostatic electron-electron repulsion, \hat{W}_{nn} is the potential operator describing the electrostatic nucleus-nucleus repulsion and \hat{V}_{ne} is the potential operator describing the electrostatic Coulomb attraction between nuclei and electrons. M_A is the ratio of the mass of nucleus A to the mass of an electron and Z_A is the atomic number of nucleus A . The variable $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between electron i and j ; $R_{AB} \equiv |\mathbf{R}_A - \mathbf{R}_B|$ is the distance between nuclei A and B , and $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$ is the distance between electron i and nucleus A . The indices $j > i$ and $B > A$ in the third and fourth terms are necessary to prevent counting the same interaction twice.

In the usual model of matter, Eq. (2.1) which is deceptively simple by its form, has to be solved for M -nuclei and N -electrons but this task is enormously complex. However, a number of reasonable approximations has been put together to reduce the complexity. The first important approximation is the Born-Oppenheimer approximation which is obtained by decoupling the dynamics of the electrons and the nuclei.

The Born-Oppenheimer approximation[16], which is valid when the electrons reach equilibrium on a time scale that is short compared to the time scale on which the nuclei move, is based on the assumption that the nuclei are much heavier than the electrons. The approximation allows the dynamics of the electrons and nuclei to be approximately decoupled as such we get independent wave-function for nuclei Ψ_n and electrons Ψ_e , with energies E_n and E_e respectively. The Hamiltonian is split into corresponding terms, \hat{H}_n and \hat{H}_e . The interaction energy between the nuclei and electrons is placed in the electronic part. The result is

$$\Psi = \Psi_n \Psi_e, \quad \hat{H} = \hat{H}_n(\mathbf{R}) + \hat{H}_e(\mathbf{r}; \mathbf{R}) \quad (2.3)$$

$$\hat{H}_n \Psi_n = E_n \Psi_n, \quad \hat{H}_e \Psi_e = E_e \Psi_e \quad (2.4)$$

and

$$E = E_e + E_n \quad (2.5)$$

is the total energy. The nuclear part is uncomplicated to handle. We therefore concern ourselves with the electronic part, which describes interacting electrons that moves in a static external potential created by the charged nuclei, $v(\mathbf{r})$.

The electronic wave-function Ψ_e , depends on nuclear coordinates ($\{\mathbf{R}_A\}$) only parametrically now. Thus for a fixed configuration of the nuclei we suppress $\{\mathbf{R}_A\}$. This many-electron wave-function, $\Psi_e = \Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, describing the system's electronic states is subject to two conditions; they must be normalized

$$\langle \Psi_e | \Psi_e \rangle = \int \int \dots \int |\Psi_e|^2 d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N = 1 \quad (2.6)$$

and antisymmetric with respect to interchange of any two electrons i and j .

$$\Psi_e(\dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) = -\Psi_e(\dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots) \quad (2.7)$$

The state Ψ_e we are interested in is the ground state wave-function Ψ_0 with energy E_0 . It is the lowest energy solution to the electronic part of the Schrödinger equation Eq. (2.4).

The electronic part of the energy operator \hat{H}_e is conventionally split into a sum of three contributions: the kinetic energy of the electrons \hat{T} , the internal potential energy (the repulsion between individual electrons) \hat{W} , and the external potential energy (typically, the attraction between the electrons and nuclei) \hat{V} . We drop the subscripts for the sake of simplicity. It is also convenient to use \hat{F} for the total internal electronic energy, i.e., $\hat{T} + \hat{W}$:

$$\hat{H}_e = \hat{T} + \hat{W} + \hat{V} = \hat{F} + \hat{V} \quad (2.8)$$

i.e.,

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) \quad (2.9)$$

The electronic energy E_e can be calculated as the expectation value of the Hamiltonian,

$$\begin{aligned} E_e &= \langle \Psi_e | \hat{H}_e | \Psi_e \rangle = \langle \Psi_e | \hat{T} + \hat{W} + \hat{V} | \Psi_e \rangle = T + W + V \\ &= \int \int \dots \int \left(-\frac{1}{2} \sum_{i=1}^N \Psi_e^* \nabla_i^2 \Psi_e + \sum_{i<j}^N \frac{|\Psi_e|^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N |\Psi_e|^2 v_{\text{ext}}(\mathbf{r}_i) \right) \\ &\quad d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (2.10)$$

Here T , W and V are introduced as the individual scalar expectation values of the corresponding operators.

The Rayleigh-Ritz variational principle[17, 18] establishes that E_0 can be obtained through a search for the many-electron wave-function by the following minimization

$$E_0 = \min_{\Psi_e} \langle \Psi_e | \hat{H}_e | \Psi_e \rangle, \quad \text{has minimum for } \Psi_e = \Psi_0 \quad (2.11)$$

where the search is over all N -electron antisymmetric wave-functions Ψ_e , normalized to unity $\langle \Psi_e | \Psi_e \rangle = 1$. A direct application of the Rayleigh-Ritz variational method involves a search for the minimizing wave-function in the space of functions of a dimensionality proportional to the number of electrons in the system. In the following, we will not consider the wave-function based methods, where the many-electron wave-function is the key but the DFT approach which is based on a reformulation of the variational theorem to involve a search over only three-dimensional functions, i.e., electron densities.

2.2 Wave-Function Based Methods

As mentioned earlier, the fundamental quantity for the wave-function based methods is the many-electron wave-function, Ψ_e , whose correct functional form is far from simple. The first step in the determination of Ψ_e is often simply an *ansatz* (an educated guess) and then reliance on the variational principle. The variational principle says that we can use any normalized wave-function to calculate the expectation value of the electronic Hamiltonian (\hat{H}_e) and we are guaranteed to get an energy above the true ground-state (GS) energy i.e., $E[\Psi_e] \geq E_0[\Psi_0]$. The equality holds only when the wave-function Ψ_e is in the true GS (Ψ_0). The advantage of the variational principle is that starting with a trial wave-function we can approach the GS energy $E_0[\Psi_0]$ from above by variationally improving the quality of the wave-function. In the following, the variational principle will be applied to minimize the energy and obtain the Hartree-Fock equation and wave-function.

2.2.1 The Hartree-Fock Formalism

The Hartree-Fock (HF) approximation, or the mean-field approximation (also called self-consistent field approximation) introduces an approximation that sometimes allows to solve a certain physical problem analytically. The HF method is more about solving complex many-body problems numerically from the study of effective non-interacting particle model as it gives important insight into the properties of

many-electron systems. What is specific for the HF method is the *ansatz* used to represent a many-body wave-function.

Hartree proposed that a simple possible *ansatz* is to construct the many-body wave-function as a product of one-electron wave-functions ($\{\phi_i(\mathbf{x}_i)\}$)[19]

$$\Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N) \quad (2.12)$$

The one-electron functions $\phi_i(\mathbf{x}_i)$ are called spin orbitals, and are composed of a spatial orbital $\varphi_i(\mathbf{r})$ and one of the two spin functions, $\alpha(s)$ or $\beta(s)$.

$$\phi(\mathbf{x}) = \varphi(\mathbf{r})\sigma(s), \quad \sigma = \alpha, \beta \quad (2.13)$$

The spin functions have the important property that they are orthonormal, i.e., $\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$ and $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$. For computational convenience, the spin orbitals themselves are usually chosen to be orthonormal also:

$$\langle \phi_i(\mathbf{x}) | \phi_j(\mathbf{x}) \rangle = \int \phi_i^*(\mathbf{x})\phi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij} \quad (2.14)$$

The *ansatz* given by Eq. (2.12) leads to the Hartree product, not in use any more, because it neglects an important property of electrons – that they are Fermi particles, and the wave-function of a system of identical fermions must be antisymmetric with respect to interchange of any pair of particles according to Eq. (2.7). Obviously, the antisymmetric requirement is not satisfied by Eq. (2.12). But we can easily force the wave-function to obey Eq. (2.7) as proposed by Fock[20]. To do this, we simply take products like (2.12), interchange their positions of all particles pairwise and construct the combinations which are *a priori* anti-symmetric. This is easy to do for two particles:

$$\Psi_e(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) - \phi_1(\mathbf{x}_2)\phi_2(\mathbf{x}_1)] = -\Psi_e(\mathbf{x}_2, \mathbf{x}_1) \quad (2.15)$$

The factor $1/\sqrt{2}$ is introduced to preserve the normalization. In this way, the Pauli exclusion principle is also satisfied.

Generally, if there are N electrons, then there are $N!$ possibilities to interchange every two electrons and write down antisymmetric terms like in Eq. (2.15). This results in a fully antisymmetric wave-function:

$$\Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \cdot \phi_{P1}(\mathbf{x}_1)\phi_{P2}(\mathbf{x}_2) \cdots \phi_{PN}(\mathbf{x}_N) \quad (2.16)$$

P runs over all permutations of electrons, $(-1)^P = 1$ for even permutations and $(-1)^P = -1$ for odd permutations of the labels $1, 2, \dots, N$. It is common and

convenient to write down the wave-functions as determinants, because Eq. (2.16) is similar to how the determinant of a matrix is determined;

$$\Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix} \quad (2.17)$$

The wave-function of this form is called a *Slater determinant*¹. In the Slater determinant each of the columns are labeled by spin orbitals and exchange of two electron coordinates will interchange two columns in the determinant, thus satisfying the anti-symmetric requirement by introducing a negative sign.

Now using the HF wave-function the electronic energy can be written as,

$$E_e^{\text{HF}} = \langle \Psi_e^{\text{HF}} | \hat{H}_e | \Psi_e^{\text{HF}} \rangle = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (2.18)$$

where

$$h_i = \int \phi_i^*(\mathbf{x}) \left[-\frac{1}{2} \nabla^2 + V(\mathbf{x}) \right] \phi_i(\mathbf{x}) \, d\mathbf{x} \quad (2.19)$$

$$J_{ij} = \iint \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{x}) \phi_i(\mathbf{x}') \, d\mathbf{x} d\mathbf{x}' \quad (2.20)$$

$$K_{ij} = \iint \phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{x}) \phi_i(\mathbf{x}') \, d\mathbf{x} d\mathbf{x}' \quad (2.21)$$

These integrals are all real, and $J_{ij} \geq K_{ij} \geq 0$. The J_{ij} are called Coulomb integrals, the K_{ij} are called exchange integrals. The above equation can be treated as an energy functional, $E^{\text{HF}}[\{\phi_i^*(\mathbf{x})\}, \{\phi_i(\mathbf{x})\}]$, and can be minimized variationally by applying Lagrange undetermined multiplier under the constraint that the spin orbitals $\{\phi_i(\mathbf{x})\}$ remain orthonormal, i.e., $\langle \phi_i(\mathbf{x}) | \phi_j(\mathbf{x}) \rangle = \delta_{ij}$. This leads to a mapping from a complex N -electron Schrödinger equation into effective one-electron Schrödinger-like equations.

$$\hat{F}_i \phi_i(\mathbf{x}_i) = \epsilon_i \phi_i(\mathbf{x}_i), \quad \hat{F}_i = -\frac{1}{2} \nabla^2 + V(\mathbf{x}_i) + V_{\text{H}}(\mathbf{x}_i) + V_{\text{x}}(\mathbf{x}_i) \quad (2.22)$$

\hat{F}_i represents a one-electron Hamiltonian, known as the Fock operator while ϵ_i and ϕ_i are the corresponding eigenvalues and eigenvectors, respectively. The first two terms in \hat{F}_i are, respectively, the kinetic energy of an electron and the external

¹That is, if we are dealing with non-degenerate states. Otherwise the wave-function might be a limited linear combination of Slater determinants.

potential. The external potential, $V(\mathbf{x}_i)$, is typically the Coulomb attraction on the i^{th} electron due to all the nuclei. The third and fourth terms approximately account for the many-body electron-electron interactions. $V_{\text{H}}(\mathbf{x}_i)$ is the Hartree potential, which is the Coulomb repulsion between the i^{th} electron and the electron density produced by the remaining $N - 1$ electrons

$$V_{\text{H}}(\mathbf{x}_i) = \int \frac{n(\mathbf{x}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{x}_j, \quad n(\mathbf{x}_j) = \sum_{j=1}^N |\phi_j(\mathbf{x}_j)|^2 \quad (2.23)$$

The fourth term solely appears from the anti-symmetric nature of the wave-function and is known as exchange potential ($V_{\text{x}}(\mathbf{x}_i)$). Unlike $V(\mathbf{x}_i)$ and $V_{\text{H}}(\mathbf{x}_i)$, $V_{\text{x}}(\mathbf{x}_i)$ does not have any classical analogy, and it can only be written as an integral operator

$$V_{\text{x}}(\mathbf{x}_i)\phi_i(\mathbf{x}_i) = \left[\sum_{j=1}^N \int \phi_j^*(\mathbf{x}_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \phi_i(\mathbf{x}_i) d\mathbf{x}_j \right] \phi_j(\mathbf{x}_j) \quad (2.24)$$

As evident from the equation above, $V_{\text{x}}(\mathbf{x}_i)$ leads to an exchange of the variable in the two spin orbitals. Furthermore, the exchange operator, $V_{\text{x}}(\mathbf{x}_i)$ is said to be a non-local operator, as the results of $V_{\text{x}}(\mathbf{x}_i)$ operating on the spin orbital $\phi_i(\mathbf{x}_i)$ will depend on the value of $\phi_i(\mathbf{x}_i)$ throughout all space. Also worth mentioning is that for $i = j$, we have the important equality $J_{ii} = K_{ii}$, and so, by construction, the HF method is self-interaction-free. Eq. (2.22) is the usual form of the HF equation, which is a linear eigenvalue problem and must be solved self consistently. The HF method is used extensively to study various materials science problems, such as adsorption[21], defects in solids[22], and electronic structure of insulators[23].

A major drawback, though, lies in the effective mean-field treatment of the Coulomb repulsion between electrons, which provides an inaccurate description of the spatial separation of the electrons as it would be in a complete many-electron interaction. This missing part is widely designated as *electron correlation*[24]. Indeed, the difference between the ground-state HF energy and the exact ground-state energy is used as the standard definition of the correlation energy in *quantum chemistry*. The *correlation* energy is typically a small fraction of the total energy. However, it can be a very important contribution to many systems of physical and chemical interest. For example, the restricted HF method cannot describe the dissociation of H_2 into two open-shell H atoms. Or, at least one quarter of the strength of hydrogen bonds between water molecules comes from correlations beyond HF. In the following we will briefly describe some of the methods which explicitly calculate the electron correlation.

2.2.2 Correlated Methods Beyond Hartree-Fock

In quantum chemistry, methods beyond HF aim to improve on HF by taking account of electron correlation. Most of these methods require more flexible wave-functions than that of a single determinant HF and usually it is obtained by means of excitations of electrons from occupied to virtual orbitals. These methods include configuration interaction (CI), Møller-Plesset perturbation theory, and coupled cluster. For CI methods, a linear combination of ground-state and excited-state Slater determinants is used rather than a single Slater determinant in HF to approximate the wave-function. Møller-Plesset perturbation theory, as the name suggests, treat electron correlation in a perturbative manner. And in the coupled cluster method, the electron correlation is handled through use of a so-called cluster operator. None of these methods was used in this thesis, so they will not be discussed any further.

2.3 Density-Functional Theory

Density-Functional Theory (DFT) differs from the wave-function based methods by using the electron density $n(\mathbf{r})$ as the central quantity. An important advantage of using the electron density over the wave-function is the much reduced dimensionality. Regardless of how many electrons one has in the system, the density is always three-dimensional. This enables DFT to be readily applied to much larger systems, hundreds or even thousands of atoms become possible. Partly for this reason, DFT has become the most widely used electronic structure approach today, particularly in the condensed matter physics community.

The electron density $n(\mathbf{r})$ is defined as the number of electrons per volume at the point \mathbf{r} in space. It is a physical quantity – it can (at least in theory) be measured. The integral of the electron density gives the total number of electrons,

$$\int n(\mathbf{r})d\mathbf{r} = N \quad (2.25)$$

The relation between $n(\mathbf{r})$ and the many-electron wave-function Ψ_e is

$$n(\mathbf{r}) = N \int \int \cdots \int |\Psi_e(\mathbf{r}\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (2.26)$$

where $\{\mathbf{x}_i\}$ represents both spin and spatial coordinates. $n(\mathbf{r})$ determines the probability of finding any of the N electrons with arbitrary spin in a region $d\mathbf{r}$ around \mathbf{r} while the other $N - 1$ electrons have arbitrary positions and spin in the state represented by Ψ_e .

If one looks at the three terms in the expression for the electronic energy Eq. (2.10), one sees that the term for the external potential V is easily rewritten in terms of the density,

$$\begin{aligned} V &= \int \int \cdots \int \sum_{i=1}^N |\Psi_e|^2 v_{\text{ext}}(\mathbf{r}_i) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= \frac{1}{N} \sum_{i=1}^N \int n(\mathbf{r}_i) v_{\text{ext}}(\mathbf{r}_i) d\mathbf{r}_i = \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2.27)$$

The other two terms of the electronic energy Eq. (2.10) are not as easy to rewrite. In the kinetic energy term T , the derivative operator between the wave-functions prevents rewriting the integrand in the form $|\Psi_e|^2$ as needed to turn the term into an expression of the electron density. In the potential energy term W , the particle positions in the denominator preclude a direct term by term integration.

A *functional* is an object that acts on a function to produce a scalar². From the way the potential energy term V was written in Eq. (2.27), it is an explicit potential energy functional $V[n]$ of the electron density. This and other functionals with the electron density $n(\mathbf{r})$ as arguments are called *density functionals*. The other terms in the electronic energy Eq. (2.10) are not in explicit density functional form, but can at least be written as functionals of the many-electron wave-function Ψ_e ³.

$$E_e = T[\Psi_e] + W[\Psi_e] + V[v_{\text{ext}}, n] = F[\Psi_e] + V[v_{\text{ext}}, n] \quad (2.28)$$

At this point, we ask a very important question central to DFT: *is it possible to also rewrite the total internal electronic energy $F[\Psi_e]$ as a density functional $F[n]$?* If such a functional exists, it is a *universal functional* in that it is independent of the external potential. *The same $F[n]$ may be used for all electronic structure problem.* The question of the existence of an $F[n]$ functional will be considered in the following.

2.3.1 The Thomas-Fermi (TF) Model

Early attempts to express the total internal energy as a density functional was first exploited in 1927 by Thomas and Fermi[25, 26]. They used some assumptions about the distribution and the interaction between electrons to approximate the kinetic

²Functionals are usually denoted with square brackets [].

³We will henceforth use $V[v, n]$ in place of $V[v_{\text{ext}}, n]$ for the sake of convenience, unless where it is otherwise necessary to write this full form.

energy while treating the electron-nucleus and electron-electron interactions in a classical manner. The electron density in each space point is set equal to a number of electrons in a fixed volume, $n(\mathbf{r}) = \Delta N / \Delta V$. A system of ΔN free non-interacting electrons in an infinite-well model of volume ΔV then gives an expression for the kinetic energy per volume. The continuity limit is then taken $\Delta V \rightarrow 0$. The result is integrated over the whole space to give the approximate *Thomas-Fermi functional* for the total kinetic energy $T_{\text{TF}}[n]$,

$$T \approx T_{\text{TF}}[n] = \frac{3}{10} (3\pi)^{2/3} \int n^{5/3}(\mathbf{r}) \, d\mathbf{r} \quad (2.29)$$

Furthermore, the *electrostatic energy of a classical repulsive gas* $J[n]$ is used as a simplistic approximation of the internal potential energy W ,

$$W \approx J[n] = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \quad (2.30)$$

The result is the *Thomas-Fermi model*:

$$E_e \approx T_{\text{TF}} + J[n] + V[v, n] \quad (2.31)$$

The Thomas-Fermi approximation to the internal electronic energy is thus

$$F[n] = T_{\text{TF}}[n] + J[n] \quad (2.32)$$

2.3.2 The Hohenberg-Kohn (HK) Theorem

The early efforts to find and use internal electronic energy functionals $F[n]$ by Thomas and Fermi, and extensions along the same ideas, were all based on ‘reasonable’ approximations. The work of Hohenberg and Kohn[27] was based on a more rigorous theoretical framework. Here we examine the two famous theorems which follows from the work of Hohenberg and Kohn:

HK I: *The first Hohenberg-Kohn theorem states that the ground state electron density $n(\mathbf{r})$ determines the external potential of a system $v_{\text{ext}}(\mathbf{r})$ up to an arbitrary additive constant (which only sets the absolute energy scale).*

The proof proceeds by *reductio ad absurdum*. Assume that there exists two local potentials $v_{\text{ext}}(\mathbf{r})$ and $v'_{\text{ext}}(\mathbf{r})$ differing by more than an additive constant, $v_{\text{ext}}(\mathbf{r}) \neq v'_{\text{ext}}(\mathbf{r}) + \text{const}$, and giving rise to the same ground-state density, $n(\mathbf{r})$. Obviously, $v_{\text{ext}}(\mathbf{r})$ and $v'_{\text{ext}}(\mathbf{r})$ belong to distinct Hamiltonians $\hat{H} = \hat{T} + \hat{W} + \hat{V}$ and $\hat{H}' =$

$\hat{T} + \hat{W} + \hat{V}'$ which give rise to non-degenerate ground-state wave-functions⁴ Ψ and Ψ' . Using the Rayleigh-Ritz variational principle, and the fact that Ψ and Ψ' have the same density $n(\mathbf{r})$, we arrive at the following inequality

$$\begin{aligned} E_0 &< \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E'_0 + \int n(\mathbf{r}) [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (2.33)$$

where E_0 and E'_0 are the ground-state energies for \hat{H} and \hat{H}' , respectively. Similarly, we can get

$$\begin{aligned} E'_0 &< \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &= E_0 - \int n(\mathbf{r}) [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (2.34)$$

Adding Eqs. (2.33) and (2.34), we get

$$E_0 + E'_0 < E'_0 + E_0 \quad (2.35)$$

which is clearly a contradiction. We therefore conclude that, for systems without degenerate GS, there cannot exist two local potentials differing by more than an additive constant which have the same GS density.

Thus the GS density $n(\mathbf{r})$ determines the potential $v_{\text{ext}}(\mathbf{r})$, which in turn determines the Hamiltonian, and thus everything about the many-body problem. In other words, the potential v_{ext} is a unique (up to an additive constant) functional of the GS density n . This means that all GS properties of the system are also consequently determined since in theory anything can be calculated from the external potential. For instance, the GS wave-function Ψ_0 is also a GS property of the system and can therefore be considered to be a functional of the GS density $\Psi_0[n]$.

The existence of the total energy functional $E_e[n]$ and an internal electronic energy functional directly follows as

$$\begin{aligned} E_e[n] &= \langle \Psi_0[n] | \hat{H}_e | \Psi_0[n] \rangle \\ &= \langle \Psi_0[n] | \hat{T} + \hat{W} + \hat{V} | \Psi_0[n] \rangle \\ &= F_{\text{HK}}[n] + V[v, n] \end{aligned} \quad (2.36)$$

where

$$F_{\text{HK}}[n] = F[\Psi_0[n]] = T[n] + W[n] \quad (2.37)$$

Here note that $F_{\text{HK}}[n]$ is only dependent on $n(\mathbf{r})$ and independent of any external potential $v(\mathbf{r})$. Thus $F_{\text{HK}}[n]$ is a universal functional of $n(\mathbf{r})$.

⁴For degenerate systems see the article by M. Levy, Phys. Rev. A **26**, 1200 (1982).

HK II: The second Hohenberg-Kohn theorem states that the total energy density functional $E_e[n]$ satisfies a variational property: the GS energy E_0 of the system considered is obtained by minimizing this functional with respect to N -electron densities n .

$$E_0 = \min_n \left\{ F[n] + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\} \quad (2.38)$$

with the minimum being reached for the exact GS density $n_0(\mathbf{r})$. We can express this as $E_0[n_0] \leq E_e[n]$.

The proof follows straightforwardly from the first theorem. Suppose Ψ is the GS wave-function corresponding to the unique GS density $n_0(\mathbf{r})$ then we define the energy of the GS by

$$E_0 = E_e[n_0] = \langle \Psi | \hat{H}_e | \Psi \rangle$$

If there is another wave-function Ψ' with an arbitrary variation from Ψ and its electron density is $n'(\mathbf{r})$, then we can obtain

$$\begin{aligned} E_0 = E_e[n_0] &= \langle \Psi | \hat{H}_e | \Psi \rangle \\ &< \langle \Psi' | \hat{H}_e | \Psi' \rangle = E_e[n'] \end{aligned} \quad (2.39)$$

So it follows that the correct density that minimizes the energy is the GS density.

The many-electron problem has thus been rewritten into what looks like a straightforward minimization with respect to a three-dimensional quantity $n(\mathbf{r})$. Yet the functional form of $F_{\text{HK}}[n]$ is not known and this poses a serious challenge for practical applications. The major part of the complexities of the many-electron problem are associated with the determination of the universal functional $F_{\text{HK}}[n]$.

2.4 The Kohn-Sham (KS) Scheme

Soon after the original Hohenberg-Kohn paper on DFT, Kohn and Sham[28] recognized that the failure of TF theory mainly resulted from the bad description of the kinetic energy. So they proposed a method (similar to the Hartree-Fock approach) for computing the main contribution to the kinetic energy functional to good accuracy, the *Kohn-Sham method*. Their idea was to map the system of many interacting electrons on to an auxiliary system of *non-interacting Kohn-Sham particles*. These particles behave as non-interacting electrons. By non-interacting electrons we refer to fictitious particles that do not interact with each other by Coulomb forces (W switched off). The particles are still regarded as indistinguishable fermions.

The first step is to write the functional form of $F_{\text{HK}}[n]$ as a sum of the kinetic energy of non-interacting electrons $T_s[n]$, the Hartree energy which is the electrostatic energy of a classical repulsive gas $J[n]$ as it was defined in the section about Thomas-Fermi model, and all the many-body quantum effects are put together into the exchange and correlation energy $E_{\text{xc}}[n]$. So the energy functional becomes

$$\begin{aligned} E_e[n] &= F_{\text{HK}}[n] + V[v, n] \\ &= T_s[n] + J[n] + E_{\text{xc}}[n] + V[v, n] \end{aligned} \quad (2.40)$$

The DFT variational principle for the GS electronic energy E_0 in Eq. (2.38) can be expressed in the new quantities,

$$E_0 = \min_n (T_s[n] + J[n] + E_{\text{xc}}[n] + V[v, n]) \quad (2.41)$$

In the language of variational calculus this energy minimization can be rewritten as a *stationary condition* for the electron density⁵

$$\frac{\delta T_s[n]}{\delta n} + \frac{\delta J[n]}{\delta n} + \frac{\delta E_{\text{xc}}[n]}{\delta n} + \frac{\delta V[v, n]}{\delta n} = 0 \quad (2.42)$$

Now we look at what the above relations correspond to when DFT is applied to the system of non-interacting KS particles. The DFT variational principle becomes

$$E_s = \min_n (T_s[n] + V[v_{\text{eff}}, n]) \quad (2.43)$$

where we use E_s as the GS energy of the system of KS particles and $v_{\text{eff}}(\mathbf{r})$ is the potential in which they move. The stationary condition becomes

$$\frac{\delta T_s[n]}{\delta n} + \frac{\delta V[v_{\text{eff}}, n]}{\delta n} = 0 \quad (2.44)$$

A comparison between the stationary conditions of the interacting and non-interacting systems Eqs. (2.42) and (2.44), shows that the same stationary $n(\mathbf{r})$ is described if

$$\frac{\delta V[v_{\text{eff}}, n]}{\delta n} = \frac{\delta V[v_{\text{ext}}, n]}{\delta n} + \frac{\delta J[n]}{\delta n} + \frac{\delta E_{\text{xc}}[n]}{\delta n} \quad (2.45)$$

The functional derivatives are calculated on both sides to give

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) \quad (2.46)$$

⁵The functional derivative $\delta F[n]/\delta n(\mathbf{r})$ is defined so that the first order change in the functional due to a change in its argument $n(\mathbf{r})$ is:

$$\delta F = \int d\mathbf{r} \frac{\delta F}{\delta n(\mathbf{r})} \delta n(\mathbf{r})$$

where $v_{\text{xc}}(\mathbf{r})$ is the exchange-correlation potential defined as:

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n} \quad (2.47)$$

This leads to the central equation in KS DFT which is the one-electron Schrödinger-like equation expressed as:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}} \right] \phi_i = \epsilon_i \phi_i \quad (2.48)$$

Here $\{\phi_i\}$ are the KS one-electron orbitals and the electron density is defined as,

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i|^2 \quad (2.49)$$

The ϵ_i 's are the energies of the KS one-electron orbitals. Clearly this is a Hartree-Fock-like single particle equation which needs to be solved iteratively.

The definition of v_{eff} Eq. (2.46) is inserted into the expression for the $V[v, n]$ functional Eq. (2.27) to derive a relation between the energies of the two systems. By identifying the terms in the relation and the energy of the non-interacting (KS) system as $E_s = \sum_{i=1}^N \epsilon_i = T_s + V_s$, the result can be written as

$$E_0 = E_s - J[n] + E_{\text{xc}}[n] - V[v_{\text{xc}}, n] \quad (2.50)$$

Equations (2.46) – (2.49) are the celebrated KS equations. We observe that v_{eff} depends on $n(\mathbf{r})$ through Eq. (2.49). So the KS equations must be solved self-consistently. The general approach is to start with an initial guess for $n(\mathbf{r})$, calculate the corresponding v_{eff} from Eq. (2.46) and then solve Eq. (2.48) for the KS orbitals. From these orbitals, we construct a new density using Eq. (2.49) and repeat the process until convergence is reached. Finally, the total energy will be calculated from Eq. (2.50) with the converged solution for the electron density. If each term in the Kohn-Sham energy functional was known, we would be able to obtain the exact ground state density and total energy. Unfortunately, there is one unknown term, the exchange-correlation (xc) functional (E_{xc}). E_{xc} includes the non-classical aspects of the electron-electron interaction along with the component of the kinetic energy of the real system different from the fictitious non-interacting system. Since E_{xc} is not known exactly, it is necessary to approximate it, which is the focus of §3.1.

2.5 Interpretation of Kohn-Sham energies

The Kohn-Sham eigenvalues, introduced as Lagrange multipliers, have no direct physical meaning, at least not that of the energies to add or subtract electrons from the interacting many-body system. The exception is the highest eigenvalue in a finite system which is minus the ionization energy.

Nevertheless, the eigenvalues have a well defined meaning within the theory and can be used to construct physically meaningful quantities. For example, they can be used to develop perturbation expressions for excitation energies, either in the form of a functional or in the form of explicit many-body calculations that use the Kohn-Sham eigenfunctions and eigenvalues as an input.

Within the Kohn-Sham scheme, the meaning of the eigenvalues, known as Janak's theorem, is that the eigenvalue is the derivative of the total energy with respect to the occupation of a state[30]:

$$\epsilon_i = \frac{\partial E}{\partial n_i} \quad (2.51)$$

2.6 Failure of DFT for Band Gap Energies

We have already mentioned (in §1.2) the inaccuracy of LDA when determining the band gap of insulators and semiconductors. This failure is intimately related to the non-analytical behaviour of the xc energy functional, as shown by J.P. Perdew and M. Levy and by L.J. Sham and M. Schlüter[31, 32]. To see this, we begin by applying Janak's theorem for the case of the HOMO for a fractional electron number $\mathcal{N} = N - \delta$ where $\delta \rightarrow 0+$, i.e.,

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N-\delta} = \epsilon_H^{N-\delta} = \epsilon_H^N \quad (2.52)$$

where ϵ_H^N is the HOMO energy of the N -electron system (here, the HOMO is the N^{th} orbital). We define ϵ_H^N as the limit when N is approached from the left (electron-deficient) side which implies that

$$\epsilon_H^N = -I_N \quad (2.53)$$

i.e., the energy of the HOMO KS orbital is the opposite of the exact ionization energy.

Similarly, Janak's theorem for the HOMO but now for a fractional electron number $\mathcal{N} = N + \delta$ where $\delta \rightarrow 0+$ gives

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N+\delta} = \epsilon_H^{N+\delta} \quad (2.54)$$

where $\epsilon_H^{N+\delta}$ is the HOMO energy from the right (excess-electron) side of the discontinuity (here, the HOMO is the $(N+1)^{\text{th}}$ orbital). Since the derivative is in fact the same for all $N < \mathcal{N} < N+1$, it is also the HOMO energy of the $(N+1)$ -electron system, $\epsilon_H^{N+\delta} = \epsilon_H^{N+1-\delta} = \epsilon_H^{N+1}$ and so we have

$$\epsilon_H^{N+1} = -A_N \quad (2.55)$$

One may naively think that $\epsilon_H^{N+\delta}$ is equal to the LUMO energy of the N -electron system ϵ_L^N (again defined as the limit from the left side, $\epsilon_L^N = \epsilon_L^{N-\delta}$, i.e., the $(N+1)^{\text{th}}$ orbital), and therefore that the LUMO KS energy equals to the opposite of the electron affinity. However, this is not the case. Let us compare $\epsilon_H^{N+\delta}$ that we can write as

$$\epsilon_H^{N+\delta} = \int \phi_H^{N+\delta}(\mathbf{r})^* \left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{N+\delta}(\mathbf{r}) \right) \phi_H^{N+\delta}(\mathbf{r}) d\mathbf{r} \quad (2.56)$$

with $\epsilon_L^{N-\delta}$ that we can write as

$$\epsilon_L^{N-\delta} = \int \phi_L^{N-\delta}(\mathbf{r})^* \left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{N-\delta}(\mathbf{r}) \right) \phi_L^{N-\delta}(\mathbf{r}) d\mathbf{r} \quad (2.57)$$

The problem is that there is nothing preventing the KS potential to have a discontinuity $v_{\text{eff}}^{N+\delta}(\mathbf{r}) \neq v_{\text{eff}}^{N-\delta}(\mathbf{r})$. Indeed, the continuity of the density implies that $n^{N+\delta}(\mathbf{r}) = n^{N-\delta}(\mathbf{r})$, but this only imposes that $v_{\text{eff}}^{N+\delta}(\mathbf{r})$ and $v_{\text{eff}}^{N-\delta}(\mathbf{r})$ be equal up to an arbitrary additive constant (according to Hohenberg-Kohn theorem). So we can have:

$$v_{\text{eff}}^{N+\delta}(\mathbf{r}) - v_{\text{eff}}^{N-\delta}(\mathbf{r}) = \Delta_{\text{xc}}^N \quad (2.58)$$

where Δ_{xc}^N is independent of \mathbf{r} . Since the two potentials just differ by an additive constant, the orbitals are continuous at the integer N , and in particular $\phi_H^{N+\delta}(\mathbf{r}) = \phi_L^{N-\delta}(\mathbf{r})$. Using this fact and Eq. (2.58), we find

$$\begin{aligned} \epsilon_H^{N+\delta} &= \int \phi_L^{N-\delta}(\mathbf{r})^* \left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{N-\delta}(\mathbf{r}) \right) \phi_L^{N-\delta}(\mathbf{r}) d\mathbf{r} + \Delta_{\text{xc}}^N \\ &= \epsilon_L^{N-\delta} + \Delta_{\text{xc}}^N \end{aligned} \quad (2.59)$$

Thus, the LUMO energy of the N -electron system is not the opposite of the exact electron affinity

$$\epsilon_L^N = -A_N - \Delta_{\text{xc}}^N \quad (2.60)$$

due to the possible discontinuity Δ_{xc}^N in the KS potential.

Such a discontinuity can only come from the xc part of the potential $v_{\text{xc}}^{\mathcal{N}}(\mathbf{r})$ since $v(\mathbf{r})$ is independent of \mathcal{N} and the Hartree potential $v_H^{\mathcal{N}}(\mathbf{r}) = \int d\mathbf{r}' n^{\mathcal{N}}(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ is

a continuous function of \mathcal{N} . So, we have

$$\Delta_{\text{xc}}^N = v_{\text{xc}}^{N+\delta}(\mathbf{r}) - v_{\text{xc}}^{N-\delta}(\mathbf{r}) = \left(\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right)_{N+\delta} - \left(\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right)_{N-\delta} \quad (2.61)$$

i.e., Δ_{xc}^N is the *derivative discontinuity* in the exchange-correlation energy functional $E_{\text{xc}}[n]$. Theoretical and numerical examples show that this discontinuity does exist[33, 34].

The fundamental gap of the N -electron system is defined as

$$E_{\text{gap}}^N = I_N - A_N \quad (2.62)$$

Using Eqs. (2.53) and (2.60), it can be expressed as

$$E_{\text{gap}}^N = \epsilon_L^N - \epsilon_H^N + \Delta_{\text{xc}}^N \quad (2.63)$$

i.e., the difference between the LUMO and HOMO energies which defines the KS gap, $E_{\text{gap}}^{\text{KS},N} = \epsilon_L^N - \epsilon_H^N$, is not equal to the exact fundamental gap of the system. The difference comes from the derivative discontinuity Δ_{xc}^N . In practice, this last term can represent an important contribution to the fundamental gap as it is absent by construction from any current approximated functional (be it LDA or gradient-corrected or more complex). This xc discontinuity Δ_{xc} is therefore the main cause of the difference between the experimental gaps and those given by LDA. In fact, Δ_{xc} accounts for about 80% of the LDA band gap error for typical insulators and semiconductors as confirmed by Knorr and Godby for a family of model semiconductors[35]. In this case, the exact potential $v_{\text{eff}}(\mathbf{r})$ (and hence, the exact $E_{\text{gap}}^{\text{KS}}$) was calculated by imposing the reproduction of quantum Monte-Carlo densities. Again $\Delta_{\text{xc}} = E_{\text{gap}}^{\text{KS}} - E_{\text{gap}} \neq 0$, accounting for 80% of the LDA error $E_{\text{gap}} - E_{\text{gap}}^{\text{LDA}}$.

2.7 Past Work on Correcting DFT Band Gap Energies

The essence of this section is to illustrate the growth in literature theories on correcting DFT band gap energies. In this regard therefore, this section has been broken down into the conceptual framework of theoretical and empirical literature that are related to the topic under study.

Perdew, Parr, Levy and Balduz[36] showed that the exact KS xc potential $v_{\text{xc}}(\mathbf{r})$ of an open system may jump discontinuously as the particle number crosses an

integer, with important physical consequences. One of such consequences is the underestimation of band gaps in common semiconductors and insulators. Perdew and Levy[31] argued that the underestimation of the gap width is due to the derivative discontinuities of the xc energy. So they emphasized the need for an energy-dependent potential in band theory even though the center of the gap was exactly predicted by the KS band structure.

Godby, Schlüter and Sham[52] obtained an accurate $v_{xc}(\mathbf{r})$ for silicon from the calculations of self-energy Σ and showed that the correct gap in Si may be obtained from DFT if the discontinuity in v_{xc} is taken into consideration. Later they showed how to calculate v_{xc} of a semiconductor from the self-energy operator Σ . See Ref. [37]. They discussed the nature of v_{xc} and investigated the features and trends found in some semiconductors and concluded that 80% of the LDA band-gap error could be accounted for by the discontinuity Δ_{xc} in v_{xc} upon the addition of an electron.

Hybertsen and Louie[6] presented a first-principles theory of the quasiparticle energies in semiconductors and insulators described in terms of the electron self-energy operator within the GW approximation. The calculated indirect band gaps they obtained for diamond, Si, and Ge were within 0.20 eV of experimental values. The calculated direct gap for LiCl was within 5% of experiment. Thus their theory was found to be suitably applicable to systems ranging from relatively small gap semiconductors (Ge) to wide gap ionic compounds (LiCl) with features extending across the entire range.

In the article by Hanke and Sham[1], a tight-binding model for the self-energy Σ_{xc} was presented and an xc potential v_{xc} and a band-gap correction was derived from this model. This xc potential derived from Σ_{xc} , scales with $n^{1/3}$ and depends analytically on the solid-state parameters ω_p , the plasma frequency, and E_p , the Penn gap. In this article, the band gap correction due to v_{xc} discontinuity was found to account for the band gap underestimation both in the small-gap semiconductors and the large-gap insulators.

In their 2006 paper, Grüning, Marini and Rubio[65] addressed the band gap problem in the standard KS scheme for small-gap semiconductors (Si), large-gap insulators (LiF), and noble-gas solids (Ar) using a method that show that the derivative discontinuity contributes by as much as 30%–50% to the energy gap. Chan and Ceder[38] proposed an efficient method for the prediction of fundamental band gaps in solids using DFT. Their method, the Δ -sol method which is based on total energy differences and derived from dielectric screening properties of electrons was

demonstrated to be a viable method for band gap prediction in solids.

Tran and Blaha^[64] used a modified version of the xc potential proposed by Becke and Johnson [J. Chem. Phys. **124**, 221101 (2006)] to calculate band gaps of some insulators and semiconductors. They observed that their modified Becke and Johnson (MBJLDA) scheme was in good agreement with experiment for all types of solids (wide gap insulators, small gap insulators and strongly correlated transition-metal oxides) considered. The accurate band gaps (within 5% of experimental values) they obtained for insulators and semiconductors with an orbital-independent xc potential that is solely dependent on semilocal quantities was the first of its kind to compete in accuracy with the more expensive hybrid and GW methods.

Functional Development

As has been said, density-functional theory (DFT) is the most popular theoretical approach for determining the electronic structures of many-body systems. Despite its enormous success, questions like how good DFT is for band gaps in semiconductors and insulators or what the best exchange-correlation (xc) functional is for treating band gaps cannot be avoided by developers and practitioners of Kohn-Sham DFT. As vague and imprecise as these questions may be, it is nonetheless important to answer them, once of course, terms like “good” and “best” have been defined and consideration made to the properties of interest (energetic, structural, dynamic, electronic).

In this chapter, the concepts and form of exchange-correlation functional are discussed. We also consider the $X\alpha$ -method, all of which forms the basis for the development of the functional that we use for calculating the band gap energies of some selected materials in this thesis.

3.1 Exchange-Correlation Functionals

For practical use of the Kohn-Sham equations we must know what the form of the exchange-correlation energy functional is. However, the exact form of E_{xc} is not known and may never be known (in a closed mathematical form). Thus since the birth of DFT some sort of approximations for E_{xc} have been used. We review here the main classes of approximate xc functionals. These classes are roughly ordered

from the simplest to the most sophisticated ones as proposed by Perdew[51] and is known as “Jacob’s ladder”. In this scheme, functionals are grouped according to their complexity on rungs of a ladder which lead from the Hartree approximation on “earth” to the exact xc functional in “heaven”. The first few rungs of this ladder are now briefly discussed as a means to introduce some of the most common types of xc functionals in widespread use. The discussion is focus on the contents of the approximations, not their performance in practical calculations. On the average, more sophisticated approximations are usually more accurate than simpler ones, even though many exceptions can be found.

3.1.1 The Local-Density Approximation (LDA)

In the *local-density approximation* (LDA), introduced by Kohn and Sham[28], the xc functional is approximated as

$$E_{\text{xc}}^{\text{LDA}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{unif}}(n(\mathbf{r})) d\mathbf{r} \quad (3.1)$$

where $\varepsilon_{\text{xc}}^{\text{unif}}$ is the exchange-correlation energy per particle of the interacting uniform electron gas with the density $n(\mathbf{r})$. The uniform electron gas represents a family of systems of interacting electrons with an arbitrary spatially constant density $n(\mathbf{r})$ that acts as a parameter. Thus, in the LDA, the exchange-correlation energy per particle of an inhomogeneous system at a spatial point of density $n(\mathbf{r})$ is approximated as the exchange-correlation energy per particle of the uniform electron gas of the same density.

The function $\varepsilon_{\text{xc}}^{\text{unif}}(n)$ is a sum of exchange and correlation contributions, $\varepsilon_{\text{xc}}^{\text{unif}}(n) = \varepsilon_{\text{x}}^{\text{unif}}(n) + \varepsilon_{\text{c}}^{\text{unif}}(n)$. The exchange energy per particle of the uniform electron gas can be calculated analytically

$$\varepsilon_{\text{x}}^{\text{unif}}(n) = c_{\text{x}} n^{1/3} \quad (3.2)$$

where $c_{\text{x}} = -(3/4)(3/\pi)^{1/3}$. Thus, we have the exact analytical expression for the exchange energy¹:

$$E_{\text{x}}^{\text{LDA}}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r} \quad (3.3)$$

The correlation energy per particle $\varepsilon_{\text{c}}^{\text{unif}}(n)$ of the uniform electron gas cannot be calculated analytically. This quantity has been obtained numerically for a number of densities n using accurate quantum Monte Carlo simulations of the UEG[39], and fitted to a parametrized function of n satisfying the known high- and low-density

¹Note that this definition differs from the average over the HF exchange energy.

expansions. Expressed in terms of the Wigner-Seitz radius $r_s = (3/4\pi n)^{1/3}$, the first terms of the high-density expansion ($r_s \rightarrow 0$) have the form

$$\varepsilon_c^{\text{unif}} = A \ln r_s + B + C r_s \ln r_s + \mathcal{O}(r_s), \quad (3.4)$$

and the first terms of the low-density expansion ($r_s \rightarrow +\infty$) have the form

$$\varepsilon_c^{\text{unif}} = \frac{a}{r_s} + \frac{b}{r_s^{3/2}} + \mathcal{O}\left(\frac{1}{r_s^2}\right), \quad (3.5)$$

where A , B , C , a , and b are constants depending on the electron spin configuration. The Perdew-Zunger[40], Perdew-Wang (PW)[41] and Vosko-Wilk-Nusair (VWN)[42] functionals are all common LDA functionals.

3.1.2 The Generalized-Gradient Approximation (GGA)

It was realized very early that only the local uniform density at each given point is not a reasonable approximation for the rapidly varying electron densities of many materials, and that the gradient of the density ($\nabla n(\mathbf{r})$) needs to be included. A first attempt was the so-called gradient-expansion approximations (GEA). The idea behind GEA is to regard LDA as the first term in a power series expansion of E_{xc} in the density's spatial variation (described by the derivatives of $n(\mathbf{r})$). The second-order GEA thus uses LDA plus the term of next lowest order in density variation, giving a functional of the form

$$E_{\text{xc}}^{\text{GEA}}[n] = E_{\text{xc}}^{\text{LDA}}[n] + \int A_{\text{xc}}(n(\mathbf{r})) s^2 + \int B_{\text{xc}}(n(\mathbf{r})) q + \dots \quad (3.6)$$

where $A_{\text{xc}}(n(\mathbf{r}))$ and $B_{\text{xc}}(n(\mathbf{r}))$ are dimensionless functions (not functionals) of $n(\mathbf{r})$, and s and q defines the appropriate measure of the density gradient both of which have been expressed on scale invariant form; the *dimensionless gradient*

$$s = \frac{|\nabla n|}{2k_F n} = \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3} n^{4/3}(\mathbf{r})} = \frac{3}{2} \left(\frac{4}{9\pi}\right)^{1/3} |\nabla r_s| \quad (3.7)$$

and the *dimensionless Laplacian*

$$q = \frac{\nabla^2 n}{(2k_F)^2 n} = \frac{\nabla^2 n(\mathbf{r})}{4(3\pi^2)^{2/3} n^{5/3}(\mathbf{r})} \quad (3.8)$$

Because there is no special direction in the uniform electron gas, there can be no term linear in ∇n . Moreover, terms linear in $\nabla^2 n$ can be recast as s^2 terms, since

$$\int d\mathbf{r} f(n) \nabla^2 n = - \int d\mathbf{r} \left(\frac{\partial f}{\partial n}\right) |\nabla n|^2 \quad (3.9)$$

via integration by parts.

In application to real systems, the GEA has generally been disappointing, indeed often worsened the results of the LDA. The failure of the GEA led to the development of generalized-gradient approximation (GGA). The xc functional is written as a function of the local density and of the local gradient of the density, usually as an “enhancement factor” F_{xc} multiplying the homogeneous electron:

$$E_{xc}^{\text{GGA}}[n] = \int \varepsilon_{xc}(n(\mathbf{r})) F_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r} \quad (3.10)$$

The enhancement factor is written in terms of r_s and the dimensionless density gradient s :

$$F_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) \rightarrow F_{xc}(r_s, s)$$

Gradient-corrected functionals are the simplest extensions of LDA to inhomogeneous systems one can think of. GGA found widespread acceptance due to their improved performance. GGA functionals are known to satisfy some known conditions that the exact functional should satisfy as well[43]. They yield much better atomic energies and binding energies than LDA, at a modest additional computational cost[44, 45]. In particular, they yield better results for the band gap in semiconductors and insulators especially for some transition-metal oxides which LDA incorrectly describes as metals[46]. Despite the improvement by GGA over LDA functionals, even greater accuracy can be obtained by using the so-called meta-GGA.

3.1.3 Meta-GGA (mGGA)

The next step in the development of gradient approximations is to incorporate the kinetic energy density or/and the Laplacian of the density. Such functionals are generally referred to as meta-GGA functionals.

The form of the functional is typically:

$$E_{xc}^{\text{mGGA}} = \int n(\mathbf{r}) \varepsilon_{xc}(n, |\nabla n|, \nabla^2 n, \tau) d\mathbf{r} \quad (3.11)$$

where the kinetic energy density τ is;

$$\tau = \frac{1}{2} \sum_i |\nabla \phi_i|^2 \quad (3.12)$$

Still higher accuracy (of course, at a higher cost) can be obtained by using the so-called hybrid schemes.

3.1.4 Hybrid Schemes

These fourth generation functionals add “exact exchange” calculated from the HF-like functional to some conventional treatment of DFT exchange and correlation:

$$E_{xc}^{\text{hybrid}} = \alpha E_x^{\text{HF}} + E_c \quad (3.13)$$

where α can be chosen to satisfy particular criteria. The B3LYP functional[47, 48], which is widely used in the quantum chemistry community, is an example. Here three adjustable parameters (a_{1-3}) are used to fit calculated values to a molecular data base. It has the following form:

$$E_{xc} = E_{xc}^{\text{LDA}} + a_1 (E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_2 \Delta E_x^{\text{GGA}} + a_3 \Delta E_c^{\text{GGA}} \quad (3.14)$$

Where E_{xc}^{LDA} , E_x^{HF} and E_x^{LDA} are the LDA exchange-correlation energy functional, Hartree-Fock exchange energy functional and LDA exchange functional respectively, and ΔE_x^{GGA} and ΔE_c^{GGA} are respectively the GGA exchange and correlation functionals. Here B88[49] and LYP[50] are commonly used as GGA exchange and correlation functionals respectively.

As mentioned earlier, the functionals currently used in density functional simulations form a natural hierarchy. Although, it cannot be claimed that there is a systematic approach to the exact functional, it is clear that improvements are being made in the underlying functional form and that the description of ground state properties is improving. The most notable recent advances being those in which the non-local nature of the exchange potential is introduced in one form or another. The current hierarchy is summarized in Table 3.1 with expected accuracy decreasing as we go down the table. This hierarchical classification is what is often referred to as the Jacob’s ladder[51].

Family	Dependencies
Hybrid	Exact exchange, $ \nabla n , n$
mGGA	$\nabla^2 n, \tau$
GGA	$ \nabla n $
LDA	n

Table 3.1: The current hierarchy of exchange functionals.

3.2 A New Density Functional

In this work, we introduce a new exchange-correlation functional in order to address the band gap problem. This new functional builds on the so-called $X\alpha$ functional. Thus, we introduce the $X\alpha$ first.

3.2.1 $X\alpha$ -Method

The $X\alpha$ -method was proposed by Slater (1951) as a simplification of the HF method. The idea of Slater was to approximate the complicated non-local Fock operator Eq. (2.22) by a simple local operator. He invoked the UEG model to produce the simplification, resulting in the $X\alpha$ equation (sometimes called the Hartree-Fock-Slater equation)

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{x\alpha}(\mathbf{r}) \right] \phi_i = \epsilon_i \phi_i \quad (3.15)$$

with the $X\alpha$ local potential

$$v_{x\alpha}(\mathbf{r}) = -\frac{3}{2}\alpha \left(\frac{3}{\pi} n(\mathbf{r}) \right)^{1/3} \quad (3.16)$$

where the parameter α was set equal to 1 in the original prescription.

If correlation is neglected, the LDA would be equivalent to the $X\alpha$ as Kohn and Sham observed by using the Dirac exchange formula

$$E_x^{\text{LDA}}[n] = -K_D[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r} \quad (3.17)$$

$$v_x^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_x^{\text{LDA}}}{\delta n} = - \left(\frac{3}{\pi} n(\mathbf{r}) \right)^{1/3} \quad (3.18)$$

then the resulting KS equation is precisely the $X\alpha$ equation with $\alpha = 2/3$.

The two different values of α result from applying the UEG approximation in different places: Slater in the exchange potential, giving $\alpha = 1$; Kohn and Sham in the exchange energy, giving $\alpha = 2/3$. The former concerns the one-electron equation; the latter emphasizes the total energy. This ambiguity has led to the use of α as an *adjustable parameter* in many $X\alpha$ calculations.

The $X\alpha$ -method may be regarded as a density-functional scheme with neglect of correlation and with approximation to the exchange-energy functional.

$$E_x^{\text{LDA}}[n] = -\frac{3}{2}\alpha K_D[n] = -\frac{9}{8}\alpha \left(\frac{3}{\pi} \right)^{1/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r} \quad (3.19)$$

which gives the $X\alpha$ potential Eq. (3.16) upon functional differentiation. The $X\alpha$ method, particularly in light of the Kohn-Sham derivation, differs from the Thomas-Fermi model of §2.3.1 only in the kinetic-energy functional. The KS approach uses a much more accurate kinetic energy functional $T_s[n]$ in the $X\alpha$ method in place of $T_{TF}[n]$ used in the TF model. This accounts for a great difference. The $X\alpha$ method constitutes a quite efficient technique for electronic-structure calculations for molecules and solids. It is easier to implement than the HF method, particularly for larger molecules and solids, and it does not entail much loss in accuracy. In spite of contrary suggestions, the $X\alpha$ formula Eq. (3.19) should not be interpreted as including correlation effects.

In §2.6, we pointed out that Δ_{xc} is usually not zero thereby accounting for most of the error encountered in using the LDA for band gap calculation. The first evidence of a non-zero Δ_{xc} in real matter was given by Godby *et al.*[52, 53] who used the so-called Sham-Schlüter equation[32, 54]

$$\begin{aligned} & \int d\mathbf{r}' v_{xc}(\mathbf{r}') \int \frac{d\omega}{2\pi} G_{KS}(\mathbf{r}, \mathbf{r}'; \omega) G(\mathbf{r}', \mathbf{r}; \omega) \\ &= \int d\mathbf{r}' d\mathbf{r}'' \int \frac{d\omega}{2\pi} G_{KS}(\mathbf{r}, \mathbf{r}'; \omega) \Sigma_{xc}(\mathbf{r}', \mathbf{r}''; \omega) G(\mathbf{r}'', \mathbf{r}; \omega) \end{aligned} \quad (3.20)$$

to calculate the xc potential from the many-body self-energy operator. Here, G is the Green's function and Σ_{xc} is the self-energy (see more in the appendix).

In 1988, Hanke and Sham derived a band-gap correction due to the v_{xc} discontinuity on the basis of the self-energy model. This gap correction Δ_{xc} analytically depends on the density average $\langle n \rangle^{1/3}$, ω_p , and E_p . A presentation of the derivation of this xc potential from a tight-binding model for Σ_{xc} according to Hanke and Sham is included in the appendix for completeness.

The final result for v_{xc} by Hanke and Sham[1] is

$$v_{xc}^{ins}(\mathbf{r}) = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \left[1 - \frac{2\omega_p}{N_{val}(\omega_p + E_p)} \right] \quad (3.21)$$

Here, N_{val} is the number of valence electrons in the unit cell, ω_p is the plasma frequency and E_p is the average gap (Penn gap)[55].

Our contribution is the use of a local density approximation for the plasma frequency:

$$\omega_p^2 = \frac{4\pi e^2}{m} n(\mathbf{r}) \quad (3.22)$$

and approximating E_p the average gap (Penn gap) as

$$E_p = c \frac{\hbar^2}{m^2} \left| \frac{\nabla n}{n} \right|^{3/2} \quad (3.23)$$

where c is an adjustable parameter.

This approximation to E_p which we have used here was considered appropriate as it is dimensionally consistent with ω_p . It is easy to observe that the dimension of ω_p is $L^{-3/2}$ (since $\omega_p \propto n^{1/2}$ and n has dimensions of inverse the cube of length, i.e., L^{-3}), meaning that we need E_p to also have dimensions of $L^{-3/2}$. $|\nabla n/n|$, has dimensions of L^{-1} hence, $|\nabla n/n|^{3/2}$ has the needed dimension of $L^{-3/2}$. Observe that apart from the term in parenthesis, v_{xc} in Eq. (3.21) is similar to the $X\alpha$ -method above.

We apply the $X\alpha$ -method and introduce the scaling factor α , which is needed to multiply the Slater exchange potential such that the xc potential for the tight-binding insulator becomes

$$v_{xc}^{\text{ins}} = -\alpha e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \left[1 - \frac{2\omega_p}{N_{\text{val}}(\omega_p + E_p)} \right] \quad (3.24)$$

with ω_p and E_p defined as above. This xc potential given by Eq. (3.24), with the two adjustable parameters α and c , was used for the calculations in this thesis.

3.2.2 The Corresponding xc Energy E_{xc}

Having obtained an expression for $v_{xc}[n]$, we proceed to determine the xc energy E_{xc}^{ins} . We can obtain the xc energy E_{xc}^{ins} corresponding to the xc potential v_{xc}^{ins} by functional integration. We take a line integral along some specified path. For instance[56]

$$E_{xc}^{\text{ins}}[n] = \int_0^1 dt \int d\mathbf{r} v_{xc}^{\text{ins}}([n_t]; \mathbf{r}) \frac{\partial n_t}{\partial t} \quad (3.25)$$

where

$$v_{xc}^{\text{ins}}([n_t]; \mathbf{r}) = \left. \frac{\delta E_{xc}^{\text{ins}}[n]}{\delta n} \right|_{n=n_t} \quad (3.26)$$

and $n_t : \mathcal{R} \rightarrow \mathcal{B}$ is a differentiable path in Banach space which is defined by $n_t = n_a + t(n_b - n_a)$. To derive Eq. (3.25), we commence with

$$E_{xc}^{\text{ins}}[n_{t'}] - E_{xc}^{\text{ins}}[n_t] = \int d\mathbf{r} v_{xc}^{\text{ins}}([n_t]; \mathbf{r}) [n_{t'}(\mathbf{r}) - n_t(\mathbf{r})] + \mathcal{O}([n_{t'} - n_t]^2) \quad (3.27)$$

where t' is very close to t . Next divide both sides by $t' - t$ and let $t' \rightarrow t$ to obtain

$$\frac{\partial E_{xc}^{\text{ins}}[n_t]}{\partial t} = \int d\mathbf{r} v_{xc}^{\text{ins}}([n_t]; \mathbf{r}) \frac{\partial n_t(\mathbf{r})}{\partial t} \quad (3.28)$$

Finally, integrate both sides of Eq. (3.28) from $t = 0$ to $t = 1$ to generate our desired result, Eq. (3.25), by incorporating the crucial endpoint identity[57]

$$E_{xc}^{\text{ins}}[n_{t=0}] = 0 \quad (3.29)$$

Knowledge of the exact relationship between E_{xc} and v_{xc} is especially important now that an active area of research involves the direct approximation of v_{xc} , in order to obtain more accurate orbital energies and densities. Thus to obtain E_{xc}^{ins} , we use the expression for v_{xc}^{ins} of Eq. (3.21) in Eq. (3.25) which gives for $n_a = 0$ and $n_b = n$,

$$\begin{aligned}
E_{xc}^{\text{ins}}[n] &= \int d\mathbf{r} \int_0^1 v_{xc}^{\text{ins}}[tn](n) dt \\
&= -e^2 \left(\frac{2\pi}{3}\right)^{1/3} \int d\mathbf{r} n \int_0^1 \left\{ (tn)^{1/3} \left[1 - \frac{4e\sqrt{\pi tn/m}}{N_{\text{val}} \left(2e\sqrt{\pi tn/m} + \frac{c\hbar^2}{m^2} \left| \frac{\nabla n}{n} \right|^{3/2} \right)} \right] \right\} dt \\
&= -e^2 \left(\frac{2\pi}{3}\right)^{1/3} \int d\mathbf{r} n \int_0^1 \left\{ (tn)^{1/3} - \frac{4e\sqrt{\pi/m} (tn)^{5/6}}{N_{\text{val}} \left(2e\sqrt{\pi/m} (tn)^{1/2} + \frac{c\hbar^2}{m^2} \left| \frac{\nabla n}{n} \right|^{3/2} \right)} \right\} dt \\
&= -e^2 \left(\frac{2\pi}{3}\right)^{1/3} \left[\int d\mathbf{r} \frac{3}{4} n^{4/3} - \int d\mathbf{r} n \int_0^1 \frac{4e\sqrt{\pi/m} (tn)^{5/6}}{N_{\text{val}} \left(2e\sqrt{\pi/m} (tn)^{1/2} + \frac{c\hbar^2}{m^2} \left| \frac{\nabla n}{n} \right|^{3/2} \right)} dt \right] \\
&= -e^2 \left(\frac{2\pi}{3}\right)^{1/3} \left[\int d\mathbf{r} \frac{3}{4} n^{4/3} - \int d\mathbf{r} \int_{t=0}^{t=1} \frac{\alpha (tn)^{5/6}}{\beta (tn)^{1/2} + \gamma} d(tn) \right] \tag{3.30}
\end{aligned}$$

with

$$\alpha = 4e\sqrt{\frac{\pi}{m}} \tag{3.31}$$

$$\beta = 2eN_{\text{val}}\sqrt{\frac{\pi}{m}} \tag{3.32}$$

$$\text{and } \gamma = N_{\text{val}} \frac{c\hbar^2}{m^2} \left| \frac{\nabla n}{n} \right|^{3/2} \tag{3.33}$$

The second integral in Eq. can be evaluated (e.g., using a software program) and after some careful algebra we obtain the energy as

$$\begin{aligned}
E_{xc}^{\text{ins}}[n] &= -e^2 \left(\frac{2\pi}{3}\right)^{1/3} \left[\int d\mathbf{r} \frac{3}{4} \left(1 - \frac{2}{N_{\text{val}}} \right) n^{4/3} + \int d\mathbf{r} \frac{\Lambda^{8/3}}{N_{\text{val}}} \left\{ \frac{12}{5} x^2 \left(x^3 - \frac{5}{2} \right) \right. \right. \\
&\quad \left. \left. + 2 \ln \left(\frac{1-x+x^2}{1+2x+x^2} \right) - \sqrt{3} \tan^{-1} \left(\frac{2x-1}{\sqrt{3}} \right) \right\} \right] \tag{3.34}
\end{aligned}$$

with

$$x = \left(\frac{n}{\Lambda^2} \right)^{1/6} \quad \text{and} \quad \Lambda = \frac{c\hbar^2}{2em^2} \sqrt{\frac{m}{\pi}} \left| \frac{\nabla n}{n} \right|^{3/2} \tag{3.35}$$

Remarks:

1. We observe that this expression for E_{xc}^{ins} is essentially the $X\alpha$ approach with a value of α which depends on n and $|\nabla n|$, therefore making the functional a GGA.

2. When $|\nabla n| = 0$, then $E_{xc}^{\text{ins}} \propto \int d\mathbf{r} n^{4/3}$ except for ($N_{\text{val}} = 2$). So the expression reduces to the $X\alpha$ case with constant α .

Having obtained this expression, our goal now is to determine reasonable values of the parameters α and c of the model. In the next chapter, we will discuss how our calculations were carried out and how we determined α and c .

In this chapter, we discuss the method we use in doing our calculations, which is basically solving the Kohn-Sham equations for each system under consideration. We begin with a description of basis sets and pseudo-potentials as they are necessary for solving the Kohn-Sham equations.

4.1 Basis Sets

In this section, we introduce the concept of basis sets which are almost always necessary for practical solution of the Kohn-Sham equations. Essentially, almost all electronic structure methods today rely on an expansion of the unknown wave function in terms of a set of basis functions. Any type of basis function may in principle be used like exponential, Gaussian, polynomial, plane-wave, spline, Slater type orbitals, and numeric atomic orbitals, etc. In this thesis, the calculations we do for periodic systems are carried out with plane wave basis sets and pseudo-potentials. Also the approach of combining plane wave basis sets and pseudo-potentials¹ is the workhorse of the present day DFT calculations for periodic systems, so we briefly discuss such methods in what follows:

¹Pseudo-potentials are intertwined with plane wave methods because they allow calculations to be done with a feasible number of plane waves.

4.1.1 Plane Waves

For the treatment of periodic systems, like solids, plane wave basis sets have become the natural choice because of Bloch's theorem. In a periodic potential, $U(\mathbf{r})$, where $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ and \mathbf{R} is the Bravais lattice vector, Bloch's theorem states that the eigenfunctions of the one-electron Hamiltonian $H = -\frac{1}{2}\nabla^2 + U(\mathbf{r})$ can be chosen to have the form of a plane wave ($e^{i\mathbf{k}\cdot\mathbf{r}}$) times a function, $u_{nk}(\mathbf{r})$, having the same periodicity as the potential $U(\mathbf{r})$:

$$\phi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{nk}(\mathbf{r}) \quad (4.1)$$

where $u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r})$. Here the index k reflects the periodicity of the system, the index n is a second quantum number, the so-called "band index", and it originates from the atomic states which form the Bloch states ϕ_{nk} : for any value of k one finds a complete set of bands n .

Bloch's theorem allows to expand the electronic wave function in terms of a discrete set of plane waves. But for a periodic solid which has electrons in the order of Avogadro's number the spacing of the \mathbf{k} points goes to zero and \mathbf{k} can be considered as a continuous variable. So far the infinite number of electrons in the solid are accounted for by an infinite number of \mathbf{k} points, and only a finite number of electronic states are occupied at each \mathbf{k} point. The occupied states at each \mathbf{k} point contribute to physical quantities such as the electronic potential, electron density, and total energy of the solid. However, the electronic wave functions at \mathbf{k} points that are very close together will be almost identical. Hence it is possible to represent them over a region of \mathbf{k} space only by that at a single \mathbf{k} point. Efficient methods have been devised to choose special finite sets of \mathbf{k} points, for obtaining an accurate electronic potential, electron density, and total energy. In this thesis, the method proposed by Monkhorst and Pack[58] has been used, in which a uniform mesh of \mathbf{k} points is generated along the three lattice vectors in reciprocal space. The magnitude of any error in the total energy or the total energy difference due to inadequacy of the \mathbf{k} point sampling can always be reduced to zero by using a denser set of \mathbf{k} points. Therefore, it is crucial to test the convergence of the results with respect to the number of \mathbf{k} points in general.

Now expanding the periodic function u_{nk} with plane waves whose wave vectors are reciprocal lattice vectors (\mathbf{G}) of the periodic crystal:

$$u_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (4.2)$$

so the electronic wave function can be rewritten as

$$\phi_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (4.3)$$

While solving one electron Schrödinger-like equation with an effective periodic potential, e.g., the Kohn-Sham potential defined in Eq. (2.46), Kohn-Sham wave function can be expanded with plane wave basis sets as described in Eq. (4.3). As a result Eq. (2.48) can be rewritten as

$$\sum_{\mathbf{G}'} \left[\frac{1}{2} |\mathbf{k} + \mathbf{G}'|^2 \delta_{\mathbf{G},\mathbf{G}'} + V_{\text{eff}}(\mathbf{G} - \mathbf{G}') \right] C_{n,\mathbf{k}+\mathbf{G}'} = \epsilon_n C_{n,\mathbf{k}+\mathbf{G}} \quad (4.4)$$

where $\delta_{\mathbf{G},\mathbf{G}'}$ is the Kronecker δ and reflects that the kinetic energy is diagonal and ϵ_n are the electronic energies. The above equation is the basic Schrödinger-like equations of a periodic crystal with a plane wave basis set.

Here the sum over \mathbf{G}' tells that one needs an infinite number of plane waves to solve Eq.(4.4). However, the coefficients $C_{n,\mathbf{k}+\mathbf{G}}$ for the plane waves with small kinetic energy are typically more important than those with large kinetic energy. Thus the plane wave basis set can be truncated to include only plane waves that have kinetic energies less than a particular energy cutoff E_{cut} ,

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}} \quad (4.5)$$

Employing a finite basis set introduces a new source of inaccuracy, which can be reduced by increasing the number of plane waves or E_{cut} . Therefore, appropriate convergence tests have to be performed in order to find an E_{cut} that is sufficiently converged to compute the property of interest with the required accuracy.

4.1.2 Pseudo-potentials

The many-electron Schrödinger equation can be very much simplified if electrons are divided in two groups: valence electrons and inner core electrons. The electrons in the inner shells are strongly bound and do not play a significant role in the chemical binding of atoms, thus forming with the nucleus an (almost) inert core. Binding properties are almost completely due to the valence electrons, especially in metals and semiconductors. The bound core electrons within plane waves basis sets, require a huge amount of basis functions for their description. Thus this leads to a contradiction that the less important core electrons will consume a lot of the computational cost. This separation suggests that inner electrons can be ignored in

a large number of cases, thereby reducing the atom to a ionic core that interacts with the valence electrons. The use of an effective interaction, a pseudo-potential, that replaces the strong ionic potential felt by the valence electrons, by a weaker pseudo-potential was introduced to solve this problem. In general, there are two main purposes of the pseudo-potential formalism. First, to use a much weaker pseudo-potential to get rid of core electrons which due to their deep potential would need to be described by many plane wave basis functions. Second, to eliminate the rapid oscillations of the valence electron wave functions in the core region.

The use of pseudo-potentials was first introduced by Fermi in 1934 but was abandoned (in spite of the simplification they introduce in calculations) until the late 50's before they gained extensive usage due to the work of Phillips and Kleinman[59, 60].

We now consider the Phillips-Kleinman construction of pseudo-potential which if formally appearing in the Kohn-Sham equations, leads, as a solution, to the pseudo-function ψ_c^{PS} . Let the exact solutions of the Schrödinger equation for the inner and valence electrons be denoted by $|\psi_c\rangle$, and $|\psi_v\rangle$ respectively. Then

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle, \quad \text{with } n = c, v \quad (4.6)$$

The valence orbitals can be written as the sum of a smooth function (called the pseudo wave-function), $|\varphi_v\rangle$, with an oscillating function that results from the orthogonalization of the valence to the inner core orbitals (we remove wiggles in valence states by canceling them by those in core states):

$$|\psi_v\rangle = |\varphi_v\rangle + \sum_c \alpha_{cv} |\psi_c\rangle \quad (4.7)$$

By multiplying with $\langle\psi_{c'}|$, one gets the expansion coefficients²:

$$\langle\psi_{c'}|\psi_v\rangle = \underbrace{\langle\psi_{c'}|\varphi_v\rangle}_{=0} + \sum_c \alpha_{cv} \underbrace{\langle\psi_{c'}|\psi_c\rangle}_{=\delta_{cc'}} \quad (4.8)$$

$$\text{whence} \quad \alpha_{c'v} = \langle\psi_{c'}|\psi_v\rangle \quad (4.9)$$

² $\langle\psi_{c'}|\varphi_v\rangle = 0$ since the core and valence states correspond to the same Hamiltonian and $\langle\psi_{c'}|\psi_c\rangle = \delta_{cc'}$ since core states at different centers do not overlap.

Now we let \hat{H} act on $|\psi_v\rangle$ of Eq. (4.7) and we obtain³:

$$\begin{aligned}
 \hat{H}|\psi_v\rangle &= \underbrace{\hat{H}|\varphi_v\rangle}_{E_v|\varphi_v\rangle} + \sum_c \alpha_{cv} \hat{H}|\psi_c\rangle \\
 &= E_v \left[|\psi_v\rangle - \sum_c \alpha_{cv} |\psi_c\rangle \right] + \sum_c \alpha_{cv} E_c |\psi_c\rangle \\
 &= E_v |\psi_v\rangle + \sum_c \alpha_{cv} (E_c - E_v) |\psi_c\rangle \\
 &\left[\hat{H} - \sum_c (E_c - E_v) \underbrace{|\psi_c\rangle\langle\psi_c|}_{\mathbb{P}} \right] |\psi_v\rangle = E_v |\psi_v\rangle
 \end{aligned} \tag{4.10}$$

This equation indicates that the states ψ_v satisfy a Schrödinger-like equation with an energy-dependent pseudo-Hamiltonian

$$\hat{H}^{\text{PK}}(E) = \hat{H} - \sum_c (E_c - E) |\psi_c\rangle\langle\psi_c| \tag{4.11}$$

It is then possible to identify the Phillips-Kleinman pseudo-potential:

$$V^{\text{PK}}(E) = V(\mathbf{r}) - \sum_c (E_c - E) |\psi_c\rangle\langle\psi_c| \tag{4.12}$$

where $V(\mathbf{r})$ is the true potential, as the effective potential in which valence electrons move. However, this pseudo-potential is non-local and depends on the eigen-energy of the electronic state one wishes to find.

The Phillips and Kleinman potential was later generalized to

$$V^{\text{PK}} = V(\mathbf{r}) + \sum_c |\psi_c\rangle\langle\xi_c| \tag{4.13}$$

where ξ_c is some set of functions.

The pseudo-potential can be cast into the form

$$\hat{V}(\mathbf{r}, \mathbf{r}') = \sum_l \sum_{m=-l}^l |Y_{lm}\rangle V_l(r, r') \langle Y_{lm}| \tag{4.14}$$

where $Y_{lm}(\theta, \phi) = P_l(\cos\theta)e^{im\phi}$ are the spherical harmonics. This expression emphasizes the fact that V_l as a function of r and r' depends on the angular momentum. The most usual forms for $V_l(r, r')$ are the separable Kleinman and Bylander form[61]

$$V_l(r, r') = v_l(r)v_l(r') \tag{4.15}$$

³The quantum mechanical operator, $\mathbb{P} \equiv |\psi_c\rangle\langle\psi_c|$ is called the projection operator. See, for example, Griffiths Introduction to Quantum Mechanics

and the semi-local form

$$V_l(r, r') = V_l(r)\delta(r - r') \quad (4.16)$$

One important class of pseudo-potentials are so called *norm-conserving pseudo-potentials*. Norm conserving pseudo-potentials require that the all-electron and pseudo valence eigenvalues agree for the chosen atomic configuration, that the all-electron and pseudo wave-function agree beyond a chosen core radius (r_c) and that the integrated density inside r_c for the all-electron wave function and pseudo wave function are the same (“norm conservation”). There are many types of norm-conserving pseudo-potentials but in this thesis we work with the pz-family of pseudo-potentials (for all calculations of interest) with the Perdew-Zunger (LDA) exchange-correlation[40]

One issue with the norm-conserving pseudo-potentials is that they can not generate smoother pseudo wave functions than the all-electron one when coming to the first row elements like O and the localized transition metals like Ni due to the “norm conservation” rule. There is hardly any improvement for the norm-conserving pseudo-potential over the all-electron counterpart. To circumvent this difficulty, Vanderbilt[62] made a radical modification to break the norm conservation rule and relax the condition that the pseudo wave function inside the core region must have the same charge (or integrated density) as the all-electron wave function. By this way, r_c can be chosen to a larger value and the pseudo wave function can be made much softer than the all-electron wave function hence much lower plane wave cutoff would be needed. Clearly, this introduces a deficit in the charge inside the core region and it is compensated with additional localized atom-centered charges. The additional charges are defined as the charge difference between the all-electron and pseudo wave functions and for convenience they are also “pseudized”. This kind of pseudo-potential, which enables much lower plane-wave cut-offs to be used in the calculations, is called an *ultrasoft pseudo-potential*.

4.2 Methodology

In this thesis, the electronic structure calculations were done using the quantum-ESPRESSO package[63]. We used the xc-potential developed in §§A.3 with norm-conserving pseudo-potentials especially the pz-family of pseudopotential (with the Perdew-Zunger (LDA) exchange-correlation). For all systems the Brillouin zone is sampled with $8 \times 8 \times 8$ Monkhorst-Pack grid. The Kohn-Sham equations were solved

with plane wave basis sets and the energy band gap which is the difference between the Kohn-Sham eigenvalues for the lowest unoccupied and highest occupied orbitals are recorded and compared to experimental values for each of the materials that was considered in this thesis.

The parameter c that appear in the definition of the Penn gap in Eq. (3.23) and the scaling factor α which we introduce as suggested by the $X\alpha$ -method were adjusted simultaneously until the best band gap energies for bulk Si and Ge systems were obtained. We call this scheme the *AUST Scheme* and denote our parameter pair by $(\text{aust}\alpha, \text{aust}c)$. After obtaining the best parameter for this system, we tested them on other systems. The results obtained from these calculations are presented in the next chapter.

CHAPTER 5

Results, Discussion and Conclusion

The results obtained are presented and discussed. These results were compared with those obtained from experiment and those from LDA calculations in literature.

5.1 Results

First, we obtained our parameter pair ($aust\alpha$, $austc$), by calculating the band gap of bulk Si and Ge systems, with different values of $aust\alpha$ & $austc$. In our search for the best pair of parameter to reproduce the “best” (as close to experimental values as possible) band gap energies, we obtain some results as shown in the following tables¹. The calculations were carried out for Si and Ge in the diamond structure having experimental lattice constants.

¹The LDA and experimental values used here are taken from F. Tran and P. Blaha Phys. Rev. Lett. **102**, 226401 (2009).

The first Table presented uses ($\text{aust}\alpha = 1.40, \text{aust}c = 0.35$)

($\text{aust}\alpha = 1.40, \text{aust}c = 0.35$)

All energies are given in eV					
Solid	Expt.	LDA		AUST Scheme	
		band gap	% error	band gap	% error
Si	1.17	0.47	59.8	1.20	2.0
Ge	0.74	0.00	100.0	0.27	63.0
ZnO	3.44	0.75	78.2	1.67	52.0
MgO	7.83	4.70	40.0	3.26	58.0
ZnS	3.91	1.84	52.9	3.56	8.9
LiF	14.20	8.94	37.0	9.37	34.0
FeO	2.40	-0.35	114.6	0.46	80.9
GaAs	1.52	0.30	80.3	1.46	3.9
		mean % error = 70.4%		mean % error = 37.8%	

Table 5.1: AUST Scheme compared to experiment for (1.40, 0.35).

We average the percent error over the number of systems studied using:

$$\langle \%e \rangle = \frac{1}{N} \sum_i^N x_i \quad (5.1)$$

where x_i is the percentage error of an individual system and $N = 8$ is the number of systems studied. For the values given in Table 5.1 above, the average percent error is

$$\langle \%e \rangle = 37.8\% \quad (5.2)$$

This is already an improvement over the 70.4% error from LDA. The next table shows more improvement using another parameter set.

(aust α = 1.58, aust c = 0.31)

All energies are given in eV					
Solid	Expt.	LDA		AUST Scheme	
		band gap	% error	band gap	% error
Si	1.17	0.47	59.8	1.55	33.0
Ge	0.74	0.00	100.0	0.34	54.0
ZnO	3.44	0.75	78.2	2.40	30.0
MgO	7.83	4.70	40.0	3.91	50.0
ZnS	3.91	1.84	52.9	3.88	0.7
LiF	14.20	8.94	37.0	10.18	28.3
FeO	2.40	-0.35	114.6	1.09	54.5
GaAs	1.52	0.30	80.3	1.56	2.7
		mean % error = 70.4%		mean % error = 31.7%	

Table 5.2: AUST Scheme compared to experiment for (1.58, 0.31).

For this set of values, the average percent error is

$$\langle \%e \rangle = 31.7\% \quad (5.3)$$

which is smaller than the previous case. The next set of parameter gives more accurate results (although, only slightly).

(aust α = 1.32, aust c = 0.31)

All energies are given in eV					
Solid	Expt.	LDA		AUST Scheme	
		band gap	% error	band gap	% error
Si	1.17	0.47	59.8	1.40	19.0
Ge	0.74	0.00	100.0	0.54	27.0
ZnO	3.44	0.75	78.2	2.78	19.0
MgO	7.83	4.70	40.0	5.11	35.0
ZnS	3.91	1.84	52.9	3.42	12.5
LiF	14.20	8.94	37.0	8.98	36.8
FeO	2.40	-0.35	114.6	0.20	91.5
GaAs	1.52	0.30	80.3	1.41	7.4
		mean % error = 70.4%		mean % error = 31.0%	

Table 5.3: AUST Scheme compared to experiment for (1.32, 0.31).

The average percent error for this pair of parameter is

$$\langle \%e \rangle = 31.0\% \quad (5.4)$$

showing yet an improvement over the last pair.

(aust α = 1.50, aust c = 0.40)

All energies are given in eV					
Solid	Expt.	LDA		AUST Scheme	
		band gap	% error	band gap	% error
Si	1.17	0.47	59.8	1.69	45.0
Ge	0.74	0.00	100.0	0.74	0.4
ZnO	3.44	0.75	78.2	3.34	3.0
MgO	7.83	4.70	40.0	5.63	28.0
ZnS	3.91	1.84	52.9	3.75	4.1
LiF	14.20	8.94	37.0	9.89	30.4
FeO	2.40	-0.35	114.6	0.79	67.2
GaAs	1.52	0.30	80.3	1.53	0.6
		mean % error = 70.4%		mean % error = 22.3%	

Table 5.4: AUST Scheme compared to experiment for (1.50, 0.40).

For this pair of parameter we obtain the average percent error to be 22.3%. This is the parameter pair we choose to work with as it gives the least average error percent. This is a far better improvement over the LDA which estimates band gap energies with error as large as 50% (70.4% in our case due to the number of systems we considered).

5.2 Discussion

Although the pair of parameter we chose to work with does not give zero error for all the materials we studied, each calculated band gap shows an improvement over the LDA result. The best improvement is in Ge (0.4% vs 100% for LDA) while the worst case is in FeO (67.2% vs 114.6% for LDA which wrongly predicts the material to be metallic). Overall, the AUST functional shows an improvement over the LDA one: 22.3% mean percentage error vs 70.4%.

5.3 Conclusion and Perspective

It is obvious that our scheme performs better than the LDA, the values obtained using the AUST Scheme are closer to experimental values than LDA values. For Ge, ZnO, ZnS and GaAs our results for the AUST Scheme are accurate to within 5% of the experimental results.

Some of the things that may be looked into for future considerations are:

- The search for a better pair of parameter than the one already obtained in this work could be continued so that closer values to the experimental values for all systems may be obtained.
- This scheme could be tested for a variety of samples with a careful observation of the behaviour over a wide range of materials.
- This scheme could be used to calculate other properties of interest: lattice parameter, binding energy, bulk moduli, bond angles, etc., and the values obtained for each of these properties compared to those obtained from experiment to understand how well the scheme works.
- The functional form of the exchange-correlation potential suggested in this work could be improved upon, possibly by proposing different definitions for the Penn gap E_p in terms of n or/and $|\nabla n|$, to obtain more accurate band gap energies in materials. For instance

$$E_p = c \frac{\hbar^2 |\nabla n|}{m^2 n^{5/6}}$$

or

$$E_p = c \frac{\hbar^2 |\nabla n|^{9/8}}{m^2 n}$$

are possible definitions for E_p that may be considered.

Hanke-Sham (HS) xc Potential

The derivation of the HS xc potential is presented here. We begin by introducing Green's function and self-energy operator because an explicit model for the self-energy Σ_{xc} of an insulator or semiconductor will be used to derive the HS functional for v_{xc} in insulators and semiconductors from Eq. (3.20)

A.1 Green's Function and Self-Energy Operator

Green's functions are the essential ingredients in many-body theory from which the relevant physical information can be extracted. For a non-relativistic N -electron system under the influence of an external potential $v(\mathbf{x})$, the one-particle Green's function is defined as

$$G(\mathbf{x}, \mathbf{x}'; t - t') = -i \left\langle \Psi_N^{(0)} \left| \mathcal{T} \left[\hat{\psi}(\mathbf{x}, t) \hat{\psi}^\dagger(\mathbf{x}', t') \right] \right| \Psi_N^{(0)} \right\rangle \quad (\text{A.1})$$

where $\mathbf{x} \equiv (\mathbf{r}, \sigma)$ symbols the space and spin coordinates, $|\Psi_N^{(0)}\rangle$ is the ground-state of the system, $\hat{\psi}(\mathbf{x}, t)$ is the annihilation operator in the Heisenberg picture, and \mathcal{T} is Wick's time-ordering operator¹. We may see that for $t > t'$, the Green's function is the probability amplitude of finding an electron with spin σ at point \mathbf{r} and time t if the electron was added to the system with spin σ' at point \mathbf{r}' and time t' . When $t < t'$, the Green's function describes the propagation of a hole created at t .

¹Note that G depends on $t - t'$ due to translational time invariance.

It has been mentioned that the relevant physical information about one-particle excitations are contained in the Green's function. To see this, we start from the Lehmann representation of the Green's function:

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \sum_n \frac{f_n(\mathbf{x})f_n^*(\mathbf{x}')}{\omega - \mathcal{E}_n + i\eta \text{sgn}(\mathcal{E}_n - \mu)} \quad (\text{A.2})$$

Here, $G(\omega)$ is the Fourier transform with respect to $\tau = t - t'$, η is a positive infinitesimal (i.e., $\eta \rightarrow 0+$), μ is the Fermi energy of the system, and

$$f_n(\mathbf{x}) = \begin{cases} \langle \Psi_N | \hat{\psi}(\mathbf{x}) | \Psi_{N+1}^{(n)} \rangle, & \mathcal{E}_n = E_{N+1}^{(n)} - E_N^{(0)} & \text{if } \mathcal{E}_n > \mu \\ \langle \Psi_{N-1}^{(n)} | \hat{\psi}(\mathbf{x}) | \Psi_N \rangle, & \mathcal{E}_n = E_N^{(0)} - E_{N-1}^{(n)} & \text{if } \mathcal{E}_n < \mu \end{cases} \quad (\text{A.3})$$

with $E_N^{(0)}$ the ground-state energy and $|\Psi_{N\pm 1}^{(n)}\rangle$ the n -th eigenstate with energy $E_{N\pm 1}^{(n)}$ of the $N \pm 1$ electron system. By taking the imaginary part of Eq. (A.2), we have the so-called spectral function:

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi} |\text{Im}G(\mathbf{x}, \mathbf{x}'; \omega)| = \sum_n f_n(\mathbf{x})f_n^*(\mathbf{x}')\delta(\omega - \mathcal{E}_n) \quad (\text{A.4})$$

which shows that $A(\mathbf{x}, \mathbf{x}'; \omega)$ is just the superposition of delta functions with weights given by the amplitudes $f_n(\mathbf{x})$ centered at each of the one-particle excitation energies \mathcal{E}_n . That is, the Green's function reflects the one-particle excitation spectra as anticipated above. Moreover, such weights (see Eq. (A.3) above), depend on the density of available eigenstates after the addition/removal of one electron.

This one-electron picture can be formally introduced with the aid of the so-called self-energy operator Σ_{xc} , which is defined through the Dyson equation

$$G^{-1}(\mathbf{x}, \mathbf{x}'; \omega) = G_H^{-1}(\mathbf{x}, \mathbf{x}'; \omega) - \Sigma_{\text{xc}}(\mathbf{x}, \mathbf{x}'; \omega) \quad (\text{A.5})$$

Here, we have used the Hartree Green's function

$$G_H^{-1}(\mathbf{x}, \mathbf{x}'; \omega) = \delta(\mathbf{x} - \mathbf{x}')[\omega - h_0(\mathbf{x})] \quad (\text{A.6})$$

that corresponds to the non-interacting system in which $h_0(\mathbf{x})$ is the one-electron Hamiltonian under the external potential $v(\mathbf{x})$ plus the classical Hartree potential $v_H(\mathbf{x})$. Then, it is evident that the self-energy contains the many-body effects due to Pauli exchange and Coulomb correlation, and that sharp structures in $G(\omega)$ are related to small expectation values of the frequency-dependent operator $\omega - \hat{h}_0 - \hat{\Sigma}(\omega)$. Moreover, if we extend the ω -dependence of the self-energy to complex frequencies,

such structures can be attributed to zeros of the operator $\omega - \hat{h}_0 - \hat{\Sigma}(\omega)$, that is, to solutions of the *non-Hermitian* eigenvalue problem

$$h_0(\mathbf{x})\phi_n^{\text{qp}}(\mathbf{x}) + \int d\mathbf{x}' \Sigma_{\text{xc}}(\mathbf{x}, \mathbf{x}'; E_n^{\text{qp}})\phi_n^{\text{qp}}(\mathbf{x}') = E_n^{\text{qp}}\phi_n^{\text{qp}}(\mathbf{x}) \quad (\text{A.7})$$

with complex energies E_n^{qp} . This is the *quasiparticle* equation, where Σ_{xc} plays the role of an effective frequency-dependent and non-local potential. We may see that the self-energy has a resemblance with the DFT xc potential $v_{\text{xc}}(\mathbf{x})$ but, of course, the two objects are not equivalent. We have to bear in mind that the local and static $v_{\text{xc}}(\mathbf{x})$ is part of the potential of the fictitious KS non-interacting system, whereas the self-energy may be thought of as the potential felt by an added/removed electron to/from the interacting system.

A.2 A Tight-Binding (TB) Model for the Self-Energy (Σ_{xc})

In their 1988 paper, Hanke and Sham used a tight-binding (TB) approximation to derive an explicit energy-dependent and nonlocal model for Σ_{xc} . They used the energy-dependent, nonlocal Σ within the time-dependent screened HF (TDSHF) approximation and use a dynamically screened Coulomb potential W to replace the bare Coulomb potential w thereby accounting for correlation effects

$$\begin{aligned} & \langle \phi_v(\mathbf{r}) | \Sigma_{\text{xc}}(\mathbf{r}, \mathbf{r}'; E) | \phi_{v'}(\mathbf{r}' - \mathbf{l}) \rangle \\ &= \frac{i}{2\pi N} \int_0^\infty dE' \sum_{\gamma, \gamma', \mathbf{m}, \mathbf{m}'} [G_{\gamma\gamma'}(-\mathbf{m}; E + E') + G_{\gamma\gamma'}(-\mathbf{m}; E - E')] \\ & \quad \times \sum_{\mathbf{q}}^{\text{BZ}} e^{-i\mathbf{q}\cdot\mathbf{m}} W_{\mathbf{m}+\mathbf{m}'\gamma v, \ell+\mathbf{m}'\gamma'v'}(\mathbf{q}, E) \end{aligned} \quad (\text{A.8})$$

G is the one-particle propagator in local-orbital representation:

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_{\substack{v, v' \\ \mathbf{l}, \mathbf{l}'}} \phi_v(\mathbf{r} - \mathbf{l}) G_{vv'}(\mathbf{l} - \mathbf{l}'; E) \phi_{v'}^*(\mathbf{r}' - \mathbf{l}') \quad (\text{A.9})$$

with

$$G_{vv'}(\mathbf{l} - \mathbf{l}'; E) = \frac{1}{N} \sum_{n, \mathbf{k}}^{\text{BZ}} \frac{c_{vn}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')} c_{v'n}^*(\mathbf{k})}{E - E_{n\mathbf{k}} + i\eta \text{sgn}(E_{n\mathbf{k}} - E_F)} \quad (\text{A.10})$$

where c_{vn} gives the eigenvectors of the orbital expansion, $E_{n\mathbf{k}}$ denotes the Bloch energy with band-index n and wave-vector \mathbf{k} , $\eta \rightarrow 0+$ and the Fermi level E_F is placed somewhere within the gap.

Using an extreme tight-binding model with,

$$\begin{aligned} c_{vn}(\mathbf{k}) &= \delta_{vn} , \\ E_{n\mathbf{k}} &= \begin{cases} E_v, & \text{valence band} \\ E_c, & \text{conduction band} \end{cases} \end{aligned} \quad (\text{A.11})$$

the one-particle propagator (the valence-band contribution) becomes

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; E) &= \frac{\delta_{v\mathbf{v}'} \delta_{\mathbf{u}'}}{E - E_v - i\eta} \\ &= \sum_{\mathbf{v}\mathbf{l}} \frac{\phi_v(\mathbf{r} - \mathbf{l}) \phi_v^*(\mathbf{r}' - \mathbf{l})}{E - E_v - i\eta} \end{aligned} \quad (\text{A.12})$$

In accordance with this TB model, we define the average or E_p gap by a Penn-type equation[55] ($E_p = E_c - E_v$) and use a *plasmon-pole* ansatz to approximate the effective interaction W in Eq. (A.8)

$$W(\mathbf{r}, \mathbf{r}'; E) = w(\mathbf{r} - \mathbf{r}') + u(\mathbf{r}, \mathbf{r}') \left[\frac{1}{E - \omega_p} - \frac{1}{E + \omega_p} \right] \quad (\text{A.13})$$

where w is the Coulomb potential, and u is given by

$$u(\mathbf{r}, \mathbf{r}') = \frac{2E_p}{\omega_p} \sum_{\mathbf{v}, \mathbf{l}} M_v(\mathbf{r} - \mathbf{l}) M_v(\mathbf{r}' - \mathbf{l}) \quad (\text{A.14})$$

with

$$M_v(\mathbf{r} - \mathbf{l}) = \int d\mathbf{r}_1 \phi_{v^+}^*(\mathbf{r}_1 - \mathbf{l}) w(\mathbf{r} - \mathbf{r}_1) \phi_{v^-}(\mathbf{r}_1 - \mathbf{l}) \quad (\text{A.15})$$

v^+ and v^- stand for valence- and conduction-band orbitals respectively.

The energy integration in Σ_{xc} can be carried out analytically using the simplified expressions Eqs. (A.12) and (A.13) for G and W . It is convenient to use the replacement $E \rightarrow iE_n$ with $E_n = (2n + 1)\pi T$ for integer n , and do the integration in the finite-temperature form, and then let $T \rightarrow 0$. The finite- T version of Σ_{xc} therefore becomes

$$\Sigma_{xc}(\mathbf{r}, \mathbf{r}'; iE_n) = -T \sum_{l=-\infty}^{\infty} u(\mathbf{r}, \mathbf{r}'; iE_l) G(\mathbf{r}, \mathbf{r}'; iE_n + i\omega_l) e^{-i(E_n + \omega_l)(-0)} \quad (\text{A.16})$$

(-0) being a negative infinitesimal, and $\omega_l = 2l\pi T$

Summing up the contributions to Eq. (A.16), Σ_{xc} becomes

$$\Sigma_{xc}(\mathbf{r}, \mathbf{r}'; iE_n) = \Sigma_x(\mathbf{r}, \mathbf{r}') + \frac{\Sigma_{c,1}(\mathbf{r}, \mathbf{r}')}{iE_n + \omega_p - E_v} + \frac{\Sigma_{c,2}(\mathbf{r}, \mathbf{r}')}{iE_n - \omega_p - E_c} \quad (\text{A.17})$$

where²

$$\begin{aligned}\Sigma_x(\mathbf{r}, \mathbf{r}') &= - \sum_{bl} \phi_b(\mathbf{r} - \mathbf{l}) w(\mathbf{r} - \mathbf{r}') \phi_b^*(\mathbf{r} - \mathbf{l}) \\ \Sigma_{c,1}(\mathbf{r}, \mathbf{r}') &= \sum_{bl} \phi_b(\mathbf{r} - \mathbf{l}) u(\mathbf{r}, \mathbf{r}') \phi_b^*(\mathbf{r} - \mathbf{l}) \\ \text{and } \Sigma_{c,2}(\mathbf{r}, \mathbf{r}') &= \sum_{al} \phi_a(\mathbf{r} - \mathbf{l}) u(\mathbf{r}, \mathbf{r}') \phi_a^*(\mathbf{r} - \mathbf{l})\end{aligned}$$

It should be noted that the model is self-interaction free (i.e., the orbitals ϕ_b do not self-interact) with respect to the nonlocal exchange contribution Σ_x . For the correlation contributions, one finds for example, from Eq. (A.17) for the real part of the bonding on-site matrix element of Σ_c

$$\langle \phi_b(\mathbf{r}) | \Sigma_c(\mathbf{r}, \mathbf{r}'; E) | \phi_b(\mathbf{r}) \rangle = V_{bb}^2 \frac{2E_p}{\omega_p(\omega_p - E_v + E)} + \mathcal{O}(V_{ba}^2) \quad (\text{A.18})$$

where V_{bb}^2 is the Coulomb square matrix element obtained by taking the bonding matrix elements of $\Sigma_{c,1}$ in Eq. (A.17) into account. Although, V_{bb}^2 describes a long-range polarization cloud, it can still be converted to a local potential. So it can be shown that, for a uniformly charged sphere with average density n surrounded by vacuum,

$$V_{bb}^2 \simeq \frac{8\pi e^4 p^2}{\Omega_0(2/a_0)} = \frac{8\pi e^4 p^2}{\Omega_0(n/4)^{1/3}} \quad (\text{A.19})$$

where we have introduced the average density $n = 4(2/a_0)^3$, with lattice constant a_0 and unit-cell volume Ω_0 and p is the dipole matrix element determined from

$$p^2 = \frac{\Omega_0 \omega_p^2}{4\pi e^2 N_{\text{val}} E_p} \quad (\text{A.20})$$

with N_{val} being the number of valence electrons in the unit cell and ω_p the plasma frequency.

The omitted matrix element V_{ba}^2 in Eq. (A.18) which is due to the bonding matrix elements of $\Sigma_{c,2}$ in Eq. (A.17) can be shown to be

$$V_{ba} = \iint \phi_a^*(\mathbf{r}) \phi_b(\mathbf{r}) w(\mathbf{r} - \mathbf{r}') \phi_a^*(\mathbf{r}') \phi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (\text{A.21})$$

Using these results, we can construct the model Σ_{xc} which acts locally on Bloch states $\psi_{\text{val},\mathbf{k}}(\mathbf{r})$ and $\psi_{\text{cond},\mathbf{k}}(\mathbf{r})$ by introducing the average density n . In a dipole form,

² a and b stand for anti-bonding (conduction-band) and bonding (valence-band) orbitals respectively.

the real parts of $\psi_{\text{val},\mathbf{k}}(\mathbf{r})$ and $\psi_{\text{cond},\mathbf{k}}(\mathbf{r})$ are given as

$$\Sigma_{\text{val}}(\mathbf{r}, E) = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \left[1 - \frac{4\pi p^2 e^2}{\Omega_0} \frac{2E_p}{\omega_p(\omega_p - E_v + E)} \right] \quad (\text{A.22})$$

$$\text{and } \Sigma_{\text{cond}}(\mathbf{r}, E) = -V_{ba} - e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \frac{4\pi p^2 e^2}{\Omega_0} \frac{2E_p}{\omega_p(\omega_p + E_c - E)} \quad (\text{A.23})$$

This analytical model for Σ_{xc} which scales as the cube root of the local density ($n^{1/3}$) forms the basis for the construction of the xc potential v_{xc} and the gap correction Δ_{xc} .

A.3 A v_{xc} for Insulators and Semiconductors

Using the analytical model obtained above for Σ_{xc} we can derive an explicit form for v_{xc}^{ins} (for the sake of simplicity, we henceforth drop the superscript unless where it is otherwise necessary) for insulating and semiconducting systems. The frequency integration on the left-hand side of Eq. (3.20) yields

$$\int d\mathbf{r}' \chi^0(\mathbf{r}, \mathbf{r}') v_{xc}(\mathbf{r}') = T \sum_n \int d\mathbf{r}' \int d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'; iE_n) \Sigma_{xc}(\mathbf{r}', \mathbf{r}''; iE_n) G(\mathbf{r}'', \mathbf{r}; iE_n) \quad (\text{A.24})$$

where $\chi^0(\mathbf{r}, \mathbf{r}')$ is the density-response of the fictitious KS system, defined by

$$\chi^0(\mathbf{r}, \mathbf{r}') = T \sum_n G(\mathbf{r}, \mathbf{r}'; iE_n) G(\mathbf{r}', \mathbf{r}; iE_n) \quad (\text{A.25})$$

carrying out the frequency sums and using the TB model of Eqs. (A.11) and (A.12) gives

$$\begin{aligned} \chi^0(\mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{v}, \mathbf{l}, \mathbf{v}', \mathbf{l}'} \phi_{\mathbf{v}}(\mathbf{r} - \mathbf{l}) \phi_{\mathbf{v}'}^*(\mathbf{r}' - \mathbf{l}') \frac{f(E_{\mathbf{v}'}) - f(E_{\mathbf{v}})}{E_{\mathbf{v}'} - E_{\mathbf{v}}} \phi_{\mathbf{v}'}(\mathbf{r}' - \mathbf{l}') \phi_{\mathbf{v}}^*(\mathbf{r} - \mathbf{l}) \\ &= -2 \sum_{\mathbf{a}, \mathbf{b}, \mathbf{l}, \mathbf{l}'} \phi_{\mathbf{b}}(\mathbf{r} - \mathbf{l}) \phi_{\mathbf{a}}(\mathbf{r} - \mathbf{l}') \frac{1}{E_c - E_{\mathbf{v}}} \phi_{\mathbf{b}}(\mathbf{r}' - \mathbf{l}') \phi_{\mathbf{a}}(\mathbf{r}' - \mathbf{l}) \end{aligned} \quad (\text{A.26})$$

where a and b denote antibonding and bonding orbitals respectively. Thus, assuming completeness of the orbitals $\phi_{\mathbf{v}}$, the LHS of Eq. (3.20) becomes³

$$\begin{aligned} &\int d\mathbf{r}' v_{xc}(\mathbf{r}') \int \frac{d\omega}{2\pi} G_{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega) G(\mathbf{r}', \mathbf{r}; \omega) \\ &= -\frac{2}{E_p} \sum_{\mathbf{a}, \mathbf{b}, \mathbf{l}, \mathbf{l}'} \phi_{\mathbf{b}}(\mathbf{r} - \mathbf{l}) \left[\sum_{\mathbf{v}, \mathbf{l}'} \phi_{\mathbf{v}}(\mathbf{r} - \mathbf{l}') \langle \phi_{\mathbf{v}}^{\mathbf{l}'} | v_{xc} | \phi_{\mathbf{b}}^{\mathbf{l}} \rangle - \sum_{\mathbf{b}', \mathbf{l}'} \phi_{\mathbf{b}'}(\mathbf{r} - \mathbf{l}') \langle \phi_{\mathbf{b}'}^{\mathbf{l}} | v_{xc} | \phi_{\mathbf{b}}^{\mathbf{l}} \rangle \right] \\ &= -\frac{2}{E_p} \left[\sum_{\mathbf{b}, \mathbf{l}} \phi_{\mathbf{b}}^2(\mathbf{r} - \mathbf{l}) v_{xc}(\mathbf{r}) - \sum_{\mathbf{b}, \mathbf{b}', \mathbf{l}, \mathbf{l}'} \phi_{\mathbf{b}}(\mathbf{r} - \mathbf{l}) \phi_{\mathbf{b}'}(\mathbf{r} - \mathbf{l}') \langle \phi_{\mathbf{b}'}^{\mathbf{l}} | v_{xc} | \phi_{\mathbf{b}}^{\mathbf{l}} \rangle \right] \end{aligned} \quad (\text{A.27})$$

³Observe that $\langle \phi_i^k | v_{xc} | \phi_j^\ell \rangle = v_{xc}(\mathbf{r}) \delta_{ij} \delta_{k\ell}$ has been used in this simplification.

with the density defined by,

$$n(\mathbf{r}) = \sum_{bl} \phi_b^2(\mathbf{r} - \mathbf{l}) \quad (\text{A.28})$$

the LHS finally becomes

$$\int d\mathbf{r}' v_{xc}(\mathbf{r}') \int \frac{d\omega}{2\pi} G_{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega) G(\mathbf{r}', \mathbf{r}; \omega) = -\frac{2}{E_p} n(\mathbf{r}) [v_{xc}(\mathbf{r}) - \langle \phi_b | v_{xc} | \phi_b \rangle] \quad (\text{A.29})$$

For the evaluation of the RHS of Eq (3.20), we split the self-energy into the bare exchange, Σ_x , and into the two correlation contributions $\Sigma_{c,1}$ and $\Sigma_{c,2}$ according to Eq. (A.17). The bare exchange part Σ_x , being energy independent, is evaluated following a similar calculation for the LHS. Thus, as in Eq. (A.27),

$$\begin{aligned} T \sum_n \int d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'; iE_n) \Sigma_x(\mathbf{r}', \mathbf{r}'') G(\mathbf{r}'', \mathbf{r}; iE_n) \\ = -\frac{2}{E_p} \left[\sum_{bl} \phi_b(\mathbf{r} - \mathbf{l}) \int d\mathbf{r}'' \Sigma_x(\mathbf{r}, \mathbf{r}'') \phi_b(\mathbf{r}'' - \mathbf{l}) - n(\mathbf{r}) \langle \phi_b^l | \Sigma_x | \phi_b^l \rangle \right] \end{aligned} \quad (\text{A.30})$$

Using the approximate form of Σ_x , given in Eq. (A.22), we have

$$\int d\mathbf{r}'' \Sigma(\mathbf{r}, \mathbf{r}'') \phi_b(\mathbf{r}'') = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \phi_b(\mathbf{r}) \quad (\text{A.31})$$

on comparing Eqs. (A.29) and (A.30), we see that the exchange part of v_{xc} is

$$v_x(\mathbf{r}) = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \quad (\text{A.32})$$

The correlation part Σ_c , being energy-dependent, usually result in frequency sums of the form

$$\begin{aligned} T \sum_n [(iE_n - E_v)(iE_n - E_{v'})(iE_n - \omega)]^{-1} \\ = \begin{cases} \frac{f(E_v)}{(E_v - E_{v'})(E_v - \omega)} + \frac{f(E_{v'})}{(E_{v'} - E_v)(E_{v'} - \omega)} + \frac{f(\omega)}{(\omega - E_v)(\omega - E_{v'})}, & \text{if } v \neq v' \\ \frac{f(\omega)}{(\omega - E_v)^2} - \frac{f(E_v)}{(\omega - E_v)^2}, & \text{if } v = v' \end{cases} \end{aligned} \quad (\text{A.33})$$

After some straightforward manipulations the contribution due to $\Sigma_{c,1}$ becomes

$$\begin{aligned} T \sum_n \int d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'; iE_n) \frac{\Sigma_{c,1}(\mathbf{r}', \mathbf{r}'')}{iE_n + \omega_p - E_v} G(\mathbf{r}'', \mathbf{r}; iE_n) \\ = -\frac{2}{E_p(E_p + \omega_p)} \left[\sum_{bl} \phi_b(\mathbf{r} - \mathbf{l}) \int d\mathbf{r}'' \Sigma_{c,1}(\mathbf{r}, \mathbf{r}'') \phi_b(\mathbf{r}'' - \mathbf{l}) - n(\mathbf{r}) \langle \phi_b^l | \Sigma_{c,1} | \phi_b^l \rangle \right] \end{aligned} \quad (\text{A.34})$$

Using the model assumption that the antibonding matrix elements of $\Sigma_{c,1}$ and the bonding matrix elements of $\Sigma_{c,2}$ vanish it can be argued that the corresponding contribution due to $\Sigma_{c,2}$ vanishes identically in Eq. (A.24). Comparing the RHS result of Eq. (A.34) with the LHS result of Eq. (A.29), and using the bonding matrix elements of $\Sigma_{c,1}$ from the self-energy model defined in Eqs. (A.18) and (A.19), we finally arrive at the following explicit expression of the xc potential:

$$v_{xc}(\mathbf{r}) = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \left[1 - \frac{4\pi p^2 e^2}{\Omega_0} \frac{2E_p}{\omega_p(\omega_p + E_p)} \right] \quad (\text{A.35})$$

or, by Eq. (A.20) for the dipole matrix element,

$$v_{xc}^{\text{ins}}(\mathbf{r}) = -e^2 \left(\frac{2\pi}{3} n(\mathbf{r}) \right)^{1/3} \left[1 - \frac{2\omega_p}{N_{\text{val}}(\omega_p + E_p)} \right] \quad (\text{A.36})$$

Thus completing the derivation of the HS xc potential for a tight-binding insulator.

Bibliography

- [1] W. Hanke, L.J. Sham Phys. Rev. B **38**, 13361 (1988)
- [2] K. Capelle, A bird's-eye view of density-functional theory,
<http://arxiv.org/abs/cond-mat/0211443>.
- [3] Fermi E (1926) Z Phys **36**:902.
- [4] Dirac PAM (1930) Proc Cam Phil Soc **26**:376.
- [5] S. Baroni and R. Resta, Phys. Rev B **33**, 7017 (1986).
- [6] M. Hybertson and S. Louie, Phys. Rev. B **34**, 5390 (1986).
- [7] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).
- [8] D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979)
- [9] D. R. Hartree, Proc. Camb. Phil. Soc. **24** 89, (1927).
- [10] R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules (Oxford University Press, New York, 1989).
- [11] R. M. Dreizler and E. K. U. Gross, Density Functional Theory (Springer-Verlag, Berlin, 1990).
- [12] R. M. Martin, Electronic Structure: Basic Theory and Practical Methods (Cambridge University Press, Cambridge, 2004).

- [13] C. Fiolhais, F. Nogueira and M. Marques (Eds.), *A Primer in Density Functional Theory* (Springer Lecture Notes in Physics Vol. 620, 2003).
- [14] K. Burke, *The ABC of DFT*,
<http://chem.ps.uci.edu/~kieron/dft/book/>
- [15] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (John Wiley & Sons, New York, 2001).
- [16] M. Born and J.R. Oppenheimer, *Ann. Phys.* **87**, 457 (1927).
- [17] J. W. Rayleigh, *Phil. Tran* **161**, 77 (1870).
- [18] W. Ritz, *J. Reine Angew. Math* **135**, 1 (1908).
- [19] D. R. Hartree, *Proc. Cambridge Phil. Soc.* **24**, 89 (1928).
- [20] V. Fock, *Z. Physik* **61**, 126 (1930).
- [21] D. P. Taylor, W. P. Hess, and M. I. McCarthy, *J. Phys. Chem. B* **101**, 7455 (1997).
- [22] P. Baranek, G. Pinarello, C. Pisani, and R. Dovesi, *Phys. Chem. Chem. Phys.* **2**, 3893 (2000).
- [23] S. Casassa, A. Ferrar, M. Busso, and C. Pisani, *J. Phys. Chem. B* **106**, 12978 (2002).
- [24] P.-O. Lödin, *Adv. Chem. Phys.* **2**, 207 (1959).
- [25] L. H. Thomas, *Proc. Camb. Phil. Soc.* **23**, 542 (1927).
- [26] E. Fermi, *Rend. Accad. Lincei.* **6**, 602 (1927).
- [27] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [28] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [29] M. Levy, *Phys. Rev.* **A26**, 1200 (1982).
- [30] J. F. Janak, *Phys. Rev. B* **18**, 7165 (1978).
- [31] J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983).
- [32] L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1983).

- [33] E. Sagvolden and J. P. Perdew, *Phys. Rev. A* **77**, 012517 (2008).
- [34] T. Gould and J. Toulouse, *Phys. Rev. A* **90**, 050502(R) (2014).
- [35] W. Knorr and R. W. Godby, *Phys. Rev. Lett.* **65**, 639 (1992); *Phys. Rev. B* **50**, 1779 (1994).
- [36] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., *Phys. Rev. Lett.* **49**, 1691 (1982).
- [37] R. W. Godby, M. Schlüter, and L. J. Sham, *Phys. Rev. B* **37**, 10159 (1987).
- [38] M. K. Y. Chan and G. Ceder, *Phys. Rev. Lett.* **105**, 196403 (2010).
- [39] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [40] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [41] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [42] S. J. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- [43] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [44] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992); **48**, 4978(E) (1993).
- [45] A. D. Becke, *J. Chem. Phys.* **96**, 2155 (1992).
- [46] P. Dufek, P. Blaha, V. Sliwko, and K. Schwarz, *Phys. Rev. B* **49**, 10170 (1994).
- [47] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [48] P. J. Stephens, J. F. Devlin, and C. F. Chabalowski, *J. Phys. Chem.* **98**, 11623 (1994)
- [49] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [50] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988)
- [51] J. P. Perdew and K. Schmidt, in *Density Functional Theory and Its Applications to Materials*, eds. V. E. Van Doren, K. Van Alsenoy, and P. Geerlings (American Institute of Physics, Melville, NY, 2001).
- [52] R. W. Godby, L. J. Sham, and M. Schlüter, *Phys. Rev. Lett.* **56**, 2415 (1986).

- [53] R. W. Godby, L. J. Sham, and M. Schlüter, *Phys. Rev. B* **36**, 6497 (1987).
- [54] L. J. Sham and M. Schlüter, *Phys. Rev. B* **32**, 3883 (1985).
- [55] D. R. Penn, *Phys. Rev.* **128**, 2093 (1962).
- [56] R. van Leeuwen and E.J. Baerends, *Phys. Rev. A* **51**, 170 (1995).
- [57] M. Levy, *Phys. Rev. A* **43**, 4637 (1991)
- [58] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [59] J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).
- [60] L. Kleinman and J. C. Phillips, *Phys. Rev.* **118**, 1153 (1960).
- [61] L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- [62] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [63] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sciauzero, Ari P Seitsonen, Alexander Smogunov, Paulo Umari, and Renata M Wentzcovitch. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502 (19pp), 2009.
- [64] F. Tran and P. Blaha *Phys. Rev. Lett.* **102**, 226401 (2009).
- [65] M. Grüning, A. Marini, and A. Rubio, *J. Chem. Phys.* **124**, 154108 (2006).