UNIVERSIDAD DE INVESTIGACION DE TECNOLOGIA EXPERIMENTAL YACHAY

Escuela de Ciencias Físicas y Nanotecnología

TÍTULO: First Principles and Machine Learning Investigations into the Atomic and Mechanical Properties of Cement Hydrates (C-S-H).

Trabajo de integración curricular presentado como requisito para la obtención del título de Físico

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For her, who is my everything.

For my family, who always supported me.

Balarezo J. Gabriel

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Resumen

Este estudio presenta una investigación exhaustiva de las propiedades magnéticas y electrónicas de los monocapas $XGeTe_3$ (X = Cr, Mn, Fe) y sus aleaciones aleatorias, utilizando la teoría del funcional de la densidad (DFT) con los funcionales PBE y PBESol, complementados con correcciones de Hubbard U. $CrGeTe_3$ exhibe un robusto orden ferromagnético (FM) con una brecha de banda calculada que concuerda bien con los datos experimentales, destacando su potencial para aplicaciones prácticas. La monocapa $MnGeTe_3$ muestra un comportamiento de medio metal (HM), lo que lo hace particularmente prometedor para aplicaciones espintrónicas. En contraste, $FeGeTe_3$ revela un estado fundamental antiferromagnético (AFM) y posibles inestabilidades dinámicas, lo que requiere una mayor exploración para optimizar sus propiedades electrónicas.

En las aleaciones aleatorias, se observaron modificaciones significativas en los momentos magnéticos y las estructuras electrónicas. Específicamente, en $Cr_{1-x}GeMn_xTe_3$, el desorden en el momento magnético sugiere estados magnéticos fundamentales complejos, beneficiosos para la espintrónica. Mientras tanto, $Cr_{1-x}GeFe_xTe_3$ demuestra efectos de fuerte hibridación, indicando su idoneidad para sensores magnéticos y aplicaciones termoeléctricas. El sistema $Fe_{1-x}GeMn_xTe_3$ revela desafíos estructurales a mayores concentraciones de Mn, pero su estabilidad termodinámica respalda su potencial uso en uniones túnel magnéticas.

En general, esta investigación resalta las considerables perspectivas tecnológicas de los monocapas $XGeTe_3$ y sus aleaciones aleatorias, abogando por un control preciso de las propiedades magnéticas y electrónicas para avanzar en sus aplicaciones en espintrónica, memorias magnéticas y dispositivos termoeléctricos.

Palabras clave: Teoría del Funcional de la Densidad, monocapas, ferromagnetismo, antiferromagnetismo, semi-metal, aleaciones aleatorias.

Abstract

This study presents a thorough investigation of the magnetic and electronic properties of $XGeTe_3$ (X = Cr, Mn, Fe) monolayers and their random alloys, utilizing density functional theory (DFT) with PBE and PBESol functionals, supplemented by Hubbard U corrections. $CrGeTe_3$ exhibits robust ferromagnetic (FM) ordering with a calculated band gap that aligns well with experimental data, highlighting its potential for practical applications. The $MnGeTe_3$ monolayer shows half-metallic (HM) behavior, making it particularly promising for spintronic applications. In contrast, $FeGeTe_3$ reveals an antiferromagnetic (AFM) ground state and potential dynamical instabilities, necessitating further exploration to optimize its electronic properties.

For the random alloys, significant modifications in magnetic moments and electronic structures were noted. Specifically, in $Cr_{1-x}GeMn_xTe_3$, magnetic moment disorder suggests complex magnetic ground states beneficial for spintronics. Meanwhile, $Cr_{1-x}GeFe_xTe_3$ demonstrates strong hybridization effects, indicating its suitability for magnetic sensors and thermoelectric applications. The $Fe_{1-x}GeMn_xTe_3$ system reveals structural challenges at higher Mn concentrations, but its thermodynamic stability supports its potential use in magnetic tunneling junctions.

Overall, this research emphasizes the considerable technological prospects of $XGeTe_3$ monolayers and their random alloys, advocating for precise control over magnetic and electronic properties to advance their applications in spintronics, magnetic memory, and thermoelectric devices.

Keywords: Density Functional Theory, monolayers, ferromagnetism, anti-ferromagnetism, half-metal,random alloys.

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Chapter 1

Introduction

1.1 Background

Concrete is the synthetic material currently produced in volumes larger than any other material on Earth. With an annual consumption of approximately 35 billion tonnes, it is only second to water in terms of global usage[1,2]. As the backbone of modern infrastructure, it provides the foundations for buildings, bridges, roads, dams, and other structures essential for societal development. Its widespread adoption arises from a unique combination of strength, versatility, and cost-effectiveness[3], rendering it indispensable to the construction industry.

Nevertheless, despite the ubiquity of concrete, the properties of its key constituent, cement, remain incompletely understood. Cement is a chemically complex material, composed of a heterogeneous mixture of minerals that undergo a series of hydration reactions upon contact with water. The principal product of cement hydration—and the primary binding phase of concrete—calcium silicate hydrate (C-S-H)[1] is the responsible for the mechanical strength, chemical and transport properties and durability of hardened cement paste and, consequently, of concrete itself[4,5,6,7]. Therefore, understanding the atomic and mechanical properties of C-S-H is of the uttermost importance to better formulate cementitious materials with enhanced performance and durability.[8]

---

[1]Cement chemistry nomenclature
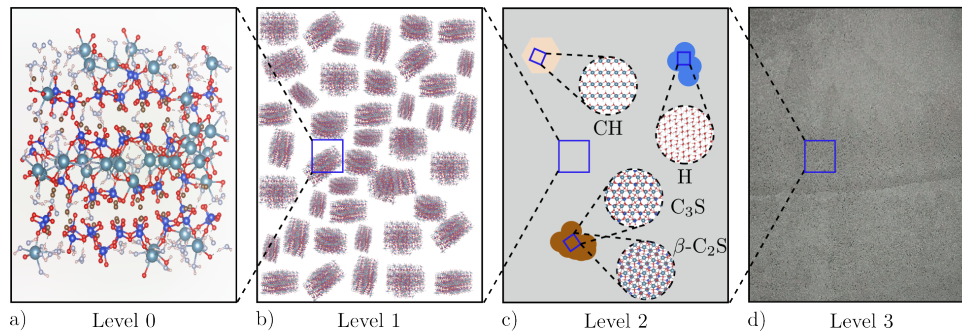
Figure 1.1: A four-level model representing the upscaling of C-S-H properties from the nanoscale to the engineering scale. (a) snapshot of C-S-H's nanostructure. (b) microstructure of C-S-H created by agglomeration of randomly oriented C-S-H nanoparticles. (c) microtexture of hardened paste composed by hydration products. (d) macrotexture of cement paste at the engineering scale. Adapted from[9].

1.2   Problem Statement

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1.3   General and Specific Objectives

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1.4   Overview

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Chapter 2

Theoretical Background

This chapter is devoted to present the theoretical foundations and formalism of Density Functional Theory (DFT) and related methods required for the development of the results presented in this work. Starting with the many-body Schrödinger equation, this chapter covers the Born-Oppenheimer approximation, the Hartree-Fock approximation, Hohenberg-Kohn theorems, the Kohn-Sham equations, exchange-correlation functionals, and definitions on Ab initio molecular dynamics (AIMD) and machine learning force fields (MLFFs), along with implementation details in the Vienna Ab initio Simulation Package (VASP).

Ultimately, the aim of this chapter is to provide a comprehensive understanding of the theoretical framework that underpins the computational methods utilised in this work, enabling the reader to grasp the principles and assumptions that govern the simulations and analyses performed throughout.

2.1 Many Body Schrödinger Equation

In the realm of materials science, comprehending particle behaviour within a system inevitably demands resorting to intricate principles of quantum mechanics. Our journey shall commence by describing the physical laws that shape the interactions among particles constituting a system—electrons and nuclei alike.

2.1.1 The Coulomb Interaction

Materials may be thought of as complex assemblies of electrons and nuclei, held together by a delicate balance between attractive Coulomb interactions—primarily between electrons and nuclei—and repulsive interactions between like-charged particles, such as electron-electron and

nucleus-nucleus pairs, which govern the overall dynamics of the material system[10,11,12]. From classical electrostatics, these interactions can be mathematically expressed as follows:

- Electron-electron interactions

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \qquad (2.1)$$

- Electron-nucleus interactions

$$\hat{V}_{nn} = \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \qquad (2.2)$$

- Electron-nuclei interactions

$$\hat{V}_{en} = - \sum_{i \neq I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \qquad (2.3)$$

where e is the electronic charge, ϵ_0 is the vacuum permittivity, Z_I and Z_J are the atomic numbers of nuclei I and J, respectively, and $\mathbf{r}_i$ and $\mathbf{R}_I$ are the position vectors of electrons and nuclei, respectively. Moreover, we must also consider the kinetic energy of the collection of electrons and nuclei

$$\hat{T} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \qquad (2.4)$$

where $\hbar$ is the reduced Planck's constant, m_e is the electron mass, and M_I is the mass of the nucleus I.

2.1.2 The Time-Independent Schrödinger Equation

The Time-Independent Schrödinger Equation (TISE) lies at the heart of non-relativistic quantum mechanics, providing a mathematical framework to describe stationary electronic states of quantum systems. It takes the following form:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (2.5)$$

where $\hat{H}$ is the Hamiltonian of the system, encompassing both kinetic and potential energies, $\psi(\mathbf{r})$ is the wavefunction of the system, and E is the energy eigenvalue associated with the state described by $\psi(\mathbf{r})$. It is important to note that Equation 2.5 is applicable to a single particle, yet a material system is composed of many electrons (N) and nuclei (M) with spatial coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ and $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M$, respectively. Therefore, we must introduce a so

called many-body wavefunction given by:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M) \tag{2.6}$$

On this basis, the many-body version of Equation 2.5 shall be constructed by combining the kinetic (Equation 2.4) and potential (Equations 2.1, 2.2, and 2.3) energy contributions, leading to the following expression:

$$\left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \right.$$
$$\left. \frac{1}{2}\sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi = E_{\text{tot}}\Psi \tag{2.7}$$

Equation 2.7 provides a complete description of the stationary states of a non-relativistic many-body system, under time-independent conditions and in the absence of external fields. Additionally, we can achieve a more compact formulation by introducing the concept of atomic units. To this end, let us consider the simplest electron-nucleus system—the hydrogen atom—where the electron orbital has an average radius $a_0 \approx 0.529\,\text{Å}$. Thereby, the Coulomb energy for such a system is given by:

$$E_{\text{Ha}} = \frac{e^2}{4\pi\epsilon_0 a_0} \tag{2.8}$$

where 'Ha' stands for Hartree. Within this framework, the Hartree energy represents the Coulomb interaction between two fundamental charges separated by a distance of one Bohr radius (a_0). Moreover, the angular momentum quantisation condition for the electron in the hydrogen atom is given by

$$m_e v a_0 = \hbar \tag{2.9}$$

Additionally, the equilibrium condition between the nuclear attraction and the electron's centrifugal force can be expressed as:

$$\frac{e^2}{4\pi\epsilon_0 a_0^2} = \frac{m_e v^2}{a_0} \tag{2.10}$$

By combining Equations 2.8, 2.9, and 2.10, we derive the following relationships:

$$\frac{e^2}{4\pi\epsilon_0 a_0} = \frac{\hbar^2}{m_e a_0^2} \tag{2.11}$$

$$\frac{1}{2}m_e v^2 = \frac{1}{2}E_{\text{Ha}} \tag{2.12}$$

This latter relation showcases that the kinetic energy is of the same order as E_{Ha}, rendering it convenient to normalise Equation 2.7 by this quantity:

$$
\begin{aligned}
\Bigg[&-\sum_i \frac{1}{2} a_0^2 \nabla_i^2 - \sum_I \frac{1}{2} \frac{1}{(M_I/m_e)} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{a_0}{|\mathbf{r}_i - \mathbf{r}_j|} \\
&+ \frac{1}{2} \sum_{I \neq J} Z_I Z_J \frac{a_0}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} Z_I \frac{a_0}{|\mathbf{r}_i - \mathbf{R}_I|} \Bigg] \Psi = \frac{E_{\text{tot}}}{E_{\text{Ha}}} \Psi
\end{aligned}
\tag{2.13}
$$

A final simplification involves setting our energy units to Ha, distance units to a_0, and mass units to m_e. The last missing constant e is set to 1, leading to the following expression:

$$
\begin{aligned}
\Bigg[&-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \\
&\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \Bigg] \Psi = E_{\text{tot}} \Psi
\end{aligned}
\tag{2.14}
$$

Ultimately, even though Equation 2.14 provides an exact method capable of yielding various properties of a material system—such as elastic, thermal, and electronic properties—a combination of mathematical complexity and computational limitations renders it intractable to solve for any realistic system. Moreover, the wavefunction contains vastly more information than is necessary to describe most observable properties of a material. Therefore, we must resort to alternative formulations that allow us to extract only the relevant information from the wavefunction whilst reducing the computational cost of the calculations. The remainder of this chapter is dedicated to presenting such alternative approaches that ultimately lead to the computational methods employed throughout this work.

2.2 The Born-Oppenheimer Approximation

For atoms in a solid, we can think of nuclei as being held immobile in a fixed position, while electrons instantaneously react to any nuclei movement. This assumption is based on the fact that nuclei are much heavier than electrons—by three to four orders of magnitude—making the former behave like classical particles. Thereby, we can rewrite the many-body wavefunction as a product of two wavefunctions:

$$
\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M) = \psi_{\mathbf{R}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \chi(\mathbf{R})
\tag{2.15}
$$

where $\psi_{\mathbf{R}}$ is the electronic wavefunction parametrised by the nuclear positions $\mathbf{R}$, and χ is the nuclear wavefunction. Furthermore, this significant mass disparity enables a systematic

approximation scheme, in which the electronic wavefunction is solved for fixed nuclei, and its solution is used as an effective potential for the nuclear dynamics afterwards. First, nuclei kinetic energy is neglected, as their positions are assumed to be fixed:

$$\sum_I \frac{\nabla_I^2}{2M_I} = 0 \quad \text{and} \quad E = E_{\text{tot}} - \sum_{I<J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{2.16}$$

Following, we define the Coulomb potential of the nuclei experienced by the electrons as:

$$V_{\text{n}}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \tag{2.17}$$

Then, Equation 2.14 can be rewritten as:

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\text{n}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi = E\Psi \tag{2.18}$$

Finally, by using Equation 2.15, we can define the electronic and nuclear Schrödinger equations as follows:

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\text{n}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \psi_{\mathbf{R}} = E_{\mathbf{R}} \psi_{\mathbf{R}} \tag{2.19}$$

$$\left[-\sum_I \frac{\nabla_I^2}{2M_I} + \sum_{I<J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E(\mathbf{R}_1, \ldots, \mathbf{R}_M) \right] \chi(\mathbf{R}) = E_{\text{tot}} \chi(\mathbf{R}) \tag{2.20}$$

where $E_{\mathbf{R}} = E(\mathbf{R}_1, \ldots, \mathbf{R}_M)$ is the electronic surface energy, which is a function of the nuclear positions, and serves as an effective potential shaping the nuclear dynamics.

2.3 Hartree-Fock Approximation

The essence of the Hartree-Fock approximation (HFA) is approximate the interacting many-electron system (Equation 2.18) by a set of non-interacting single-particle problems subject to an effective mean-field potential[13,14,15]. As a means to this, we first rewrite the total wavefunction for a system with N electrons as the product of single-electron wavefunctions—often referred to as the Hartree approximation[16]—as showcased in Equation 2.21.

$$\Psi^H(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_{i=1}^N \phi_i(\mathbf{r}_i) \tag{2.21}$$

Following, we construct the total energy functional as the expectation value of the Hamiltonian operator:

$$E^H[\{\phi_i\}] = \left\langle \Psi^H \middle| \hat{H} \middle| \Psi^H \right\rangle \tag{2.22}$$

Expanding Equation 2.22:

$$E^H[\{\phi_i\}] = \sum_{i=1}^{N} \int \phi_i^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} + V_\mathrm{n}(\mathbf{r}) \right) \phi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{i \neq j} \int \int \frac{|\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.23)$$

where the first term adds up the kinetic energy and electron-nuclear attraction overall electrons, whilst the second accounts for the classical electron-electron repulsion energy averaged over the electron density distribution. In order to find the set of orbitals $\{\phi_i\}$ that minimises the total energy functional we use the variational principle where we shall impose the orthonormality condition:

$$\int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} \quad (2.24)$$

for what we introduce the Lagrange multipliers λ_{ij} to enforce these constraints and define the Lagrangian:

$$\mathcal{L} = E^H[\{\phi_i\}] - \sum_{i=1}^{N} \lambda_{ij}(\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (2.25)$$

which ultimately simplifies to:

$$\mathcal{L} = E^H[\{\phi_i\}] - \sum_{i=1}^{N} \varepsilon_i(\langle \phi_i | \phi_i \rangle - 1) \quad (2.26)$$

Then, we need to compute the derivative of $\mathcal{L}$ with respect to ϕ_i^* and set it to zero:

$$\frac{\delta \mathcal{L}}{\delta \phi_i^*}(\mathbf{r}) = 0 \quad (2.27)$$

which yield to the Hartree equation:

$$\left[-\frac{\nabla^2}{2} + V_\mathrm{n}(\mathbf{r}) + V_i^H(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (2.28)$$

where $V_n(\mathbf{r})$ represents the electrostatic interaction between electrons and nuclei, and the Hartree potential

$$V_i^H(\mathbf{r}) = \sum_{j \neq i} \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.29)$$

accounts for the average electrostatic interaction experienced by the i-th electron due to all other electrons in the system. This effective mean-field potential replaces the electron-electron interactions, effectively simplifying the many-body problem into single-particle problems.

2.3.1 The Pauli Exclusion Principle

So far, we have introduced the Hartree approximation, which assumes that the many-electron wavefunction can be expressed as a product of single-particle wavefunctions. However, this approach does not account for the indistinguishability of electrons and the Pauli exclusion principle, which states that no two fermions—half spin particles, such as electrons—can reside in the same quantum state simultaneously. In doing so, it imposes a restriction on the possible configurations of electrons in a system that shall be accounted for.

In order to achieve this, V. Fock[17] introduced a different approximation to the wavefunction by using a Slater determinant—a mathematical construct that combines one-electron wavefunctions in such a way that satisfies the antisymmetry principle. This is done by expressing the overall wavefunction as the determinant of a matrix of single-electron wavefunctions:

$$
\Psi^{HF}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}
\begin{vmatrix}
\phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \ldots & \phi_1(\mathbf{r}_N) \\
\phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \ldots & \phi_2(\mathbf{r}_N) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_N)
\end{vmatrix}
\tag{2.30}
$$

where $1/\sqrt{N!}$ is a normalisation factor. To illustrate this, consider a two-electron system with single-particle wavefunctions $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$. The Slater determinant for this system would be:

$$
\Psi^{HF}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}
\begin{vmatrix}
\phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) \\
\phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2)
\end{vmatrix}
= \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \right]
\tag{2.31}
$$

Evidently, $\Psi^{HF}(\mathbf{r}_1,\mathbf{r}_2) = -\Psi^{HF}(\mathbf{r}_2,\mathbf{r}_1)$, which satisfies the antisymmetr principle.

2.3.2 The Hartree-Fock Equations

The Hartree-Fock equations are derived in a similar manner we addressed the Hartree equations. We first define the total energy with the Hartree-Fock wavefunction (Equation 2.30)

$$
\begin{aligned}
E^{HF}[\{\phi_i\}] &= \left\langle \Psi^{HF} \middle| \hat{H} \middle| \Psi^{HF} \right\rangle \\
&= \sum_i \langle \phi_i | \frac{\nabla^2}{2} + V_\mathrm{n}(\mathbf{r}) | \phi_i \rangle \\
&+ \frac{1}{2} \sum_{i \neq j} \langle \phi_i \phi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \phi_i \phi_j \rangle \\
&- \frac{1}{2} \sum_{i \neq j} \langle \phi_i \phi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \phi_j \phi_i \rangle
\end{aligned}
\tag{2.32}
$$

Consecutively, using the variational principle, we derive the Hartree-Fock equations:

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_i^H(\mathbf{r}) + \right] \phi_i(\mathbf{r}) - \sum_{j \neq i} \langle \phi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \phi_i \rangle \phi_j(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{2.33}$$

Noticeably, Equation 2.33 has an extra term compared with the Hartree equation (Equation 2.28). This term is called the "exchange" term[12], and describes the effects of exchange between electrons. It is convenient to try to express the Hartree-Fock equations in a more compact form, so we define the single-particle and total densities as

$$\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2 \tag{2.34}$$

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}) \tag{2.35}$$

so the Hartree potential can be expressed as

$$V_i^H(\mathbf{r}) = \sum_{j \neq i} \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \int \frac{\rho(\mathbf{r}') - \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{2.36}$$

Therefore, the single-particle exchange density can be constructed as

$$\rho_i^X(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{\phi_i(\mathbf{r})\phi_i^*(\mathbf{r})} \tag{2.37}$$

Finally, the Hartree-Fock equations take the form

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_i^H(\mathbf{r}) + V_i^X(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{2.38}$$

where V_i^X stands for the exchange potential

$$V_i^X(\mathbf{r}) = - \int \frac{\rho_i^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{2.39}$$

2.4   Density Functional Theory

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2.4.1   First Hohenberg-Kohn Theorem

2.4.2   Second Hohenberg-Kohn Theorem

2.4.3   Kohn-Sham Equations

2.4.4   Exchange-Correlation Functionals

2.5   Ab initio Molecular Dynamics

2.5.1   Born-Oppenheimer Molecular Dynamics

2.5.2   Car-Parrinello Molecular Dynamics

2.6   Machine Learning Force Fields

2.7   Computational Implementation in VASP

2.7.1   Plane Wave Basis Set

2.7.2   K-Point Sampling and Cutoff Energy

2.7.3   Pseudopotentials

2.8   Density of States

Chapter 3

Methodology

Chapter 4

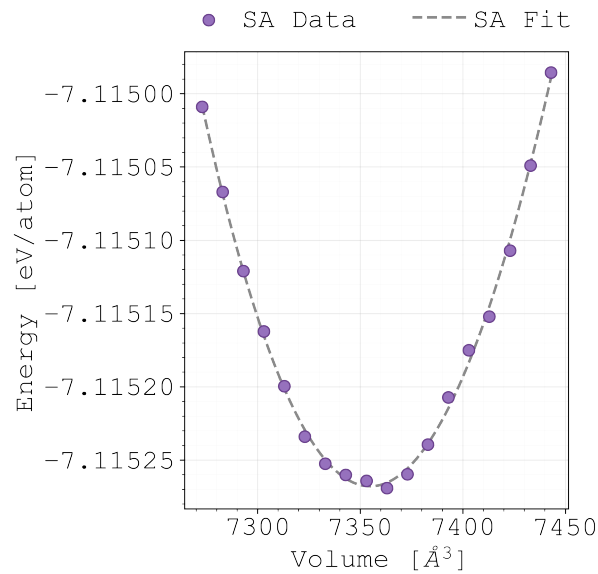# Results & Discussion

4.1 My results

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Figure 4.1: A schematic representation of the DFT formalism. The many-body wavefunction is replaced by a single-particle wavefunction, which is used to calculate the electron density. The electron density is then used to calculate the total energy of the system. Adapted from[10].

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