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Doctoral Dissertation

First-Principles Calculations on the Origin
of Mechanical Properties and Electronic
Structures of $3d$, $4d$, and $5d$
Transition Metal Monocarbides

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Abstract

Much is not systematically known about the origin of mechanical properties of $5d$ transition metal carbides including tungsten carbide, which is applied as main materials of cutting instruments, dies, and other wear-resistant parts. In order to understand the microscopic origin of hardness in the carbides, the mechanical properties and electronic structures of $5d$ transition metal monocarbides MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$) in five different crystal structures (NaCl-, WC-, ZnS-, CsCl-, and NiAs-type structures) are analyzed using first-principles calculations based on the density functional theory. Our results would indicate that in terms of the Debye temperature, WC-type WC and NiAs-type ReC have the highest and second highest hardness among all of the MC , respectively. By examining the Debye temperature in the series, it is found out that MC in the ranges of less than and more than half filled $5d$ shells are brittle and ductile, respectively. Our results would indicate that filling in the bonding and anti-bonding states contributes to brittleness and ductility. The Debye temperature could be a key to understanding the origin of hardness in terms of bulk and shear moduli. In order to understand hardness in more detail, we consider bulk modulus. Our calculations show that the bulk moduli of the $5d$ transition metal carbides universally follow those of the homogeneous electron gas model, depending on interstitial electron density. This analysis might indicate that the origin of mechanical properties is the interstitial electron density. In addition, we evaluate some other structural properties such as equilibrium volume, formation enthalpy, and elastic constants to investigate structural stability. On the basis of the theoretical findings, we discuss the microscopic mechanisms of hardness and brittleness in $3d$, $4d$, and $5d$ transition metal carbides MC ($3d$: $M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$. $4d$: $M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$. $5d$: $M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).

Chapter 1

Introduction

Elastic properties of transition metal carbides such as TiC, ZrC, VC, NbC, Cr₃C₂, Mo₂C, and WC were reported in previous researches [1, 2]. The correlation between elastic properties such as Young's modulus and sample porosity was studied [1]. The previous research indicates that as the sample porosity increases, Young's modulus decreases. The temperature dependency of Young's modulus within the temperature range of 103 K to 1373 K for TiC, ZrC, VC, NbC, Cr₃C₂, Mo₂C, and WC was also investigated [2]. These materials were manufactured by sintering their powders and using other methods.

Hard materials are important in engineering. Transition metal carbides attract much attention as hard materials, because they have remarkable physical properties such as high hardness, high strength, high melting temperature, high stiffness, wear resistance, durability, and chemical stability. Therefore transition metal carbides are key materials in both fundamental studies and technological applications in the field of structural materials. Researches for hard materials, which have physical properties of high hardness and high strength, have been intensively conducted for the last decades [3]. Hardness is related to both elastic and plastic deformation resistance, and strength is determined by failure or plastic flow of materials [3]. The description above is a general idea. However, from experience, it is considered that there is a correlation of hardness versus bulk modulus and shear modulus. This idea is supported by the previous researches [4, 5]. The previous researches show correlations of the Vickers hardness versus G/B and B by using bulk modulus B and shear modulus G . Furthermore, a correlation between the Vickers hardness and the Debye temperature was reported [5]. The Debye temperature would be an important factor for hardness because acoustic velocity is a universal physical quantity.

In particular, tungsten carbide is a remarkably interesting material in 5d transition metal carbides in the following aspects. Tungsten carbide has two forms: ditungsten carbide (W₂C) [6] and tungsten monocarbide (WC) [7]. WC phase is a dominant constituent in Co-bonded WC composites, which are utilized as cutting instruments, dies, and other wear-resistant parts. Co-bonded WC composites are manufactured by mixing and sintering WC and Co powders within the range of the temperatures from 1350 °C to 1450 °C [8]. When the sintered samples are cooled, thermal residual stresses are produced because the coefficient of the thermal expansion of WC is different from that of Co. Previous theoretical and

experimental results indicate that the thermal residual stress of WC is compressive, while that of Co is tensile [8, 9, 10, 11, 12, 13]. The previous research [8] reports that neutron diffraction is suitable enough to measure the residual strain and distribution of WC because the penetration depth of neutron diffraction is higher than that of X-ray diffraction. In addition, the effect of WC particle size in Co-bonded WC composites was studied. The WC particle size was reported to be from 0.5 μm to 5 μm [8]. When the WC particle size is large (around 5 μm), both the average residual stress of WC and that of Co are small. On the other hand, when WC particle size is small (around 0.5 μm), both the average residual stress of WC and that of Co are large.

The reason why we should pay attention to WC is as follows. Our target materials are cutting tool materials. Co-bonded WC composites are excellent as cutting tool materials. When we cut materials, cutting tool materials are pressed on the materials. In this case, the cutting tool materials are compressive. In Co-bonded WC composites, WC is more dominant than Co when we apply Co-bonded WC composites which are used in order to cut materials. The following are the reasons. In Co-bonded WC composites, the residual stress of WC is compressive, while that of Co is tensile. Co acts as a binder and WC has better elastic properties than Co does. For these reasons, we will deal with WC in the present study.

Until around the 1950s, the structure of WC had been considered to be either of the following two space groups: $P6/mmm$ and $P\bar{6}m2$. The crystal structure of WC was identified by using neutron diffraction in 1960. By this experiment, the crystal structure of WC was found to be $P\bar{6}m2$ [14]. WC has a simple hexagonal unit cell [15] and anisotropic mechanical properties [16].

The previous researches of WC [17, 18, 19, 20, 21, 22] mention that the contribution of $5d$ states to the hybridization between $5d$ transition metal and carbon is a dominant factor for hardness. In the previous researches, the hybridization is dp bonding between transition metal and carbon atoms. Bonding between metal and carbon may be anisotropic because carbon has anisotropic bonds. The previous researches would indicate that covalent and metallic bonds increase and decrease anisotropic mechanical properties, respectively.

Our target materials are cutting tool materials. In designing them, brittle and ductile properties are required because if a material is too brittle, it is breakable, while if a material is too ductile, it is difficult for the material to maintain its shape. The brittleness and ductility related to fracture and plastic deformation of materials are empirically predictable by elastic properties. By using the bulk modulus B and shear modulus G of the material, Pugh's modulus ratio B/G provides the prediction of brittleness and ductility [23]. There should be a suitable range of B/G for cutting tool materials with brittle and ductile properties. For this reason, a systematic study of brittleness and ductility is important. Transition metal carbides including WC have not been systematically studied from the viewpoint of bulk modulus, shear modulus, brittleness, ductility, the Debye temperature, and hardness. Our study is supported by a paper published in 2018, which reports results of systematic calculations performed by the density functional theory on mechanical properties of $3d$, $4d$, and $5d$ transition metal nitrides in cubic Mn_4N -type structure ($Pm\bar{3}m$) [5]. The paper also indicates that a correlation of the Vickers hardness versus the Debye temperature, mass density, and molecular weight.

Despite its physical and industrial importance, much is not known yet about the origin of its mechanical properties from the viewpoint of electronic-structure levels because it is difficult to grow large single WC crystals [7]. Although there are previous individual studies of calculations [17, 18], much is not systematically known about the origin of mechanical properties in the $5d$ transition metal carbides including tungsten carbide.

1.1 Purpose of the present study

Understanding the microscopic origin of mechanical properties on WC is crucial for further developments of hard material researches. In particular, it may be important to study the electronic origin of elastic properties such as bulk modulus and elastic constants for the following two reasons: High bulk modulus for covalent solids indicates high hardness [24] and elastic constants are related to anisotropic chemical bonds. It is known that the number of valence electrons would be correlated with elastic and electronic properties of crystals [25].

As mentioned above, it is difficult to grow large single WC crystals [7]. However, multicrystalline WC is experimentally produced. In addition, multicrystalline HfC and TaC among the $5d$ transition metal monocarbides are also experimentally produced. Previous experimental results show that the bulk moduli of multicrystalline HfC, TaC, and WC are 243 GPa, 345 GPa, and 330 GPa, respectively [26].

1.2 Materials to be studied

In the present study, we investigate electronic structures and mechanical properties for a series of $5d$ transition metal monocarbides using first-principles calculations. To analyze the effects of valence electrons, we study seven different transition metal monocarbides: HfC, TaC, WC, ReC, OsC, IrC, and PtC. To investigate the difference of their stabilities and mechanical properties, we consider five different structures: NaCl (rock-salt, $Fm\bar{3}m$), WC ($P\bar{6}m2$), ZnS (zinc-blende, $F\bar{4}3m$), CsCl ($Pm\bar{3}m$), and NiAs ($P6_3/mmc$) type structures, which are shown in Figs. 1.1, 1.2, 1.3, 1.4, and 1.5, respectively. We will discuss the origin of hardness on WC under these conditions. The Debye temperature is a criterion for estimating the contribution of one set of bulk modulus and shear modulus to hardness. Our results would indicate that WC-type WC and NiAs-type ReC have the highest and second highest hardness in the $5d$ transition metal carbides, respectively. They would indicate the following two results: Bonding and anti-bonding states contribute to brittleness and ductility, respectively and are qualitatively related to the origin of hardness. The chemical trends seen in the series of the carbides provide a clue to understand the cohesive properties of hard carbide materials.

In order to understand hardness in more detail, we consider bulk modulus. Our calculations show that the bulk moduli of the $5d$ transition metal carbides universally follow those of the homogeneous electron gas model, depending on interstitial electron density. This analysis might indicate that the origin of mechanical properties is the interstitial electron density.

Moreover, we calculate some other structural properties such as equilibrium volume, formation enthalpy, and elastic constants to investigate structural stability. On the basis of the

calculation results, we discuss the microscopic mechanisms of hardness and brittleness in $3d$, $4d$, and $5d$ transition metal carbides MC ($3d$: $M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$. $4d$: $M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$. $5d$: $M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).

Our main discussions are conducted in Chapters 1, 4, 5, and 8. The descriptions of all the chapters in the present study are as follows:

- Chapter 1 describes the introduction of the present study.
- In Chapter 2, the density functional theory is described as the fundamental theory of the present study.
- In Chapter 3, elastic mechanics of crystals is described.
- Chapter 4 deals with the computational methods and details.
- Chapter 5 presents the main discussion of our study.
- Chapters 6 and 7 provide additional information for supporting the discussion in Chapter 5.
- Chapter 8 attempts a comparison between the electron density of the homogeneous electron gas model and the interstitial electron densities of the $5d$ transition metal monocarbides in order to explain the bulk-modulus dependence of the materials.
- Chapter 9 provides the conclusion of the dissertation.

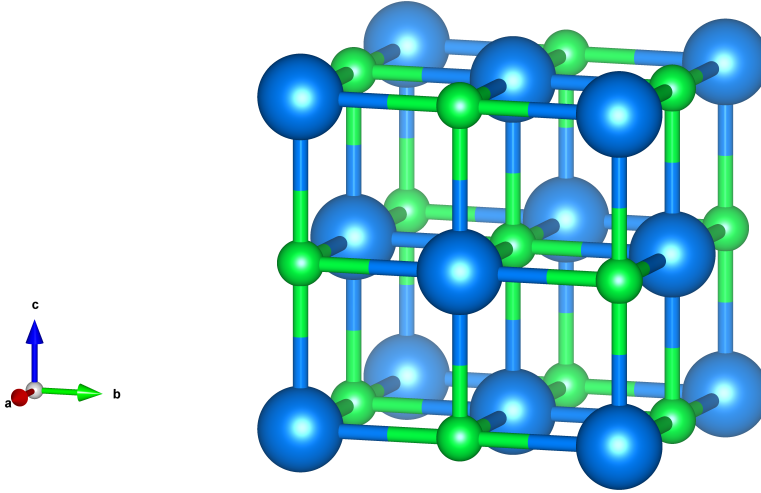


Figure 1.1: NaCl type structure. The large blue and small green spheres represent the transition metal M atoms and carbon C atoms, respectively.

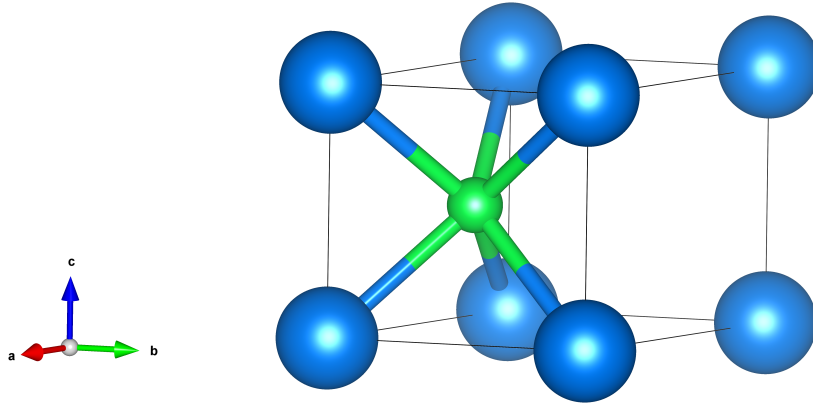


Figure 1.2: WC type structure. The large blue and small green spheres represent the transition metal M atoms and carbon C atoms, respectively.

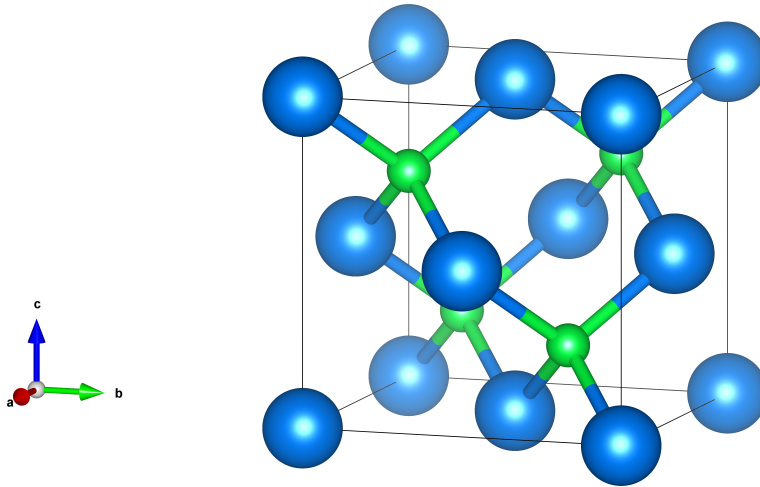


Figure 1.3: ZnS type structure. The large blue and small green spheres represent the transition metal M atoms and carbon C atoms, respectively.

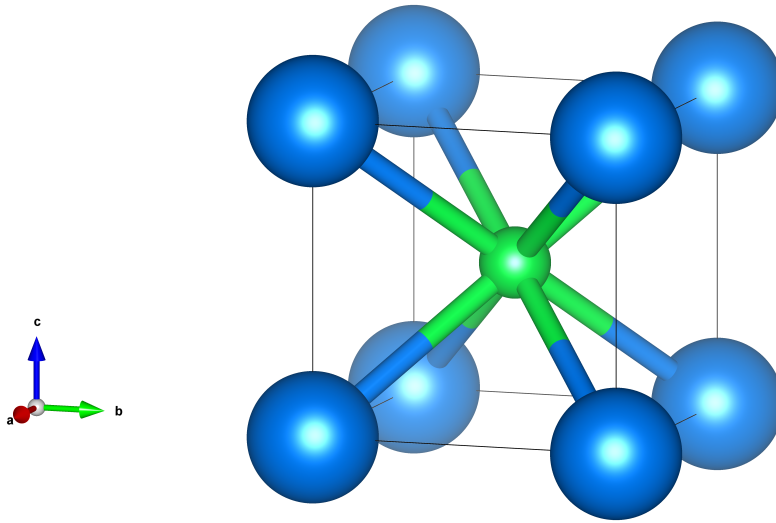


Figure 1.4: CsCl type structure. The large blue and small green spheres represent the transition metal M atoms and carbon C atoms, respectively.

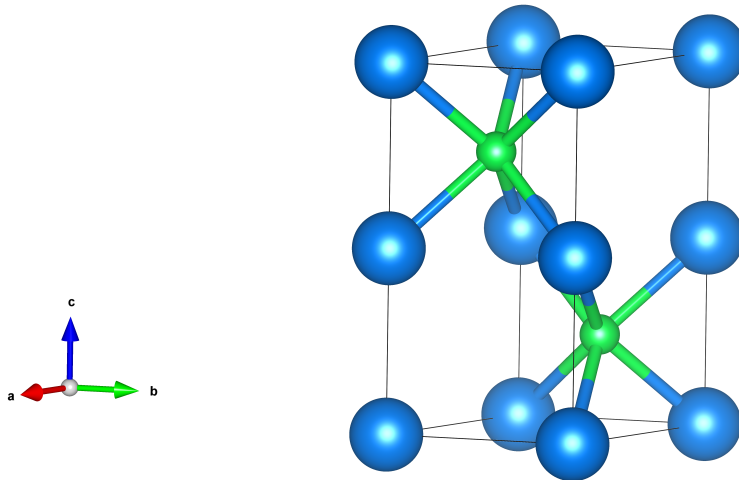


Figure 1.5: NiAs type structure. The large blue and small green spheres represent the transition metal M atoms and carbon C atoms, respectively.

Chapter 2

Density Functional Theory

First-principles electronic structure calculations are based on the laws of quantum mechanics and utilize the fundamental constants of physics with few empirical values or without any empirical values. Using the first-principles electronic structure calculations, we can gain deep and perceptive insight into the origin of mechanical, electronic, optical, and magnetic properties of materials and molecules. The number of applications based on the density functional theory has increased in materials science, solid state physics, and chemical physics. The full-potential linearized augmented plane wave (FLAPW) method, which is a first-principles electronic structure calculation of an all-electron algorithm based on the density functional theory, has been widely and universally used in the field of condensed matter physics of all atoms of the periodic table. In particular, it can be applied to structural materials, transition metals, rare-earths, surfaces, clusters, organic molecules, inorganic molecules, compact structure materials, single-crystal materials, multicrystalline materials, and so forth. The FLAPW method accurately and precisely calculates the atomic forces exerted on all the atoms in a considered system. This advantage leads to optimization.

2.1 Born-Oppenheimer Approximation

When we attempt to understand and study the physical properties of materials, we are confronted with difficulties and heavy calculations of quantum mechanics concerning the materials. From the basic quantum mechanical point of view, it is necessary that we consider the many-body problem, which is the problem of describing the system with an extraordinarily large number of electron-electron, electron-the-others, and the-others-the-others interactions. It cannot be directly solved analytically nor numerically because of the difficulties and heavy calculations.

In order to conquer the difficulties and heavy calculations of the many-body problem, we often use an approximation for performing quantum mechanical or first-principles calculations. When we apply quantum mechanics to a group of atoms, we should note that nuclei are much heavier than electrons. The mass of a proton or a neutron is about 1800 times heavier than that of an electron. In other words, except in the case of the strong correlation between

the movements of an electron and a nucleus, we can recognize that the motion of an electron is much faster than that of a nucleus because of the enormous difference between the mass of an electron and the mass of a nucleus. We can ignore all the quantum mechanical effects of nuclei due to the relatively slow movements of the nuclei while the states of electrons are changing very rapidly compared with those of the nuclei. We can assume all the nuclei to be frozen at their fixed positions, and we can presume that the states of all the electrons are instantaneously determined by the positions of all the nuclei. If we can solve the equation of the states of all the electrons with the positions of all the nuclei fixed or frozen, then we can obtain the states of the minimum or lowest total electronic energy (the ground state of the total electronic energy). We have only to calculate the movements of all the electrons determined by the configuration of all the nuclei. This idea is called the Born-Oppenheimer approximation or the Adiabatic approximation. Namely, this approximation indicates the disentanglement between the movements of all the electrons and those of all the nuclei.

We will consider a system composed of atoms. Under this approximation, the positions of all the nuclei are fixed while the states of electrons are changing rapidly. That is, the movements of both an electron and a nucleus are obviously distinguished and separated. Therefore the wave function Ψ_{total} of the system is allowed to be distinguished into two terms: the wave function $\varphi_{\text{electron}}$ of all the electrons and the wave function χ_{nucleus} of all the nuclei. The wave function Ψ_{total} of the system is written as

$$\Psi_{\text{total}}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots) = \varphi_{\text{electron}}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots) \chi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots). \quad (2.1)$$

Here, note that the semicolon in $\varphi_{\text{electron}}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots)$ indicates that $\mathbf{R}_n$ ($n = 1, 2, \dots$) is taken as a parameter when the state of the electronic subsystem is solved.

We consider the stationary Schrödinger equation (the eigenequation) of the system described as

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots) \Psi_{\text{total}}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots) = E \Psi_{\text{total}}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots), \quad (2.2)$$

where E is the eigenvalue of the Hamiltonian $\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots)$ of the system. The non-relativistic Hamiltonian of the system is written as

$$\begin{aligned} & \mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots) \\ &= \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,n} \frac{1}{4\pi\epsilon_0} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} \\ &+ \sum_n \frac{\mathbf{P}_n^2}{2M_n} + \frac{1}{2} \sum_{n \neq m} \frac{1}{4\pi\epsilon_0} \frac{Z_n Z_m e^2}{|\mathbf{R}_n - \mathbf{R}_m|}. \end{aligned} \quad (2.3)$$

The mass of the i th electron is m , and the mass of the n th nucleus is M_n . The kinetic momentum operator of the i th electron is $\mathbf{p}_i$ and the kinetic momentum operator of the n th nucleus is $\mathbf{P}_n$. The two constants e and ϵ_0 suggest the charge of an electron and the electric permittivity of free space, respectively. The n th parameters $Z_n e$ (Z_n : integer) and $\mathbf{R}_n$ denote

the charge and position of the n th nucleus, respectively. The i th parameter $\mathbf{r}_i$ indicates the position related to the state of the i th electron. Here, note that the Hamiltonian of the system is only an example. The inner structures of all the nuclei are ignored. A nucleus is regarded as a point particle with its mass and charge. All of the magnetic interactions and all of the nuclear spins are ignored. Although the Hamiltonian is fundamental, the Hamiltonian would be reliable enough to calculate all the physical properties of a material if the eigenvalues, eigenstates, and eigenfunctions of the Hamiltonian could be solved exactly. We will solve the eigenequation of the Hamiltonian in the Born-Oppenheimer approximation.

In solving the eigenequation of the Hamiltonian (Eq. 2.2) and (Eq. 2.3) in the Born-Oppenheimer approximation, we divide the Hamiltonian $\mathcal{H}$ into three terms: the Hamiltonian $\mathcal{H}_{\text{electron}}$ of the subsystem of all the electrons, the Hamiltonian $\mathcal{H}_{\text{nucleus}}$ of the subsystem of all the nuclei, and the interaction Hamiltonian $\mathcal{H}_{\text{electron-nucleus}}$ between electrons and nuclei. The Hamiltonian $\mathcal{H}_{\text{electron}}$ is distinguished into two terms: the kinetic energy T_{electron} of all the electrons and the interaction potential energy $U_{\text{electron-electron}}$ between electrons and electrons. The Hamiltonian $\mathcal{H}_{\text{nucleus}}$ is divided into two terms: the kinetic energy T_{nucleus} of all the nuclei and the interaction potential energy $U_{\text{nucleus-nucleus}}$ between nuclei and nuclei. The Hamiltonian $\mathcal{H}_{\text{electron}}$, kinetic energy T_{electron} , and interaction potential energy $U_{\text{electron-electron}}$ of the electrons are written as

$$\begin{aligned}\mathcal{H}_{\text{electron}} &= T_{\text{electron}} + U_{\text{electron-electron}}, \\ T_{\text{electron}} &= - \sum_i \frac{\hbar^2}{2m} \nabla_i^2, \\ U_{\text{electron-electron}} &= \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}.\end{aligned}\tag{2.4}$$

Here, note that the kinetic momentum operator $\mathbf{p}_i$ and kinetic energy $\mathbf{p}_i^2/2m$ of the i th electron are described as

$$\begin{aligned}\mathbf{p}_i &= \frac{\hbar}{i} \nabla_i = \begin{pmatrix} \frac{\hbar}{i} \frac{\partial}{\partial x_i} \\ \frac{\hbar}{i} \frac{\partial}{\partial y_i} \\ \frac{\hbar}{i} \frac{\partial}{\partial z_i} \end{pmatrix}, \\ \frac{\mathbf{p}_i^2}{2m} &= \frac{-\hbar^2}{2m} \Delta_i = \frac{-\hbar^2}{2m} \nabla_i^2 = \frac{-\hbar^2}{2m} \nabla_i \cdot \nabla_i = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right),\end{aligned}\tag{2.5}$$

where the position vector $\mathbf{r}_i$ of the i th electron in the Cartesian coordinates is defined as

$$\mathbf{r}_i = (x_i \quad y_i \quad z_i).\tag{2.6}$$

The Hamiltonian $\mathcal{H}_{\text{nucleus}}$, kinetic energy T_{nucleus} , and interaction potential energy $U_{\text{nucleus-nucleus}}$

of the nuclei are written as

$$\begin{aligned}
\mathcal{H}_{\text{nucleus}} &= T_{\text{nucleus}} + U_{\text{nucleus-nucleus}}, \\
T_{\text{nucleus}} &= - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2, \\
U_{\text{nucleus-nucleus}} &= \frac{1}{2} \sum_{n \neq m} \frac{1}{4\pi\epsilon_0} \frac{Z_n Z_m e^2}{|\mathbf{R}_n - \mathbf{R}_m|}.
\end{aligned} \tag{2.7}$$

Here, note that the kinetic momentum operator $\mathbf{P}_n$ and kinetic energy $\mathbf{P}_n^2/2m$ of the n th nucleus are described as

$$\begin{aligned}
\mathbf{P}_n &= \frac{\hbar}{i} \nabla_n = \begin{pmatrix} \frac{\hbar}{i} \frac{\partial}{\partial X_n} \\ \frac{\hbar}{i} \frac{\partial}{\partial Y_n} \\ \frac{\hbar}{i} \frac{\partial}{\partial Z_n} \end{pmatrix}, \\
\frac{\mathbf{P}_n^2}{2M_n} &= \frac{-\hbar^2}{2M_n} \Delta_n = \frac{-\hbar^2}{2M_n} \nabla_n^2 = \frac{-\hbar^2}{2M_n} \nabla_n \cdot \nabla_n = \frac{-\hbar^2}{2M_n} \left(\frac{\partial^2}{\partial X_n^2} + \frac{\partial^2}{\partial Y_n^2} + \frac{\partial^2}{\partial Z_n^2} \right),
\end{aligned} \tag{2.8}$$

where the position vector $\mathbf{R}_n$ of the n th nucleus in the Cartesian coordinates is defined as

$$\mathbf{R}_n = (X_n \ Y_n \ Z_n). \tag{2.9}$$

The interaction Hamiltonian $\mathcal{H}_{\text{electron-nucleus}}$ is described as

$$\mathcal{H}_{\text{electron-nucleus}} = - \sum_{i,n} \frac{1}{4\pi\epsilon_0} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|}. \tag{2.10}$$

We introduce two sets of notations for the coordinates of all the electrons and all the nuclei. The notations of the electrons and nuclei are respectively written as

$$\begin{aligned}
\tilde{\mathbf{r}} &= \{\mathbf{r}_1, \mathbf{r}_2, \dots\}, \\
\tilde{\mathbf{R}} &= \{\mathbf{R}_1, \mathbf{R}_2, \dots\}.
\end{aligned} \tag{2.11}$$

In order to ensure a better understanding, we rearrange the eigenequation of the Hamiltonian (Eq. 2.2) and (Eq. 2.3). It is as follows:

$$\begin{aligned}
& [\mathcal{H}_{\text{electron}} + \mathcal{H}_{\text{electron-nucleus}} + \mathcal{H}_{\text{nucleus}}] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&= E \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
& [\mathcal{H}_{\text{electron}} + \mathcal{H}_{\text{electron-nucleus}}] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&= [E - \mathcal{H}_{\text{nucleus}}] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&= \frac{1}{\varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}})} \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) [\mathcal{H}_{\text{electron}} + \mathcal{H}_{\text{electron-nucleus}}] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \\
&= \frac{1}{\varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}})} [E - \mathcal{H}_{\text{nucleus}}] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}).
\end{aligned} \tag{2.12}$$

Because of $\chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \neq 0$, we obtain the rearranged eigenequation described as

$$\begin{aligned} & \frac{1}{\varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}})} \left[\mathcal{H}_{\text{electron}}(\tilde{\mathbf{r}}) + \mathcal{H}_{\text{electron-nucleus}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \\ &= \frac{1}{\varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}})} \left[E - \mathcal{H}_{\text{nucleus}}(\tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}). \end{aligned} \quad (2.13)$$

The left side of (Eq. 2.13) cannot equal a constant, a function of only $\tilde{\mathbf{r}}$, or a function of only $\tilde{\mathbf{R}}$. The same goes for the right side. Physical insight, however, makes it possible to assume that because all of the nuclei can be regarded as the fixed point particles at their stationary positions when the ground state of the electronic subsystem is solved, the eigenequation for the electronic states described as

$$\left[\mathcal{H}_{\text{electron}}(\tilde{\mathbf{r}}) + \mathcal{H}_{\text{electron-nucleus}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) = \mathcal{E}(\tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \quad (2.14)$$

can be solved with all the nuclei remaining in the nuclear configuration $\tilde{\mathbf{R}}$, where $\mathcal{E}(\tilde{\mathbf{R}})$ is the electronic eigenenergy in the nuclear configuration $\tilde{\mathbf{R}}$. By inserting the above eigenequation (Eq. 2.14) into the equation (Eq. 2.13), we obtain

$$\begin{aligned} & \left[\mathcal{H}_{\text{nucleus}}(\tilde{\mathbf{R}}) + \mathcal{E}(\tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\ &= E \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}). \end{aligned} \quad (2.15)$$

The above equation (Eq. 2.15) says that the movements of all the nuclei are distinguished from those of all the electrons. We obtain the methodology for solving the eigenequation of the Hamiltonian of the system, although it is approximately done. Since the variables $\tilde{\mathbf{r}}$ and $\tilde{\mathbf{R}}$ in (Eq. 2.13) are not exactly separated, the exact solution to the problem (Eq. 2.13) of the Hamiltonian cannot be obtained. The application of the separation of the variables $\tilde{\mathbf{r}}$ and $\tilde{\mathbf{R}}$ to the eigenequation of the Hamiltonian (Eq. 2.2) is effective, although it causes the accuracy problem in the Born-Oppenheimer approximation.

The electronic energy $\mathcal{E}(\tilde{\mathbf{R}})$ is regarded as the adiabatic contribution to the nuclear potential energy. The electronic wave function $\varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}})$ is regarded as the dominant factor of the non-adiabatic contribution to the nuclear potential energy. The non-adiabatic contribution is derived from (Eq. 2.15). Multiplying the left and right sides of (Eq. 2.15) by

$\varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}})$ enables us to obtain the equation represented as

$$\begin{aligned}
& \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \left[\mathcal{H}_{\text{nucleus}}(\tilde{\mathbf{R}}) + \mathcal{E}(\tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&= E \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
& \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \left[T_{\text{nucleus}}(\tilde{\mathbf{R}}) + U_{\text{nucleus-nucleus}}(\tilde{\mathbf{R}}) + \mathcal{E}(\tilde{\mathbf{R}}) \right] \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&= E \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
& \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \left[U_{\text{nucleus-nucleus}}(\tilde{\mathbf{R}}) + \mathcal{E}(\tilde{\mathbf{R}}) \right] \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&+ \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \sum_n \left(\frac{-\hbar^2}{2M_n} \nabla_n^2 \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \right) \\
&+ \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \sum_n \left(\frac{-\hbar^2}{2M_n} \nabla_n^2 \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \\
&+ \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \sum_n \frac{-\hbar^2}{M_n} \left(\nabla_n \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right) \cdot \left(\nabla_n \chi_{\text{nucleus}}(\tilde{\mathbf{R}}) \right) \\
&= E \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \chi_{\text{nucleus}}(\tilde{\mathbf{R}}).
\end{aligned} \tag{2.16}$$

Here, we use the relation written as

$$\nabla_n^2 (\varphi \chi) = \varphi \nabla_n^2 \chi + \chi \nabla_n^2 \varphi + 2 (\nabla_n \varphi) \cdot (\nabla_n \chi). \tag{2.17}$$

By integrating over the electronic configuration $\tilde{\mathbf{r}} = \{\mathbf{r}_1, \mathbf{r}_2, \dots\}$, we obtain the equation written as

$$\begin{aligned}
& \left[- \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 + \Phi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots) \right] \chi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots) \\
&= E \chi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots),
\end{aligned} \tag{2.18}$$

where $\Phi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots)$ is the nuclear potential energy. Here, we use the relation written as

$$\int \dots \int \prod_i d\mathbf{r}_i \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) = 1. \tag{2.19}$$

The nuclear potential energy $\Phi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots)$ is described as

$$\begin{aligned}
\Phi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots) &= U_{\text{nucleus-nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots) + \mathcal{E}(\mathbf{R}_1, \mathbf{R}_2, \dots) \\
&+ \Phi_{\text{non-adiabatic}}(\mathbf{R}_1, \mathbf{R}_2, \dots).
\end{aligned} \tag{2.20}$$

Here, the term $\Phi_{\text{non-adiabatic}}(\mathbf{R}_1, \mathbf{R}_2, \dots)$ in the nuclear potential energy $\Phi_{\text{nucleus}}(\mathbf{R}_1, \mathbf{R}_2, \dots)$ is the non-adiabatic contribution. The non-adiabatic potential energy $\Phi_{\text{non-adiabatic}}(\mathbf{R}_1, \mathbf{R}_2, \dots)$

is described as

$$\begin{aligned}
& \Phi_{\text{non-adiabatic}}(\mathbf{R}_1, \mathbf{R}_2, \dots) \\
&= - \sum_n \frac{\hbar^2}{M_n} \left[\int \cdots \int \prod_i d\mathbf{r}_i \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \left(\nabla_n \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right) \right] \cdot \nabla_n \\
&\quad - \sum_n \frac{\hbar^2}{2M_n} \int \cdots \int \prod_i d\mathbf{r}_i \varphi_{\text{electron}}^*(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \left(\nabla_n^2 \varphi_{\text{electron}}(\tilde{\mathbf{r}}; \tilde{\mathbf{R}}) \right).
\end{aligned} \tag{2.21}$$

Because the movements of the nuclei are much slower than those of the electrons, the non-adiabatic potential energy is usually small. The non-adiabatic contribution is ignored or perturbatively calculated. The non-adiabatic contribution is very significant in order to calculate physical properties of a solid which are derived by the interaction between electrons and lattice vibrations.

The above nuclear eigenequation (Eq. 2.18) can be regarded as the classical-nuclear equation of motion because the mass of nucleus is larger than that of electron and because the movements of all the nuclei are slower than those of all the electrons. Namely, when we assume different nuclear configurations ($\tilde{\mathbf{R}} = \tilde{\mathbf{R}}_1, \tilde{\mathbf{R}}_2, \dots$), we can obtain the different nuclear potential energies $\Phi_{\text{nucleus}}(\tilde{\mathbf{R}})$. In addition, ions and ion cores are often substituted for nuclei because core electrons related to nuclei play a much less role than valence electrons in determining the physical properties of a solid.

2.2 One-Electron Approximation

In order to solve many-particle problems, we assume an independent particle or electron in an effective potential. The interactions of all the electrons with one another are ignored. This approximation is called “the one-electron approximation” or “the independent-particle approximation.”

We assume a periodic system which has an effective potential $U_{\text{eff}}(\mathbf{r})$ with periodicity. The eigenstates $\psi(\mathbf{r})$ of the one-electron Hamiltonian $\mathcal{H}$ described as

$$\begin{aligned}
\mathcal{H} &= \frac{-\hbar^2}{2m} \nabla^2 + U_{\text{eff}}(\mathbf{r}), \\
\mathcal{H}\psi(\mathbf{r}) &= \mathcal{E}\psi(\mathbf{r}),
\end{aligned} \tag{2.22}$$

where $\mathcal{E}$ is the eigenvalue of this eigenequation and the effective potential $U_{\text{eff}}(\mathbf{r})$ satisfies the relation written as $U_{\text{eff}}(\mathbf{r} + \mathbf{R}) = U_{\text{eff}}(\mathbf{r})$ for all the Bravais lattice vectors $\mathbf{R}$ in a Bravais lattice, can be written as

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n,\mathbf{k}}(\mathbf{r}). \tag{2.23}$$

Here, $\mathbf{k}$ is a wave vector, the index n is regarded as the band index, and a function $u_{n,\mathbf{k}}(\mathbf{r})$ has the periodicity of the Bravais lattice:

$$u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r}). \tag{2.24}$$

This is called the Bloch theorem [27]. The Bloch theorem implies the relation described as

$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R})\psi_{n,\mathbf{k}}(\mathbf{r}). \quad (2.25)$$

Hartree discovered an approximation. In the approximation, the N -particle wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is described as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_{\mathbf{k}_1}(\mathbf{r}_1)\psi_{\mathbf{k}_2}(\mathbf{r}_2) \cdots \psi_{\mathbf{k}_N}(\mathbf{r}_N), \quad (2.26)$$

where $\psi_{\mathbf{k}_i}(\mathbf{r})$ is the $\mathbf{k}_i$ th one-electron orbital. This approximation is called the Hartree approximation [28]. The Hartree approximation is in good agreement with a case where all the electronic wave functions are localized in the system.

In order to consider quantum-mechanical phenomena beyond the Hartree approximation, we assume another approximation. In the approximation, we construct an anti-symmetric N -particle state. The anti-symmetric N -particle wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is written as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\mathbf{k}_1}(\mathbf{r}_1) & \psi_{\mathbf{k}_1}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_1}(\mathbf{r}_N) \\ \psi_{\mathbf{k}_2}(\mathbf{r}_1) & \psi_{\mathbf{k}_2}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_2}(\mathbf{r}_N) \\ \vdots & \vdots & & \vdots \\ \psi_{\mathbf{k}_N}(\mathbf{r}_1) & \psi_{\mathbf{k}_N}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_N}(\mathbf{r}_N) \end{vmatrix}. \quad (2.27)$$

This wave function is called the Slater determinant [29, 30, 31]. By using the Slater determinant, we obtain the eigenequation described as

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{eff}}(\mathbf{r}) \right) \psi_{\mathbf{k}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) + V_{\text{Fock}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}), \quad (2.28)$$

where the Hartree term $V_{\text{Hartree}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})$ and the Fock term E_{Fock} are described as

$$\begin{aligned} V_{\text{Hartree}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) &= \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}), \\ V_{\text{Fock}}(\mathbf{r}) &= - \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}'), \\ \rho(\mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}'), \\ \rho(\mathbf{r}) &= \rho(\mathbf{r}, \mathbf{r}) = \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} |\psi_{\mathbf{k}}(\mathbf{r})|^2. \end{aligned} \quad (2.29)$$

Here, $\mathbb{Z}_{\psi}$ includes all the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ and $\mathbf{k}$ is an integer vector. The summation within $\mathbb{Z}_{\psi}$ is described as

$$\sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} 1 = N. \quad (2.30)$$

$\varepsilon_{\mathbf{k}}$ is the $\mathbf{k}$ th eigenvalue and $\psi_{\mathbf{k}}(\mathbf{r})$ is the $\mathbf{k}$ th one-electron wave function. This eigenequation is called the Hartree-Fock equation. This approximation is called the Hartree-Fock approximation [32].

2.3 Kohn-Sham Equation

The density functional theory for electronic structure calculations of materials is based on the Hohenberg-Kohn theorems (for further proof of the Hohenberg-Kohn theorems and detailed information of the density functional theory, see Appendix A and see also Appendix A as to the notation of the physical quantities in this section). In the density functional theory, the Kohn-Sham equation, which will be described in this section, is based on the Hohenberg-Kohn theorems.

The first Hohenberg-Kohn theorem produces the ground-state total energy and other physical properties of materials by using the ground-state electron density. The second Hohenberg-Kohn theorem yields the fundamental principle of calculating the ground-state electron density. In order to calculate the ground-state electron density simply and easily, we will derive an eigenequation which leads to the ground-state electron density $\rho(\mathbf{r})$. The energy functional $E_v[\rho(\cdot)]$ of the system with many-body effects is redefined as

$$\begin{aligned}
E_v[\rho(\cdot)] &= F_v[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \\
&= T_v[\rho(\cdot)] + U_v[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \\
&= T_s[\rho(\cdot)] + (T_v[\rho(\cdot)] - T_s[\rho(\cdot)]) + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&\quad + \left(U_v[\rho(\cdot)] - \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \\
&= T_s[\rho(\cdot)] + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}),
\end{aligned} \tag{2.31}$$

where the exchange-correlation energy $E_{\text{xc}}[\rho(\cdot)]$ is defined as

$$\begin{aligned}
E_{\text{xc}}[\rho(\cdot)] &= (T_v[\rho(\cdot)] - T_s[\rho(\cdot)]) + \left(U_v[\rho(\cdot)] - \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \\
&= F_v[\rho(\cdot)] - T_s[\rho(\cdot)] - \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\end{aligned} \tag{2.32}$$

and the functional $F_v[\rho(\cdot)]$ independent of the external potential energy $v_{\text{ext}}(\mathbf{r})$ is written as

$$F_v[\rho(\cdot)] = T_v[\rho(\cdot)] + U_v[\rho(\cdot)]. \tag{2.33}$$

Here, $T_v[\rho(\cdot)]$ is the kinetic energy functional and $U_v[\rho(\cdot)]$ is the electron-electron interaction potential energy functional. $T_s[\rho(\cdot)]$ is the kinetic energy functional of a virtual one-electron system or a virtual single-particle system.

We assume a virtual one-electron equation described as

$$\begin{aligned}
& \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \\
& \rho(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \\
& N = \int d\mathbf{r} \rho(\mathbf{r}),
\end{aligned} \tag{2.34}$$

where N is the number of all the electrons, ε_i is the i th eigenvalue of the eigenequation, $v_{\text{eff}}(\mathbf{r})$ is an effective potential energy, $\rho(\mathbf{r})$ is the electron density of the system, and $\psi_i(\mathbf{r})$ is the i th eigenfunction of the eigenequation.

Under the condition that the electronic number N is constant, by using the method of Lagrange multipliers, the least-energy principle of the ground state generates the relation described as

$$\delta \left[E_v[\rho(\cdot)] - \mu \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \right] = 0. \tag{2.35}$$

Here, note that μ is an undetermined multiplier. The undetermined multiplier μ is independent of the other parameters (*i.e.*, μ is independent of the electron density $\rho(\mathbf{r})$). We focus on variations δF depending on the electron density $\rho(\mathbf{r})$ in order to obtain the functional derivative $\delta F / \delta \rho(\mathbf{r})$. As a result, we obtain the relation written as

$$\begin{aligned}
& \delta E_v[\rho(\cdot)] - (\delta \mu) \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) - \mu \delta \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) = 0 \\
& \delta E_v[\rho(\cdot)] - \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \delta \mu - \mu \int d\mathbf{r} \delta \rho(\mathbf{r}) + \mu \delta N = 0 \\
& \delta E_v[\rho(\cdot)] - \mu \int d\mathbf{r} \delta \rho(\mathbf{r}) - \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \delta \mu + \mu \delta N = 0 \\
& \delta T_s[\rho(\cdot)] + \delta \left(\frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) + \delta E_{\text{xc}}[\rho(\cdot)] \\
& + \delta \left(\int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \right) - \mu \int d\mathbf{r} \delta \rho(\mathbf{r}) - \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \delta \mu + \mu \delta N = 0 \\
& \delta T_s[\rho(\cdot)] + e^2 \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta \rho(\mathbf{r}) + \delta E_{\text{xc}}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) \delta \rho(\mathbf{r}) \\
& + \int d\mathbf{r} \rho(\mathbf{r}) \delta v_{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r} \delta \rho(\mathbf{r}) - \left(\int d\mathbf{r} \rho(\mathbf{r}) - N \right) \delta \mu + \mu \delta N = 0 \\
& \frac{\delta T_s[\rho(\cdot)]}{\delta \rho(\mathbf{r})} + e^2 \int d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho(\cdot)]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) - \mu = 0.
\end{aligned} \tag{2.36}$$

There exists $\delta N = 0$ because N is a constant. The external potential energy $v_{\text{ext}}(\mathbf{r})$ is related to the electron density $\rho(\mathbf{r})$. The external potential energy $v_{\text{ext}}(\mathbf{r})$ is fixed because

we determine the condition of the system, although we imaginarily change the functional variation $\delta\rho(\mathbf{r})$. Therefore we define the relation described as $\delta v_{\text{ext}}(\mathbf{r}) = 0$. The functional derivative $\delta F/\delta f$ of a functional F is described as

$$\delta F = \int \frac{\delta F}{\delta f} \delta f dx, \quad (2.37)$$

where f is a function and the function f equals $f(x)$.

We define the effective potential $v_{\text{eff}}(\mathbf{r})$ so that the functional derivative $\delta T_s[\rho(\cdot)]/\delta\rho(\mathbf{r})$ of the kinetic energy functional $T_s[\rho(\cdot)]$ in (Eq. 2.34) may be exactly the same as that in (Eq. 2.36). If we solve the eigenequation (Eq. 2.34), then we obtain the relation described as

$$\begin{aligned} T_s[\rho(\cdot)] &= \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi_i(\mathbf{r}) \\ &= \sum_{i=1}^N \varepsilon_i - \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) \psi_i(\mathbf{r}) \\ &= \sum_{i=1}^N \varepsilon_i - \sum_{i=1}^N \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \\ &= \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \\ &= \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}). \end{aligned} \quad (2.38)$$

Here, note that the i th eigenvalue ε_i and the external potential energy $v_{\text{eff}}(\mathbf{r})$ are related to the electron density $\rho(\mathbf{r})$ because the i th eigenvalue ε_i and the external potential energy $v_{\text{eff}}(\mathbf{r})$ are determined from the electron density $\rho(\mathbf{r})$ by solving the eigenequation (Eq. 2.34).

In order to obtain the functional derivative $\delta T_s[\rho(\cdot)]/\delta\rho(\mathbf{r})$, we use the variational principle of the stationary Schrödinger equation. The following four different variations are described as

$$\begin{aligned} \rho(\mathbf{r}) &\rightarrow \rho(\mathbf{r}) + \delta\rho(\mathbf{r}), \\ v_{\text{eff}}(\mathbf{r}) &\rightarrow v_{\text{eff}}(\mathbf{r}) + \delta v_{\text{eff}}(\mathbf{r}), \\ \psi_i(\mathbf{r}) &\rightarrow \psi_i(\mathbf{r}) + \delta\psi_i(\mathbf{r}), \\ \varepsilon_i &\rightarrow \varepsilon_i + \delta\varepsilon_i. \end{aligned} \quad (2.39)$$

Considering the above four variations, we focus on the first-order variations of the eigenequation (Eq. 2.34). The variation of the eigenequation (Eq. 2.34) is described as

$$\begin{aligned} \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \delta\psi_i(\mathbf{r}) + \left(\delta \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \right) \psi_i(\mathbf{r}) &= (\delta\varepsilon_i) \psi_i(\mathbf{r}) + \varepsilon_i \delta\psi_i(\mathbf{r}) \\ \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \delta\psi_i(\mathbf{r}) + \psi_i(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) &= \psi_i(\mathbf{r}) \delta\varepsilon_i + \varepsilon_i \delta\psi_i(\mathbf{r}). \end{aligned} \quad (2.40)$$

Multiplying the left and right sides of the above equation (Eq. 2.40) by $\psi_i^*(\mathbf{r})$ and integrating the equation enables us to obtain the equation represented as

$$\begin{aligned}
& \psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \delta\psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) \\
&= \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \delta\varepsilon_i + \psi_i^*(\mathbf{r}) \varepsilon_i \delta\psi_i(\mathbf{r}) \\
& \quad \int d\mathbf{r} \left(\psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \right) \delta\psi_i(\mathbf{r}) + \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) \\
&= \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta\varepsilon_i + \int d\mathbf{r} \psi_i^*(\mathbf{r}) \varepsilon_i \delta\psi_i(\mathbf{r}) \\
& \quad \int d\mathbf{r} \left(\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) \right)^* \delta\psi_i(\mathbf{r}) + \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) \\
&= \left(\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \right) \delta\varepsilon_i + \varepsilon_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r}) \\
& \quad \int d\mathbf{r} (\varepsilon_i \psi_i(\mathbf{r}))^* \delta\psi_i(\mathbf{r}) + \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) \\
&= \left(\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \right) \delta\varepsilon_i + \varepsilon_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r}) \\
& \quad \varepsilon_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r}) + \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) \\
&= \left(\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \right) \delta\varepsilon_i + \varepsilon_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r}), \\
& \quad \therefore \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) = \left(\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \right) \delta\varepsilon_i.
\end{aligned} \tag{2.41}$$

Here, ε_i is a real number and we assume that the difference between the integrations of the two surface terms $\lim_{x,y, \text{ or } z \rightarrow \infty} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r})$ and $\lim_{x,y, \text{ or } z \rightarrow -\infty} \psi_i^*(\mathbf{r}) \delta\psi_i(\mathbf{r})$ vanishes. Summing all the values from the 1st value through the N th value in each of the left and right sides of the above equation (Eq. 2.41) enables us to obtain the relation described as

$$\begin{aligned}
& \sum_{i=1}^N \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}}(\mathbf{r}) = \sum_{i=1}^N \left(\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \right) \delta\varepsilon_i \\
& \quad \int d\mathbf{r} \left(\sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \right) \delta v_{\text{eff}}(\mathbf{r}) = \sum_{i=1}^N \delta\varepsilon_i \\
& \quad \int d\mathbf{r} \rho(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) = \sum_{i=1}^N \delta\varepsilon_i.
\end{aligned} \tag{2.42}$$

Here, note that because the i th eigenfunction $\psi_i(\mathbf{r})$ is complete-orthonormal, the integration of the i th function $\psi_i(\mathbf{r})$ is described as

$$\int d\mathbf{r} |\psi_i(\mathbf{r})|^2 = 1. \tag{2.43}$$

By using the equations (Eq. 2.38) and (Eq. 2.42), the functional derivation $\delta T_s[\rho(\cdot)]/\delta\rho(\mathbf{r})$ is written as

$$\begin{aligned}
\delta T_s[\rho(\cdot)] &= \delta \left(\sum_{i=1}^N \varepsilon_i \right) - \delta \left(\int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) \right) \\
&= \sum_{i=1}^N \delta \varepsilon_i - \int d\mathbf{r} \rho(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \delta \rho(\mathbf{r}) \\
&= \int d\mathbf{r} \rho(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) - \int d\mathbf{r} \rho(\mathbf{r}) \delta v_{\text{eff}}(\mathbf{r}) - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \delta \rho(\mathbf{r}) \\
&= - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \delta \rho(\mathbf{r}) \\
\frac{\delta T_s[\rho(\cdot)]}{\delta \rho(\mathbf{r})} &= -v_{\text{eff}}(\mathbf{r}).
\end{aligned} \tag{2.44}$$

By using (Eq. 2.36) and (Eq. 2.44), the effective potential energy $v_{\text{eff}}(\mathbf{r})$ is described as

$$\begin{aligned}
v_{\text{eff}}(\mathbf{r}) &= -\frac{\delta T_s[\rho(\cdot)]}{\delta \rho(\mathbf{r})} \\
&= \frac{e^2}{4\pi\varepsilon_0} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho(\cdot)]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) - \mu \\
&= \frac{e^2}{4\pi\varepsilon_0} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{\text{xc}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) - \mu,
\end{aligned} \tag{2.45}$$

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

$$\mu_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho(\cdot)]}{\delta \rho(\mathbf{r})}. \tag{2.46}$$

By using the equations (Eq. 2.31), (Eq. 2.38), and (Eq. 2.45), we obtain the energy functional

$E_v[\rho(\cdot)]$ written as

$$\begin{aligned}
& E_v[\rho(\cdot)] \\
&= T_s[\rho(\cdot)] + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\
&= \sum_{i=1}^N \epsilon_i - \int d\mathbf{r} v_{\text{eff}}(\mathbf{r})\rho(\mathbf{r}) + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&\quad + E_{xc}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\
&= \sum_{i=1}^N \epsilon_i - \int d\mathbf{r} \left(\frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) - \mu \right) \rho(\mathbf{r}) \\
&\quad + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\
&= \sum_{i=1}^N \epsilon_i - \int d\mathbf{r} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} \mu_{xc}(\mathbf{r})\rho(\mathbf{r}) - \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + \mu \int d\mathbf{r} \rho(\mathbf{r}) \\
&\quad + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\cdot)] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\
&= \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\cdot)] - \int d\mathbf{r} \mu_{xc}(\mathbf{r})\rho(\mathbf{r}) + \mu N.
\end{aligned} \tag{2.47}$$

The calculation of the N -electrons ground state leads to the self-consistent calculation of the one-electron eigenequation (Eq. 2.34) with the effective potential energy $v_{\text{eff}}(\mathbf{r})$ in the definition (Eq. 2.45). The one-electron eigenequation (Eq. 2.34) is called the Kohn-Sham equation. As the exchange-correlation energy functional becomes more exact, the ground-state energy derived from the eigenfunctions of the Kohn-Sham equation is more exactly calculated, although the eigenfunctions or orbitals derived from the Kohn-Sham equation are virtual.

The undetermined multiplier μ fixes the number N of all the electrons. The original of the effective potential is arbitrary and is not determined because the vacuum levels cannot be defined in all the crystal systems. Note that adding a value to the undetermined multiplier μ only decreases the eigenvalues of the eigenequation (Eq. 2.34). Therefore we need not concretely consider the undetermined multiplier μ . Determining a rule that all of the electrons occupy electronic orbitals in ascending order from the lowest energy level and fixing the number of all the electrons are sufficient and important for this calculation.

Dividing the single-particle kinetic energy and the Hartree term $E^{\text{Hartree}}[\rho(\cdot)]$, which is a long-range interaction described as

$$E^{\text{Hartree}}[\rho(\cdot)] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2}{4\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{2.48}$$

from the total energy of the system is the quintessence of the Kohn-Sham equation. Therefore all the interactions except for the Hartree term and the external potential energy can be regarded as short-range interactions. This is reasonable. When we focus on a local electron density function $\rho(\mathbf{r})$ at a local position vector $\mathbf{r}$, the exchange-correlation energy $E_{\text{xc}}[\rho(\cdot)]$ is approximately described as follows:

$$\begin{aligned} E_{\text{xc}}^{\text{LDA}}[\rho(\cdot)] &= \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r})), \\ E_{\text{xc}}^{\text{GGA}}[\rho(\cdot)] &= \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \dots). \end{aligned} \tag{2.49}$$

Here, note that the terms $\varepsilon_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r}))$ and $\varepsilon_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \dots)$ are functions of the electron density $\rho(\mathbf{r})$ and so on. The approximation method of the exchange-correlation energy $E_{\text{xc}}^{\text{LDA}}[\rho(\cdot)]$ is called the local density approximation (LDA) and that of the exchange-correlation energy $E_{\text{xc}}^{\text{GGA}}[\rho(\cdot)]$ is called the generalized-gradient approximation (GGA). In the present study, we applied the generalized-gradient approximation to our first-principles calculations.

2.4 Full-Potential Linearized Augmented Plane Wave Method

In order to solve the Kohn-Sham equation which has the effective potential with periodicity, plane wave function basis sets are often selected. This choice is compatible with the periodic conditions. When we consider electronic states near atomic nuclei, an unrealistically large number of plane wave functions would be necessary in order to calculate electronic states near atomic nuclei.

In 1937, Slater proposed an idea that plane wave functions are augmented in the sites near atomic nuclei by atomic-like functions. This idea is called the augmented plane wave (APW) method [33, 34, 35, 36, 37]. The augmented plane wave method has been the most popular scheme to calculate electronic states by using the density functional theory. The augmented plane wave method, however, has a problem. The problem is that the energy dependence of the secular equation makes it difficult to diagonalize the matrix elements.

In order to conquer the APW method problem, Andersen proposed an approximate representation of the energy dependence in the linearized form for diagonalizing the matrix elements. This idea is called the linearized augmented plane wave (LAPW) method [38, 39, 40, 41, 42, 43, 44]. Moreover, Koelling and Arbman applied the LAPW method to their calculation using a model potential within the muffin-tin approximation. The linearized augmented plane wave method yields accurate calculation results of close-packed structure systems. The method does not work well in low-symmetric and non-close-packed structure systems.

In order to conquer the LAPW method problem, the full-potential linearized plane wave (FLAPW) method was proposed [45, 46, 47, 48, 49, 50, 51]. The method is the linearized plane wave method extended in terms of the treatment of the potential energy and charge

density without the shape approximation because the LAPW method allows a straightforward extension to the treatment of crystal potentials with general shapes. The full-potential linearized plane wave method yields accurate calculation results of low-symmetric, non-close-packed structure, absorbing, and open systems. Relativistic effects can be added in the form of a scalar-relativistic treatment [52] and the second variational method [53] including spin-orbit coupling into the FLAPW method. The domain of the system in the FLAPW method is divided into two regions: the interstitial region and the maffin-tin region. In the maffin-tin region, potentials are expressed as a multiplication by radial wave functions and spherical surface harmonics.

Chapter 3

Elastic Mechanics of Crystalline Materials

3.1 Crystal Structures, Bravais Lattices, Space Groups, and Crystal Systems

The number of possible structures which a crystal can have is infinite. We can classify crystalline materials as 230 space groups, 32 crystal classes, 14 Bravais lattices, and 7 crystal systems. Each classification is concrete and specific.

Crystal Structure: A periodic array of physical matter and objects such as atoms, molecules, electronic charge distribution, and current distribution is considered as a crystal. The contents (*e.g.*, the location of atoms) of a repetitive unit cell within a crystal and the repetitive lattices (or repetitive point array) of the unit cell are completely described as a crystal structure.

Bravais Lattice: The array of discrete points which a periodic unit cell within a crystal generates is written as a linear combination of three (“primitive” or “conventional”) basis vectors. The Bravais lattice vector $\mathbf{R}$ in three-dimensional space is described as

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (n_1, n_2, n_3 \text{ integers}). \quad (3.1)$$

Here, note that the i th (primitive or conventional) basis vector $\mathbf{a}_i$ ($i = 1, 2, 3$) generates discrete points and spans three-dimensional space.

Space Group: Every crystal is invariant under symmetry operations which involve pure translations such as lattice translations, pure rotations, pure reflections, and combinations of translations, rotations, and reflections. A symmetry operation ($\alpha|\mathbf{a}$) of a crystal is written as

$$\mathbf{r}' = (\alpha|\mathbf{a})\mathbf{r} = \alpha\mathbf{r} + \mathbf{a}. \quad (3.2)$$

Here, $\mathbf{r}$ is a three-dimensional position vector before the symmetry operation, $\mathbf{r}'$ is the three-dimensional position vector after the symmetry operation, $\boldsymbol{\alpha}$ is a 3×3 rotation matrix, and $\mathbf{a}$ is a translation. Note that $\mathbf{a}$ is not necessarily a lattice translation. The complete set of the symmetry operations $(\boldsymbol{\alpha}|\mathbf{a})$ of a crystal which restore the crystal to itself is regarded as a space group.

Crystal Class: The operations $(\boldsymbol{\alpha}|\mathbf{0})$ of a crystalline material are considered as a crystal class, that is, the point group of the crystal. Restoring the crystal to itself is not imposed under the operations $(\boldsymbol{\alpha}|\mathbf{0})$, although the operations could accidentally restore the crystal to itself. In other words, the “macroscopic” physical properties of a crystalline solid are invariant under the operations $(\boldsymbol{\alpha}|\mathbf{0})$ of its point group related to its space group whose elements are $(\boldsymbol{\alpha}|\mathbf{a})$.

Crystal System: The angles α , β , and γ between two basis vectors $\mathbf{a}_i$, $\mathbf{a}_j$ ($i, j = 1, 2, 3$) are written as

$$\cos \alpha = \frac{\mathbf{a}_2 \cdot \mathbf{a}_3}{|\mathbf{a}_2||\mathbf{a}_3|}, \quad \cos \beta = \frac{\mathbf{a}_3 \cdot \mathbf{a}_1}{|\mathbf{a}_3||\mathbf{a}_1|}, \quad \cos \gamma = \frac{\mathbf{a}_1 \cdot \mathbf{a}_2}{|\mathbf{a}_1||\mathbf{a}_2|}. \quad (3.3)$$

The classification of a periodic unit cell according to the seven crystal systems is shown in Table 3.1. Here, note that the length of the three basis vectors is described as

$$a = |\mathbf{a}_1|, \quad b = |\mathbf{a}_2|, \quad c = |\mathbf{a}_3|. \quad (3.4)$$

Table 3.1: The classification of a periodic unit cell within a crystal according to the seven crystal systems. The “not-equal symbol ($\neq$)” indicates that “equality” is not imposed under the symmetry operations, although it could occur accidentally.

Crystal System	Description of Nonprimitive Cell
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = \pi/2, \beta \neq \pi/2$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = \pi/2$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = \pi/2$
Trigonal (Rhombohedral)	$a = b = c, \alpha = \beta = \gamma \neq \pi/2 < 2\pi/3$
Hexagonal	$a = b \neq c, \alpha = \beta = \pi/2, \gamma = 2\pi/3$
Cubic	$a = b = c, \alpha = \beta = \gamma = \pi/2$

3.2 Normal Strain, Shearing Strain, and Rotation

First, we consider a material without an external force in Cartesian coordinates, also called xyz three-dimensional space. We set the origin $\mathbf{O} = (0, 0, 0)$ of the Cartesian coordinates. A position vector $\mathbf{A}$ in the material from the origin $\mathbf{O}$ of the space is written as $\mathbf{A} = (x_a, y_a, z_a)$. Hereafter for simplicity, the position vector $\mathbf{A}$ is represented as $\mathbf{A} = (x, y, z)$. A position vector $\mathbf{B} = (x + dx, y + dy, z + dz)$ is defined as a neighborhood of the position vector $\mathbf{A} = (x, y, z)$. Here, note that dx , dy , and dz are infinitesimal values ($|dx| \ll 1$, $|dy| \ll 1$, $|dz| \ll 1$).

Second, we consider the material with an external force. When the material is deformed by the external force, the position vector $\mathbf{A} = (x, y, z)$ moves to the position vector $\mathbf{A}' = (X, Y, Z)$. The displacement vector of the position vector $\mathbf{A} = (x, y, z)$ by the external force is written as $\mathbf{u} = \mathbf{u}(x, y, z) = (u, v, w)$. The relation between the position vectors $\mathbf{A}$ and $\mathbf{A}'$ are described as

$$\begin{aligned} X &= x + u(x, y, z), \\ Y &= y + v(x, y, z), \\ Z &= z + w(x, y, z). \end{aligned} \tag{3.5}$$

When the material is deformed by the external force, the position vector $\mathbf{B} = (x + dx, y + dy, z + dz)$ moves to the position vector $\mathbf{B}' = (X + dX, Y + dY, Z + dZ)$. The displacement vector of the position vector $\mathbf{B}$ by the external force is written as $\mathbf{u}(x, y, z) + d\mathbf{u}(x, y, z) = (u + du, v + dv, w + dw)$. The relation between the position vectors $\mathbf{B}$ and $\mathbf{B}'$ are described

as

$$\begin{aligned}
X + dX &= x + dx + u + du \\
&= x + dx + u + \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz, \\
Y + dY &= y + dy + v + dv \\
&= y + dy + v + \frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial y}dy + \frac{\partial v}{\partial z}dz, \\
Z + dZ &= z + dz + w + dw \\
&= z + dz + w + \frac{\partial w}{\partial x}dx + \frac{\partial w}{\partial y}dy + \frac{\partial w}{\partial z}dz.
\end{aligned} \tag{3.6}$$

Here, note that du , dv , and dw are infinitesimal values ($|du| \ll 1$, $|dv| \ll 1$, $|dw| \ll 1$).

By (Eq. 3.5) and (Eq.3.6), we obtain the relation between (dX, dY, dZ) and (dx, dy, dz) described as

$$\begin{aligned}
dX &= dx + du(x, y, z) = dx + \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz, \\
dY &= dy + dv(x, y, z) = dy + \frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial y}dy + \frac{\partial v}{\partial z}dz, \\
dZ &= dz + dw(x, y, z) = dz + \frac{\partial w}{\partial x}dx + \frac{\partial w}{\partial y}dy + \frac{\partial w}{\partial z}dz.
\end{aligned} \tag{3.7}$$

Therefore the relative displacement vector $d\mathbf{u}(x, y, z) = (du, dv, dw)$ between the position vectors $\mathbf{A}$ and $\mathbf{B}$ is written as

$$\begin{aligned}
du &= dX - dx = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz \\
&= \frac{\partial u}{\partial x}dx + \left[\frac{1}{2} \left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} \right) + \frac{1}{2} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] dy + \left[\frac{1}{2} \left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} \right) + \frac{1}{2} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \right] dz, \\
dv &= dY - dy = \frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial y}dy + \frac{\partial v}{\partial z}dz \\
&= \left[\frac{1}{2} \left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right) + \frac{1}{2} \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \right] dx + \frac{\partial v}{\partial y}dy + \left[\frac{1}{2} \left(\frac{\partial v}{\partial z} - \frac{\partial w}{\partial y} \right) + \frac{1}{2} \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) \right] dz, \\
dw &= dZ - dz = \frac{\partial w}{\partial x}dx + \frac{\partial w}{\partial y}dy + \frac{\partial w}{\partial z}dz \\
&= \left[\frac{1}{2} \left(\frac{\partial w}{\partial x} - \frac{\partial u}{\partial z} \right) + \frac{1}{2} \left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) \right] dx + \left[\frac{1}{2} \left(\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} \right) + \frac{1}{2} \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \right] dy + \frac{\partial w}{\partial z}dz.
\end{aligned} \tag{3.8}$$

We obtain normal strains, shearing strains, and rotations in (Eq. 3.8). Normal strains are

defined as

$$\begin{aligned}\varepsilon_1 &= \frac{\partial u}{\partial x}, \\ \varepsilon_2 &= \frac{\partial v}{\partial y}, \\ \varepsilon_3 &= \frac{\partial w}{\partial z}.\end{aligned}\tag{3.9}$$

Shearing strains are defined as

$$\begin{aligned}\varepsilon_4 &= \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}, \\ \varepsilon_5 &= \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}, \\ \varepsilon_6 &= \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}.\end{aligned}\tag{3.10}$$

Rotations are defined as

$$\begin{aligned}\omega_x &= \frac{1}{2} \left(\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} \right), \\ \omega_y &= \frac{1}{2} \left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} \right), \\ \omega_z &= \frac{1}{2} \left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right).\end{aligned}\tag{3.11}$$

Here, note that we adopt the Voigt notation for each strain.

When we use the definitions of normal strains, shearing strains, and rotations and we rearrange the relative displacement vector $d\mathbf{u}(x, y, z) = (du, dv, dw)$ between the position vectors $\mathbf{A}$ and $\mathbf{B}$ as a matrix representation of a linear transformation, we obtain a matrix equation written as

$$\begin{pmatrix} du \\ dv \\ dw \end{pmatrix} = \begin{pmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{pmatrix} \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix} + \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix} \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix}.\tag{3.12}$$

We regard the above equation (Eq. 3.12) as an elastic deformation.

We can ignore all the rotations of the material because rotating the material does not affect all the elastic properties of the material. Namely, we can disregard the effect of all the rotations. We can ignore the second term of (Eq. 3.12). We obtain the equation of an elastic deformation without the effect of rotations described as

$$\begin{pmatrix} du \\ dv \\ dw \end{pmatrix} = \begin{pmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{pmatrix} \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix}.\tag{3.13}$$

We can apply the matrix representation (Eq. 3.13) to basis vectors or lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ of a unit cell in the material. In the Cartesian coordinates, we define the lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ as

$$\mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix}, \quad \mathbf{c} = \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix}. \quad (3.14)$$

When the material is deformed, the lattice vectors are distorted at the same time. Their distorted lattice vectors $\mathbf{a}'$, $\mathbf{b}'$, and $\mathbf{c}'$ are defined as

$$\mathbf{a}' = \begin{pmatrix} a'_x \\ a'_y \\ a'_z \end{pmatrix}, \quad \mathbf{b}' = \begin{pmatrix} b'_x \\ b'_y \\ b'_z \end{pmatrix}, \quad \mathbf{c}' = \begin{pmatrix} c'_x \\ c'_y \\ c'_z \end{pmatrix}. \quad (3.15)$$

We regard the components of (dx, dy, dz) within the matrix representation (Eq. 3.13) as those of a lattice vector. We obtain the relation between the lattice vectors ($\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$) and their distorted lattice vectors ($\mathbf{a}'$, $\mathbf{b}'$, and $\mathbf{c}'$) written as

$$\begin{pmatrix} a'_x & b'_x & c'_x \\ a'_y & b'_y & c'_y \\ a'_z & b'_z & c'_z \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix} \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}, \quad (3.16)$$

$$(\mathbf{a}' \quad \mathbf{b}' \quad \mathbf{c}') = \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix} (\mathbf{a} \quad \mathbf{b} \quad \mathbf{c}).$$

Here, note the roles of (dx, dy, dz) and (du, dv, dw) . Namely, (dx, dy, dz) indicates the components of a lattice vector in a unit cell. (du, dv, dw) , however, suggests the relative displacement between the starting point and ending point of the lattice vector. Therefore we must add the 3×3 identity matrix to (Eq. 3.13) because the lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are not distorted when the material is not deformed. Here, note that the 3×3 matrix D , which is written as

$$D = \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix}, \quad (3.17)$$

is called distortion matrix.

3.3 Elasticity and Hooke's Law

Elastic properties are conventionally described by using the Lagrangian theory of elasticity [54]. In this theory, a solid is regarded as a continuous body, as an anisotropic, isotropic, or homogeneous medium, and as an elastic body with stress and strain. We consider the free

energy F of the solid. When the strain notation $\boldsymbol{\varepsilon}$ with the i th strain ε_i ($i = 1, 2, \dots, 6$) is defined as

$$\boldsymbol{\varepsilon} = (\varepsilon_1 \quad \varepsilon_2 \quad \varepsilon_3 \quad \varepsilon_4 \quad \varepsilon_5 \quad \varepsilon_6), \quad (3.18)$$

the free energy $F(\boldsymbol{\varepsilon}, T)$ per unit volume at a finite temperature T is expanded as

$$\begin{aligned} F(\boldsymbol{\varepsilon}, T) = & F(0, T_0) + \sum_{i=1}^6 \left(\frac{\partial}{\partial \varepsilon_i} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} \varepsilon_i + \left(\frac{\partial}{\partial T} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} (T - T_0) \\ & + \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 \left(\frac{\partial^2}{\partial \varepsilon_i \partial \varepsilon_j} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} \varepsilon_i \varepsilon_j + \sum_{i=1}^6 \left(\frac{\partial^2}{\partial \varepsilon_i \partial T} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} \varepsilon_i (T - T_0) \\ & + \frac{1}{2} \left(\frac{\partial^2}{\partial T^2} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} (T - T_0)^2 + \dots \end{aligned} \quad (3.19)$$

Here, note that T_0 is a temperature.

Concerning the expansion of the free energy $F(\boldsymbol{\varepsilon}, T)$, we consider only the linear and quadratic terms among stresses, strains, and the temperature. The i th stress σ_i is defined as

$$\begin{aligned} \sigma_i(\boldsymbol{\varepsilon}, T) = & \frac{\partial}{\partial \varepsilon_i} F(\boldsymbol{\varepsilon}, T) \\ = & \left(\frac{\partial}{\partial \varepsilon_i} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} + \sum_{j=1}^6 \left(\frac{\partial^2}{\partial \varepsilon_i \partial \varepsilon_j} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} \varepsilon_j \\ & + \left(\frac{\partial^2}{\partial \varepsilon_i \partial T} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} (T - T_0). \end{aligned} \quad (3.20)$$

When we consider the natural state, where all the strains ε_i ($i = 1, 2, \dots, 6$) are zero and the temperature T equals T_0 , the solid is not strained and all the stresses of the solid are zero. Therefore we obtain the relation described as

$$\sigma_i(\mathbf{0}, T_0) = \left(\frac{\partial}{\partial \varepsilon_i} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}} = 0. \quad (3.21)$$

In addition, we can assume the relation described as

$$F(\mathbf{0}, T_0) = 0 \quad (3.22)$$

because we can determine the origin of the free energy. The entropy $S(\mathbf{0}, T_0)$ of the system at the natural state is defined as

$$S(\mathbf{0}, T_0) = - \left(\frac{\partial}{\partial T} F(\boldsymbol{\varepsilon}, T) \right) \Big|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}}. \quad (3.23)$$

The ij th elastic constant $C_{ij}(\mathbf{0}, T_0)$ at the natural state is defined as

$$C_{ij}(\mathbf{0}, T_0) = \left(\frac{\partial^2}{\partial \varepsilon_i \partial \varepsilon_j} F(\boldsymbol{\varepsilon}, T) \right) \bigg|_{\substack{\boldsymbol{\varepsilon}=\mathbf{0}, \\ T=T_0}}. \quad (3.24)$$

When we assume the condition described as

$$T = T_0 = 0 \text{ [K]}, \quad (3.25)$$

we obtain the expansion of the total energy $E(\boldsymbol{\varepsilon})$ described as

$$E(\boldsymbol{\varepsilon}) = E(\mathbf{0}) + \frac{V_0}{2} \sum_{i,j=1}^6 C_{ij} \varepsilon_i \varepsilon_j + O(\varepsilon^3). \quad (3.26)$$

Here, $E(\boldsymbol{\varepsilon})/V_0$ equals $F(\boldsymbol{\varepsilon}, 0)$, V_0 is the volume of the system at the natural state, the ij th elastic constant C_{ij} at the natural state equals $C_{ij}(\mathbf{0}, 0)$, and ε is one of the strains ε_i ($i = 1, 2, \dots, 6$).

By using (Eq. 3.26), the i th stress σ_i is described as

$$\begin{aligned} \sigma_i &= \frac{\partial}{\partial \varepsilon_i} \left(\frac{E(\boldsymbol{\varepsilon})}{V_0} \right) = \sum_{j=1}^6 C_{ij} \varepsilon_j, \\ C_{ij} &= \frac{\partial^2}{\partial \varepsilon_i \partial \varepsilon_j} \left(\frac{E(\boldsymbol{\varepsilon})}{V_0} \right) = \frac{\partial^2}{\partial \varepsilon_j \partial \varepsilon_i} \left(\frac{E(\boldsymbol{\varepsilon})}{V_0} \right). \end{aligned} \quad (3.27)$$

Therefore we obtain the stress-strain relation written as

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}. \quad (3.28)$$

This relation is called Hooke's law. Moreover, by using the symmetry in (Eq. 3.27), the stress-strain relation is rewritten as

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}. \quad (3.29)$$

This relation is called Generalized Hooke's law. As to elastic constants according to crystal systems, see Appendix B.

3.4 Pugh’s Modulus Ratio

Pugh’s modulus ratio [23], which is defined as the ratio B/G , is often used as an important criterion for determining brittle–ductile properties. By Pugh’s criterion, low and high B/G may indicate brittle and ductile properties, respectively. The well-known and useful critical value B/G is around 1.75 [55, 56, 57, 58, 59, 60, 61, 62, 63]. The quoted descriptions from Pugh’s paper [23] are written as follows:

1. “The quotient, K/G , is an indication of the extent of the plastic range for a pure metal, so that a high value of K/G is associated with malleability and a low value with brittleness.”
2. “In view of the lack of suitable experimental data it is not intended to press the correlation too far, but merely to put metals in order of malleability and to note whether very brittle and very malleable metals have the expected values of K/G and Poisson’s ratio.”
3. “Among the f.c.c. metals of high melting point in table 4, K/G varies from 1.74 for iridium to 6.14 for gold indicating on the present proposed correlation that pure gold is the most malleable f.c.c. metal and iridium the least malleable.”
4. “In materials with low K/G , which are expected to be brittle, the stress concentration at the root of a crack will be high since plastic flow is relatively difficult. This adds to the brittleness of these materials deduced from the value of K/G . Thus brittleness is a co-operative phenomenon, and will appear fairly sharply below a given value of K/G in pure metals.”
5. “In the hexagonal group the lack of slip modes causes these metals to be generally more brittle than the cubic metals but there is still a wide range of malleability.”

Here, note that K/G in Pugh’s paper is the same as B/G in the present study.

The first quoted description insists that B/G be a criterion for distinguishing brittle materials from ductile materials. The second quoted description expresses that when he discovered the criterion B/G , he had to research how malleable face-centered cubic metals are due to lack of his experimental data. In other words, from the viewpoint of plastic properties (*i.e.*, malleable or ductile properties), materials can be divided into brittleness and ductility. The third quoted description indicates that iridium has the lowest value $B/G = 1.74$ in his experimental data concerning the face-centered cubic metals. Therefore this description would suggest that the critical value of the criterion B/G is approximate 1.74. The fourth quoted description indicates that brittleness is related to plastic deformation. Therefore the value B/G of the least malleable iridium in his experimental data concerning face-centered cubic metals can be regarded as a value close to the critical value. This idea is sufficiently justified. At present, the well-known and useful critical value B/G is around 1.75 [55, 56, 57, 58, 59, 60, 61, 62, 63]. Here, note the fifth quoted description. He dealt with face-centered cubic metals and hexagonal close-packed metals in his paper. The fifth

description, however, indicates that the hexagonal close-packed metals do not contribute to the discovery of the critical value B/G . The values B/G of the hexagonal close-packed metals in his paper can be ignored under this situation. Therefore we focus on the face-centered cubic metals in his paper for a better understanding of the critical value B/G .

3.5 Debye Temperature

Mechanical properties such as hardness are related to thermodynamical parameters such as the Debye temperature [64], thermal expansion, melting temperature, and specific heat [65]. The Debye temperature is an important parameter of a solid. The Debye temperature is related to the acoustic properties, which arise from atomic vibrations and phonons. We can estimate the Debye temperature by using a simplified method where the Debye temperature is calculated from the elastic constants of the solid. This idea is proposed by Anderson [66]. This approximation is useful for all of the crystals when we can use the Voigt, Reuss, and Hill approximations. For further information about the Voigt, Reuss, and Hill approximations, see Appendix B.

In the simplified method by Anderson, the Debye temperature is determined from the single-crystal elastic constants of the solids without high performance computers because we can use the Voigt, Reuss, and Hill approximations, which are well-known methods for the calculations of isotropic polycrystalline elastic constants. In his theory, the averaged sound or acoustic velocity of the polycrystalline or isotropic solid is estimated accurately. It is shown that the Debye temperature is proportional to the averaged acoustic velocity.

We give mathematical proof of the simplified method by Anderson and the concrete formulation of the Debye temperature in the approximations. We consider elastic waves in the material because the Debye temperature is related to atomic vibrations and phonons. We assume the periodic boundary conditions of a cuboid unit cell in the material because we deal with propagation velocities of the elastic waves. Therefore in the Cartesian coordinates, the wave vector $\mathbf{k} = (k_x, k_y, k_z)$ of the wave propagation is described as

$$\begin{aligned} k_i &= \frac{2\pi n_i}{L_i}, \\ n_i &= 0, \pm 1, \pm 2, \dots, \\ i &= x, y, z, \end{aligned} \tag{3.30}$$

where k_i is the i th component of the wave vector $\mathbf{k}$, L_i is the i th length of the cuboid unit cell and n_i is an integer. We obtain the relation of the wave vector $\mathbf{k}$ described as

$$\begin{aligned} \mathbf{k}^2 &= k_x^2 + k_y^2 + k_z^2 \\ &= \left(\frac{2\pi}{L_x}\right)^2 n_x^2 + \left(\frac{2\pi}{L_y}\right)^2 n_y^2 + \left(\frac{2\pi}{L_z}\right)^2 n_z^2 \\ &\approx \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2). \end{aligned} \tag{3.31}$$

Here, we assume the approximation described as

$$L_i \approx L \quad (3.32)$$

and assume that the volume $V = L_x L_y L_z$ of the unit cell is large enough. Note that if we deal with an isotropic body, then we obtain the rigorous relation described as

$$L_i = L. \quad (3.33)$$

We assume the wave relation or approximation described as

$$\lambda = \frac{2\pi}{k} = \frac{v(\nu)}{\nu}, \quad (3.34)$$

where k , $v(\nu)$, λ , and ν are the absolute value, the propagation velocity (the phase velocity), the wavelength, and the frequency of the wave vector $\mathbf{k}$, respectively. By using (Eq. 3.31) and (Eq. 3.34), we obtain the relation described as

$$n_x^2 + n_y^2 + n_z^2 \approx \left(\frac{kL}{2\pi}\right)^2 = \left(\frac{L}{\lambda}\right)^2 = \left(\frac{L\nu}{v(\nu)}\right)^2. \quad (3.35)$$

We consider the number $N(\nu)$ of all the elastic wave states (n_x, n_y, n_z) included in a sphere with its radius L/λ . The number $N(\nu)$ is related to the degrees of freedom in the system. The number $N(\nu)$ is described as

$$\begin{aligned} N(\nu) &= \frac{4\pi}{3} \left(\frac{L}{\lambda}\right)^3 \\ &= \frac{4\pi}{3} \left(\frac{L\nu}{v(\nu)}\right)^3 \\ &= \frac{4\pi}{3} \left(\frac{\nu}{v(\nu)}\right)^3 L^3 \\ &= \frac{4\pi}{3} \left(\frac{\nu}{v(\nu)}\right)^3 V \end{aligned} \quad (3.36)$$

because the volume of the sphere with the radius L/λ indicates the number $N(\nu)$.

We consider the density of elastic wave states at the frequency ν . In the polar coordinates, the propagation velocity $v(\nu)$ is written as

$$v(\nu) = \frac{1}{\Omega} \int_0^\pi d\theta \int_0^{2\pi} d\phi \frac{\sin \theta}{v(\nu, \theta, \phi)^3}. \quad (3.37)$$

Here, $v(\nu, \theta, \phi)$ is the propagation velocity at the frequency ν in the direction (θ, ϕ) inside the material and Ω is the normalization constant described as

$$\Omega = \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin \theta = 2\pi [-\cos \theta]_{\theta=0}^\pi = 4\pi. \quad (3.38)$$

When we assume that the propagation velocity $v(\nu)$ is the constant velocity v , we obtain the density $\rho(\nu)$ of elastic wave states described as

$$\rho(\nu) = \frac{d}{d\nu} N(\nu) = \frac{d}{d\nu} \left(\frac{4\pi V}{3} \frac{1}{v^3} \nu^3 \right) = 4\pi V \frac{1}{v^3} \nu^2. \quad (3.39)$$

Here, the approximation of $v(\nu) = v$ is justified in the acoustic region (*i.e.*, the frequency ν is low) because $v(\nu)$ is average enough in all the directions inside the material, shown in (Eq. 3.37).

In the case of a polycrystalline or isotropic material, we only consider two transverse acoustic velocities v_t and one longitudinal acoustic propagation velocity v_l of the material. When we define the relation described as

$$v_1 = v_t, \quad v_2 = v_t, \quad v_3 = v_l, \quad (3.40)$$

the averaged acoustic propagation velocity v_m is defined as

$$\begin{aligned} v_m &= \left(\frac{1}{3} \sum_{i=1}^3 \frac{1}{\Omega} \int_0^\pi d\theta \int_0^{2\pi} d\phi \frac{\sin \theta}{v_i(\nu, \theta, \phi)^3} \right)^{-1/3} \\ &= \left(\frac{1}{3} \sum_{i=1}^3 \frac{1}{v_i^3} \right)^{-1/3} \\ &= \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}. \end{aligned} \quad (3.41)$$

Here, $v_i(\nu, \theta, \phi)$ is the i th propagation velocity at the frequency ν in the direction (θ, ϕ) . Without numerical calculations of complicated propagation velocity formulation, by using the three invariant velocities for all the directions, we can simplify the averaged propagation velocity because we assume the isotropic body.

By using (Eq. 3.39), the density $\rho^{\text{Debye}}(\nu)$ of all the elastic wave states with the two transverse acoustic velocities v_t and one longitudinal acoustic velocity v_l is calculated as

$$\begin{aligned} \rho^{\text{Debye}}(\nu) &= 2\rho_t(\nu) + \rho_l(\nu) \\ &= \sum_{i=1}^3 4\pi V \frac{1}{v_i^3} \nu^2 \\ &= 4\pi V \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \nu^2 \\ &= 12\pi V \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right] \nu^2 \\ &= 12\pi V \frac{\nu^2}{v_m^3}. \end{aligned} \quad (3.42)$$

Because the number $3N - 6$ of the degrees of freedom in the system is invariant, we obtain the relation described as

$$\begin{aligned}
\int_0^{\nu^{\text{Debye}}} d\nu \rho^{\text{Debye}}(\nu) &= \int_0^{\nu^{\text{Debye}}} d\nu \frac{12\pi V}{v_m^3} \nu^2 \\
&= \frac{12\pi V}{v_m^3} \left[\frac{\nu^3}{3} \right]_{\nu=0}^{\nu^{\text{Debye}}} \\
&= 4\pi V \frac{(\nu^{\text{Debye}})^3}{v_m^3} \\
&= 3N - 6 \\
&\approx 3N,
\end{aligned} \tag{3.43}$$

where N is the number of all the atoms in the volume V and ν^{Debye} is the Debye frequency. Therefore the Debye frequency is described as

$$\nu^{\text{Debye}} = \left(\frac{3N}{4\pi V} \right)^{1/3} v_m. \tag{3.44}$$

The Debye temperature is defined as

$$\Theta^{\text{Debye}} = \left(\frac{3N}{4\pi V} \right)^{1/3} \left(\frac{h v_m}{k_B} \right). \tag{3.45}$$

Here, h is Planck's constant and k_B is Boltzmann's constant. The Debye temperature depends on the averaged acoustic velocity. We can obtain the averaged acoustic velocity of the isotropic body in the Voigt, Reuss, and Hill approximations.

In order to obtain the averaged acoustic velocity, we consider elastic wave equations of the isotropic and homogeneous continuous body. In the Cartesian coordinates, the elastic wave equations are described as

$$\begin{aligned}
\rho \frac{\partial^2 u}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right), \\
\rho \frac{\partial^2 v}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial y} + \mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right), \\
\rho \frac{\partial^2 w}{\partial t^2} &= (\lambda + \mu) \frac{\partial \Delta}{\partial z} + \mu \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right), \\
\Delta &= \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}.
\end{aligned} \tag{3.46}$$

In order to solve (Eq. 3.46), we assume the three wave functions described as

$$\begin{aligned}
u &= A_1 \exp[i(\omega t - k_1 x - k_2 y - k_3 z)], \\
v &= A_2 \exp[i(\omega t - k_1 x - k_2 y - k_3 z)], \\
w &= A_3 \exp[i(\omega t - k_1 x - k_2 y - k_3 z)].
\end{aligned} \tag{3.47}$$

Here, note the following definitions. ρ is the mass density of the material. λ and μ are the first and second Lamé parameters, respectively. $\mathbf{A} = (A_1, A_2, A_3)$ is the polarization vector indicating the amplitude of the wave. $\mathbf{k} = (k_1, k_2, k_3)$ is the wave vector. $\mathbf{r} = (x, y, z)$ is the position vector. $\mathbf{u} = (u, v, w)$ is the displacement vector of the wave. t indicates time. ω is the angular frequency of the wave. Therefore we obtain the secular equation of the elastic wave equations described as

$$\begin{vmatrix} (\lambda + \mu)k_1^2 + \mu k^2 - \rho\omega^2 & (\lambda + \mu)k_1k_2 & (\lambda + \mu)k_1k_3 \\ (\lambda + \mu)k_1k_2 & (\lambda + \mu)k_2^2 + \mu k^2 - \rho\omega^2 & (\lambda + \mu)k_2k_3 \\ (\lambda + \mu)k_1k_3 & (\lambda + \mu)k_2k_3 & (\lambda + \mu)k_3^2 + \mu k^2 - \rho\omega^2 \end{vmatrix} = 0. \quad (3.48)$$

This secular equation yields the relations described as

$$\begin{aligned} \rho\omega^2 &= (\lambda + 2\mu)k^2, \\ \rho\omega^2 &= \mu k^2 \text{ (multiple root)}. \end{aligned} \quad (3.49)$$

Here, we define the direction cosines (ℓ, m, n) as the propagation direction of the wave vector $\mathbf{k}$:

$$k_1 = \ell k, \quad k_2 = mk, \quad k_3 = nk. \quad (3.50)$$

The two solutions indicate the relations described as

$$\begin{aligned} \ell A_2 - mA_1 &= 0, \quad mA_3 - nA_2 = 0, \quad nA_1 - \ell A_3 = 0 \text{ (if } \rho\omega^2 = (\lambda + 2\mu)k^2), \\ \ell A_1 + mA_2 + nA_3 &= 0 \text{ (if } \rho\omega^2 = \mu k^2). \end{aligned} \quad (3.51)$$

The first relation in (Eq. 3.51) indicates that the wave vector $\mathbf{k}$ is parallel to the polarization vector $\mathbf{A}$ because the relation between the direction cosines and the polarization vector $\mathbf{A}$ is written as

$$\begin{pmatrix} \ell \\ m \\ n \end{pmatrix} \times \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} = \mathbf{0}. \quad (3.52)$$

The second relation in (Eq. 3.51) shows that the wave vector $\mathbf{k}$ is perpendicular to the polarization vector $\mathbf{A}$ because the relation between them is described as

$$\mathbf{k} \cdot \mathbf{A} = 0. \quad (3.53)$$

By using (Eq. 3.49), we obtain the longitudinal and transverse acoustic velocities described as

$$\begin{aligned} v_l &= \frac{\omega}{k} = \sqrt{\frac{\lambda + 2\mu}{\rho}} = \sqrt{\frac{1}{\rho} \left(B - \frac{2}{3}G + 2G \right)} = \sqrt{\frac{1}{\rho} \left(B + \frac{4}{3}G \right)} = \sqrt{\frac{3B + 4G}{3\rho}}, \\ v_t &= \frac{\omega}{k} = \sqrt{\frac{\mu}{\rho}} = \sqrt{\frac{G}{\rho}}. \end{aligned} \quad (3.54)$$

Here, the first and second Lamé parameters are described as

$$\begin{aligned}\lambda &= B - \frac{2}{3}G \\ \mu &= G,\end{aligned}\tag{3.55}$$

where B and G are the bulk modulus and shear modulus of the isotropic body, respectively.

The simplified method by Anderson is one of the standard methods for calculating the Debye temperature from the single-crystal elastic constants of a solid. Anderson shows that the experimentally measured acoustic velocities of the polycrystalline solids are closely approximated by a simple averaging scheme of the single-crystal elastic constants. In the present study, we have applied the Debye temperature to a criterion for estimating the contribution of the bulk modulus and shear modulus to the hardness among materials. Here, note that the mass density of any one of the materials is almost the same as that of another of the materials.

Chapter 4

Computational Methods and Details

We perform the first-principles electronic structure calculations based on the density functional theory (DFT). The generalized gradient approximation by Perdew, Burke, and Ernzerhof (GGA-PBE) [67] is used to describe the exchange-correlation functional. The calculations are performed by using the HiLAPW code, which employs the scalar-relativistic all-electron full-potential linearized augmented plane wave (FLAPW) method [45, 46, 52, 68, 69]. We adopt the cutoff energies of 20 Ry and 160 Ry for the wave function basis set and the potential basis set, respectively. The muffin-tin radii for C and transition metals M are 0.7 Å and 1.1 Å, respectively. We use the improved tetrahedron method for $\mathbf{k}$ -space integration with uniform $\mathbf{k}$ -meshes ($12 \times 12 \times 12$), which gives enough accuracy for the present study.

The total energy $E(V)$ as a function of volume V per formula unit is calculated and fitted to Murnaghan's equation of state [70] to obtain equilibrium volume V_0 and bulk modulus B_0 at ambient pressure (0 GPa) and zero temperature (0 K) for all materials and structures. In the case of hexagonal systems, we calculate $E(V)$ by finding a lattice constant ratio c/a which gives the total energy minimum for a given V .

To clarify the structural stability of the 5d transition metal monocarbides MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$), the formation enthalpies $\Delta H(MC)$ are calculated as

$$\Delta H(MC) = E(MC) - E(M) - E(C), \quad (4.1)$$

where $E(MC)$, $E(M)$, and $E(C)$ are the total energies of MC , elemental M and C crystals, respectively. We use hcp-Hf, bcc-Ta, bcc-W, hcp-Re, hcp-Os, fcc-Ir, fcc-Pt, and diamond-C for the reference energies of M and C.

Single-crystal elastic constants are determined by the three equilibrium lattice vectors ($\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$) and their distorted lattice vectors ($\mathbf{a}'$, $\mathbf{b}'$, and $\mathbf{c}'$). The distorted lattice vectors are calculated via a matrix multiplication:

$$(\mathbf{a}' \quad \mathbf{b}' \quad \mathbf{c}') = \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix} (\mathbf{a} \quad \mathbf{b} \quad \mathbf{c}), \quad (4.2)$$

where ε_i is the i th strain tensor component in the Voigt notation ($xx = 1$, $yy = 2$, $zz = 3$, $yz = 4$, $xz = 5$, and $xy = 6$). Here, the indices 1–3 are related to normal strain components,

and the indices 4–6 are related to shear strain components (see the proof of (Eq. 3.16)). We employ the strain values $\varepsilon_i = 0.00, \pm 0.01, \pm 0.02, \pm 0.03$ to obtain the distorted lattice vectors.

The elastic constants C_{ij} in the Voigt notation ($i, j = 1, 2, \dots, 6$) are the coefficients which express a linear relation between stress σ_i and strain ε_j as $\sigma_i = \sum_{j=1}^6 C_{ij}\varepsilon_j$. C_{ij} can be calculated by the total energies as a function of the strains $\boldsymbol{\varepsilon} = [\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6]$ around an equilibrium volume V_0 . The total energy $E(\boldsymbol{\varepsilon})$ of the system with the strains $\boldsymbol{\varepsilon}$ is written as

$$E(\boldsymbol{\varepsilon}) = E(\mathbf{0}) + \frac{V_0}{2} \sum_{i,j=1}^6 C_{ij}\varepsilon_i\varepsilon_j + O(\varepsilon^3), \quad (4.3)$$

where ε is one of the strains ε_i ($i = 1, 2, \dots, 6$) and $E(\mathbf{0})$ is the total energy at V_0 , *i.e.*, $\boldsymbol{\varepsilon} = \mathbf{0}$.

The total energy $E(\boldsymbol{\varepsilon})$ as a function of the strain $\boldsymbol{\varepsilon}$ is fitted to a quadratic function in order to obtain elastic constants. Three, five, and twenty-one quadratic functions of strains are required in cubic, hexagonal, and triclinic systems, respectively because cubic, hexagonal, and triclinic systems have three, five, and twenty-one independent elastic constants, respectively. For example, the hexagonal system has the five independent elastic constants C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} . As shown in Fig. 4.1, black, red, blue, green, and cyan solid circles represent five different curves of total energy $E(\boldsymbol{\varepsilon})$ versus elastic deformation with the strain $\boldsymbol{\varepsilon}$. By using the curvatures of the curves, the hexagonal elastic constants are obtained.

Once C_{ij} are calculated, we can estimate several important mechanical parameters such as bulk modulus B and shear modulus G which represent resistance of volume dilation and resistance of shear flow, respectively. Averaged (polycrystalline) B and G are calculated from single crystal C_{ij} under two main approximations by Voigt [71] and Reuss [72] as upper and lower bounds for elastic moduli. B and G under the Voigt approximation (B^V and G^V) and the Reuss approximation (B^R and G^R) are written as

$$\begin{aligned} 9B^V &= C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{23} + C_{31}), \\ 15G^V &= C_{11} + C_{22} + C_{33} - (C_{12} + C_{23} + C_{31}) \\ &\quad + 3(C_{44} + C_{55} + C_{66}), \end{aligned} \quad (4.4)$$

$$\begin{aligned} 1/B^R &= s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{23} + s_{31}), \\ 15/G^R &= 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) \\ &\quad + 3(s_{44} + s_{55} + s_{66}), \end{aligned} \quad (4.5)$$

where s_{ij} is the ij th compliance constant calculated as $s_{ij} = (C^{-1})_{ij}$. Here, note that C is the elastic constant matrix.

Multicrystalline HfC, TaC, and WC are experimentally produced [26]. In order to compare our calculations with previous experimental results, the single-crystalline orientation effect of our calculations should be reduced. The results of our single-crystalline calculations

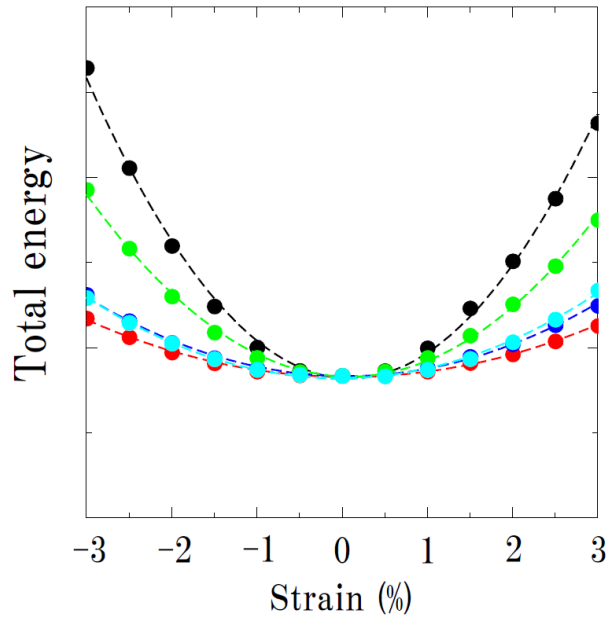


Figure 4.1: Conceptual diagram of curves of total energy versus strains in the hexagonal system. Black, red, blue, green, and cyan solid circles represent five different curves of total energy versus elastic deformation with the strain ϵ . By using the curvatures of the curves, the hexagonal elastic constants are obtained.

are converted to polycrystalline values. Actual effective moduli of polycrystals are approximated by the arithmetic average of the two bounds known as the Voigt-Reuss-Hill (VRH) approximation [73] (B^H and G^H) in the following forms:

$$\begin{aligned} B^H &= \frac{1}{2} (B^V + B^R), \\ G^H &= \frac{1}{2} (G^V + G^R). \end{aligned} \tag{4.6}$$

Hard material samples such as WC are usually prepared as polycrystalline forms with random orientations. Therefore, in this paper, we mainly show elastic moduli estimated under the VRH approximation.

Pugh's modulus ratio [23], which is defined as the ratio B/G , is often used as an important criterion for determining brittle-ductile properties. By Pugh's criterion, low and high B/G may indicate brittle and ductile properties, respectively. The well-known and useful critical value B/G is around 1.75 [55, 56, 57, 58, 59, 60, 61, 62, 63] (see Sect. 3.4).

Young's modulus Y expresses resistance of contraction. High Young's modulus indicates high stiffness. Poisson's ratio is used to estimate ductility, *i.e.*, low and high Poisson's ratios indicate brittle and ductile properties, respectively. Using B and G , we can also estimate Young's modulus Y and Poisson's ratio ν as

$$Y = \frac{9BG}{3B + G}, \tag{4.7}$$

$$\nu = \frac{3B - 2G}{2(3B + G)}. \tag{4.8}$$

To estimate Y and ν , we use B^H and G^H .

Chapter 5

5d Transition Metal Monocarbides

5.1 Cutting Technology and Cutting Tool Materials

Cutting technology, shown in Fig. 5.1, is a fundamental and essential technology for industry. In order to develop cutting technology, skilled workers have been designing by trial and error on the basis of their sense and experience. However, as long as they depend entirely upon their sense and experience, it would be difficult to develop the cutting technology such as cutting tool materials.

We need to evaluate and understand the part which cannot be completely measured in terms of their sense and experience. Materials used for making cutting tools need to be very hard. From the viewpoint of classical mechanics, many researchers have been theoretically studying and experimenting with the hardness. At first, the problem of physical phenomena such as mechanical properties seems able to be solved from the viewpoint of classical mechanics. However, when we consider the origin of the problem, we find the problem to be that of quantum mechanical phenomenon after all. Therefore research on the basis of quantum mechanics needs to be conducted to analyze the origin of hardness or microscopic phenomena. However, concerning the origin of hardness, few researches have been conducted from the viewpoint of quantum mechanics. As a result, the problem of the origin of hardness has not convincingly been solved.

In order to understand the origin of hardness, we have analyzed the quantum mechanical phenomena which occur inside materials, using a theoretical-physical calculation method called “first-principles calculation”. In addition, we have evaluated parts which cannot be measured only through human sense and experience. The present study would indicate that filling in the bonding and anti-bonding states contributes to brittleness and ductility in terms of electronic properties. As a result, we have understood the parts which cannot be understood only through human sense and experience and have clarified an important factor which cannot be measured simply with the traditional evaluation methods.

Many researchers have not regarded hardness as a universal physical quantity because the value of hardness can differ according to traditional methods of experimental measurement. These traditional estimation methods such as the Shore hardness and the Vickers hardness do not have physical universality. In order to understand hardness as a universal physical

quantity independent of various experimental measurement methods, the Debye temperature, which is related to acoustic propagation velocity, is used as a criterion for estimating the contribution of bulk modulus and shear modulus to hardness. We have found out a universal criterion for the estimation of hardness.

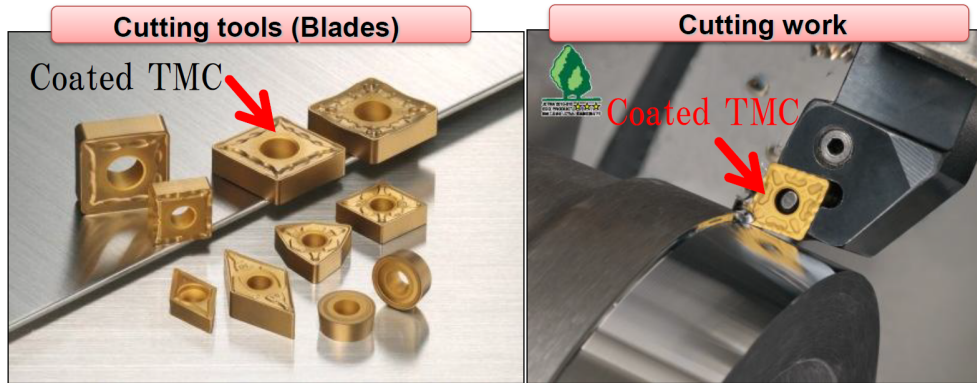


Figure 5.1: Cutting blades and cutting work. The left and right figures show cutting blades and cutting work, respectively. Yellow blades are coated transition metal carbides (TMCs). In the right figure, a rotated material is cutted. These figures are offered by Sumitomo Electric Industries, Ltd.

5.2 Results and Discussion

5.2.1 Structural Determination

We show three fundamental properties of MC in the five crystal structures: the equilibrium volumes V_0 , bulk moduli B_0 , and formation enthalpies ΔH calculated at ambient pressure (0 GPa) and zero temperature (0 K). The calculated V_0 , ΔH , and B_0 are shown in Figs. 5.2, 5.3, and 5.4, respectively.

Figure 5.2 clearly shows the smooth downward convex curves of V_0 vs. MC for each crystal structure. ReC has the minimum V_0 among the 5d TM carbides in all the crystal structures except for the ZnS-type structure in which the minimum V_0 shifts to OsC. Therefore, in particular, WC, ReC, and OsC can be relatively dense materials independent of the crystal structures. This result indicates that the element combinations of M and C are a very important factor to synthesize high-density materials. This parabolic behavior as a function of the number of valence electrons is a typical feature seen in the cohesive properties of elemental transition metals, indicating that the cohesion in the transition metal carbides studied here is also dominated by the dd bonding of the transition metal atoms. The reported experimental V_0 of HfC (NaCl-type structure), TaC (NaCl-type structure), and WC (WC-type structure) with polycrystalline forms [26] are also plotted in Fig. 5.2, showing good agreement with the calculated V_0 .

MC in the ZnS-type structure have the largest V_0 and MC except for PtC in the CsCl-type structure have the smallest V_0 , as shown in Fig. 5.2. V_0 of PtC in the NaCl-type structure is slightly smaller than that in the CsCl-type structure. There may be a correlation between the structure trends in V_0 and the coordination numbers (CN) in the crystal structures. CN is four in the ZnS-type structure, six in the WC-, NaCl-, and NiAs-type structures, and eight in the CsCl-type structure. Generally, Fig. 5.2 might indicate that as the coordination number in a structure becomes higher and lower, V_0 becomes lower and higher, respectively.

To clarify thermodynamical stabilities among the crystal structures, the calculated $\Delta H(MC)$ with respect to the elemental M and C crystals are plotted in Fig. 5.3. Figure 5.3 shows that the minimum $\Delta H(MC)$ in all the crystal structures are as follows: HfC and TaC (NaCl-type), WC and ReC (WC-type), and OsC, IrC, and PtC (ZnS-type). Negative $\Delta H(MC)$ indicates that the MC phase is stable against segregation into elemental M and C phases. HfC, TaC, and WC in the most stable crystal structures have the negative $\Delta H(MC)$. Therefore our result shows that it is difficult to synthesize ReC, OsC, IrC, and PtC in the thermodynamically stable phases at ambient pressure (0 GPa) and zero temperature (0 K), though only $\Delta H(\text{ReC})$ in the WC-type structure is slightly higher than 0 eV. Actually, to the best of our knowledge, multicrystalline NaCl-type HfC, NaCl-type TaC, and WC-type WC have been experimentally produced [26]. The calculated $\Delta H(\text{HfC})$, $\Delta H(\text{TaC})$, and $\Delta H(\text{WC})$ in the most thermodynamically stable structures are consistent with the previous experiment [26].

Figure 5.4 shows that B_0 of all the calculated materials are higher than 150 GPa. As shown in Fig. 5.4, ReC in the NiAs-type and WC-type structures have the highest and second highest B_0 among the calculated materials, respectively, suggesting that they would be distinguished into low-compressibility compounds, though ReC is not thermodynamically

stable. The calculated B_0 - MC curves show the upward convex curves with the maximum B_0 of ReC in all the crystal structures except for the NaCl-type structure, though WC has the highest B_0 in the NaCl-type structure. The reported experimental B_0 of multicrystalline HfC (NaCl-type), TaC (NaCl-type), and WC (WC-type) are also plotted in Fig. 5.4 [26], showing good agreement with our calculated B_0 . Comparing the B_0 - MC curve (Fig. 5.4) with the V_0 - MC curve (Fig. 5.2), we can speculate a strong correlation between V_0 and B_0 , *i.e.*, as V_0 becomes smaller, B_0 becomes higher. The calculated results of V_0 and B_0 would indicate that a $5d$ shell is half filled between WC and ReC. These results might suggest that WC and ReC are the border between bonding and anti-bonding states regarding the $5d$ orbital.

Common parabolic behavior as a function of the number of valence electrons seen both in the B_0 - MC curve (Fig. 5.4) and in the V_0 - MC curve (Fig. 5.2) indicates the dominance of the dd bonding in the cohesive properties just like those in the transition metals. The calculated results might suggest that WC and ReC are nearly located between bonding and anti-bonding states regarding the dd bonding, as will be mentioned in Subsect. 5.2.5.

The effects of spin-orbit coupling (SOC) on B_0 are examined to check the calculation conditions especially for the heavy-element materials. Our calculated results show that the B_0 difference of WC in the WC-type structure with and without SOC is approximately less than 1%, suggesting negligible effects of SOC on B_0 .

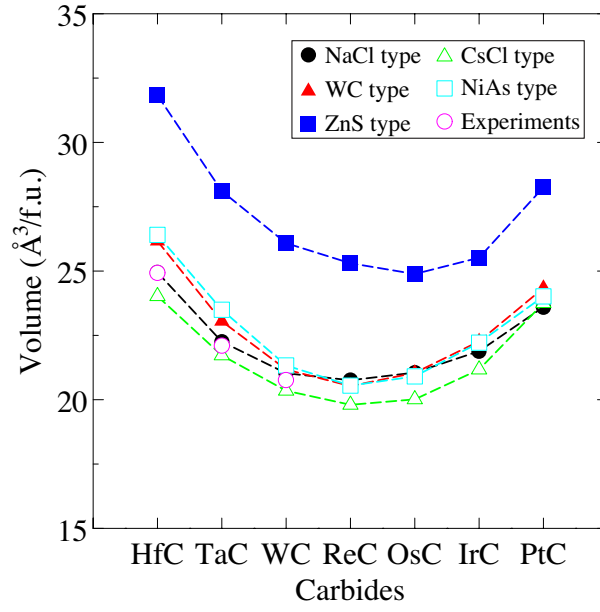


Figure 5.2: Equilibrium volume V_0 ($\text{\AA}^3/\text{f.u.}$) of MC ($M = \text{Hf}, \text{Ta}, \text{W}, \text{Re}, \text{Os}, \text{Ir}, \text{and Pt}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures. The pink open circles represent the previous experimental data [26], and the others represent our calculations.

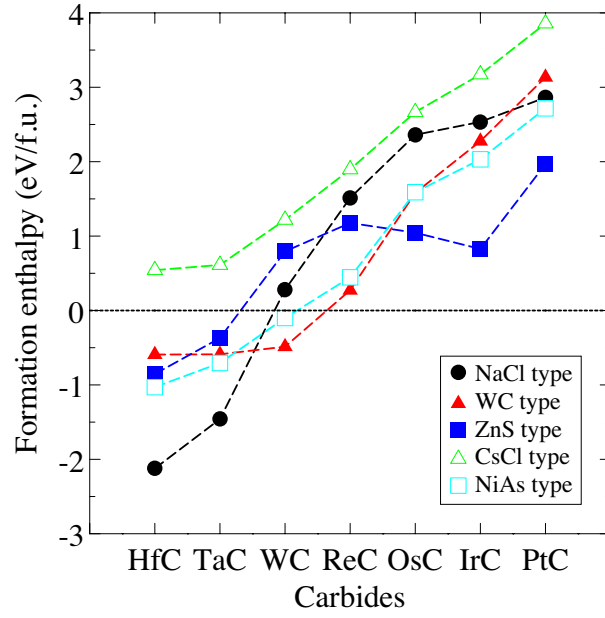


Figure 5.3: Formation enthalpies ΔH (eV/f.u.) of MC ($M = \text{Hf}, \text{Ta}, \text{W}, \text{Re}, \text{Os}, \text{Ir}, \text{and Pt}$). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively at ambient pressure (0 GPa) and zero temperature (0 K).

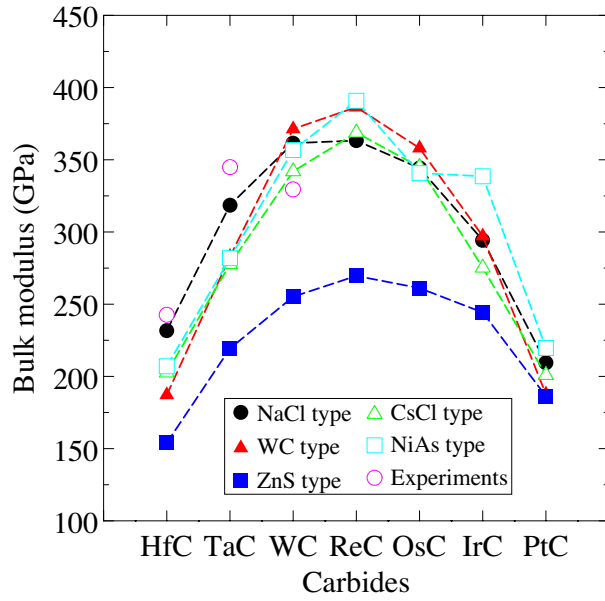


Figure 5.4: Bulk moduli B_0 (GPa), evaluated from Murnaghan's equation of state, of MC ($M = \text{Hf}, \text{Ta}, \text{W}, \text{Re}, \text{Os}, \text{Ir}, \text{and Pt}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures. The pink open circles represent the previous experimental data [26], and the others represent our calculations.

5.2.2 Elastic Constants

Analyzing elastic constants enables us to obtain and understand basic information on anisotropic mechanical properties, and also provides us remarkably useful information to estimate the hardness of compounds. The calculated elastic constants C_{ij} of *MC* are listed in Tables 5.1 (NaCl-type), 5.2 (WC-type), 5.3 (ZnS-type), 5.4 (CsCl-type), and 5.5 (NiAs-type). Because of the crystal symmetries, only three components (C_{11} , C_{12} , and C_{44}) in the cubic systems and only five components (C_{11} , C_{12} , C_{13} , C_{33} , and C_{44}) in the hexagonal systems are non-zero values.

We find the negative C_{44} values of ReC, OsC, and IrC in the NaCl-type structure (Table 5.1), HfC in the WC-type structure (Table 5.2), and HfC, TaC, OsC, IrC, and PtC in the CsCl-type structure (Table 5.4). The negative C_{44} values indicate that they are mechanically unstable with respect to the strain ε_4 by which the total energy can decrease from the equilibrium state $\varepsilon = \mathbf{0}$. The mechanically unstable property on ε_4 also occurs in *5d* TM mononitrides such as NaCl-type WN [74]. We actually confirm that the total energy of HfC in the equilibrium WC-type structure decreases by applying the non-zero ε_4 . Therefore comparing the mechanical stabilities on ε_4 with the thermodynamical stabilities ΔH shown in Fig. 5.3, we can predict that it is difficult to synthesize the mechanically unstable materials even in thermodynamically stable and metastable phases.

The trends of all the non-zero elastic constants in the mechanically stable *MC* might roughly indicate upward convex curves as functions of the atomic number of *5d* TMs. Regarding the diagonal components except for C_{44} , WC or ReC in all the crystal structures except for the ZnS-type structure has the maximum value, though C_{11} of TaC is the highest in the ZnS-type structure. In the hexagonal systems (WC-type and NiAs-type structures), the calculated C_{33} values are higher than C_{11} , as shown in Tables 5.2 and 5.5. This result indicates that these crystals are stiffer for the strains along the *c* axis than along the *a* axis. Therefore the compressibility of them is lower along the *c* axis than along the *a* axis.

Regarding the off-diagonal components, OsC in all the crystal structures except for the ZnS-type and CsCl-type structures have the highest values, though C_{12} of ReC and HfC are the highest in the ZnS-type and CsCl-type structures, respectively. Considering the minimum off-diagonal components in all the crystal structures, we find out that C_{12} of WC and C_{13} of HfC are the smallest in the CsCl-type and NiAs-type structures, respectively. This result about the minimum C_{12} of WC in the CsCl-type structure is opposite to the trends of B_0 .

Comparing the diagonal components except for C_{44} with the off-diagonal components, we may find out that the diagonal components more strongly contribute to bulk modulus than the off-diagonal components. This is because the maximum of B_0 and the diagonal components are the same and the trends of the diagonal components are similar to those of B_0 . In addition, regarding the positive C_{44} , WC in all the crystal structures except for the NaCl-type and ZnS-type structures have the maximum, though TaC and IrC have the highest in the NaCl-type and ZnS-type structures, respectively.

Table 5.1: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NaCl-type MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
HfC	499	98	168	231	1.28	430	0.19
TaC	755	109	178	324	1.43	551	0.22
WC	798	150	126	366	1.97	476	0.28
ReC	656	218	-70	364	-	-	-
OsC	553	239	-76	344	-	-	-
*IrC	440	227	-52	-	-	-	-
PtC	229	211	58	217	7.57	82	0.44

Table 5.2: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of WC-type MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
*HfC	356	87	91	485	-73	-	-	-	-
TaC	542	146	114	763	69	286	2.02	365	0.29
WC	674	232	161	942	284	375	1.40	652	0.21
ReC	702	202	209	934	171	394	1.75	569	0.26
OsC	450	350	218	853	93	364	3.87	260	0.38
IrC	452	222	157	737	67	298	2.70	295	0.33
PtC	240	169	149	387	16	197	5.91	95	0.42

Table 5.3: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of ZnS-type MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
HfC	172	149	103	156	3.44	124	0.37
TaC	317	173	154	221	1.95	290	0.28
WC	314	231	151	258	2.86	243	0.34
ReC	296	264	130	274	4.64	165	0.40
OsC	298	188	158	225	2.18	269	0.30
IrC	274	131	203	178	1.33	321	0.20
PtC	192	185	51	187	9.18	59	0.45

Table 5.4: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of CsCl-type MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
HfC	153	235	-245	208	-	-	-
TaC	507	171	-24	283	-	-	-
WC	923	52	140	342	1.52	554	0.23
ReC	920	92	55	368	2.61	375	0.33
OsC	820	114	-41	349	-	-	-
IrC	588	119	-19	275	-	-	-
PtC	278	169	-31	206	-	-	-

Table 5.5: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NiAs-type MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
HfC	382	131	50	585	91	200	1.57	315	0.24
TaC	540	111	154	701	138	288	1.57	454	0.24
WC	585	230	218	830	321	367	1.51	598	0.23
ReC	684	178	237	867	278	389	1.46	651	0.22
OsC	468	257	268	767	182	357	2.41	391	0.32
IrC	479	188	128	827	123	292	1.84	403	0.27
PtC	316	127	178	417	44	219	3.17	188	0.36

5.2.3 Elastic Moduli and Chemical Bonds

Hard materials have both high bulk modulus, which expresses their low compressibility, and high shear modulus, which expresses resistance of their shear deformation. Therefore bulk modulus and shear modulus are one set of the most important values to estimate the hardness of a material. We calculate elastic moduli: bulk modulus, shear modulus, Young's modulus, Poisson's ratio, and Pugh's modulus ratio. Using the calculated C_{ij} values, we estimate the bulk moduli B^H and the shear moduli G^H of all the MC materials except for the negative- C_{44} materials. Using B^H and G^H , we also calculate Young's moduli Y^H , Poisson's ratios ν^H , and Pugh's modulus ratio B^H/G^H . The calculated B^H , B^H/G^H , Y^H , and ν^H are also listed in Tables 5.1 (NaCl-type), 5.2 (WC-type), 5.3 (ZnS-type), 5.4 (CsCl-type), and 5.5 (NiAs-type).

Regarding bulk moduli, to confirm the difference between the anisotropic single-crystal and isotropic polycrystalline effects, we calculate the averaged bulk moduli B^H under VRH approximation by which anisotropic single-crystal elastic constants can be converted into isotropic polycrystalline elastic moduli. The calculated bulk moduli B^H shown in Tables 5.1–5.5 are in good agreement with the bulk moduli B_0 shown in Fig. 5.4, which are obtained by Murnaghan's equation of state. This result may indicate that the difference between the anisotropic single-crystal and isotropic polycrystalline effects is negligible only as far as bulk modulus, *i.e.*, the volume dilation of a material with pressure, is concerned.

Not only the bulk modulus but also the shear modulus is related to the hardness of materials. The calculated G^H values of MC determine their resistance of the averaged shear strains. We plot G^H of MC in Fig. 5.5. Regarding the calculated G^H values, WC in the WC-type structure and ReC in the NiAs-type structure are the largest and second largest, respectively. Because high shear modulus indicates anisotropic chemical bonds in materials, this result may suggest that the dominant bonds in WC-type WC and NiAs-type ReC are covalent. On the other hand, MC in the ZnS-type structure roughly have lower G^H than the other MC . This result may indicate that the key bonds in ZnS-type MC are metallic and ionic.

The stiffness of materials is one of the fundamental mechanical properties. Young's modulus is often employed to estimate the stiffness of materials. High Young's modulus suggests high stiffness. The calculated Y^H values shown in Tables 5.1–5.5 determine their resistance of the averaged uniaxial strains. Regarding the calculated Y^H values, WC in the WC-type structure and ReC in the NiAs-type structure are the largest (652 GPa) and second largest (651 GPa), respectively. We can predict that they are the stiffest in MC . Because high Young's modulus indicates strong and directional chemical bonds in materials, this result may suggest that the dominant bonds in WC-type WC and NiAs-type ReC are covalent. On the other hand, MC in the ZnS-type structure roughly have lower Y^H than the other MC . This result may indicate that the key bonds in ZnS-type MC are metallic and ionic. The trends of the calculated Y^H are in good agreement with those of G^H .

Poisson's ratio is an important criterion for roughly identifying main chemical bonds in materials. Poisson's ratio ν is defined as $\nu = -\varepsilon_t/\varepsilon_l$, where ε_t and ε_l are transverse and longitudinal strains in the direction of stretching force, respectively. Relatively low Poisson's ratio of materials would suggest directional covalent bonds. Namely, the roughly

representative criterion of Poisson's ratio is about 0.2 for covalent materials such as silicon, while it is about 0.3–0.4 for ionic materials and 0.5 for a pure-ionic limit [55].

The calculated ν^H values are shown in Tables 5.1–5.5. To confirm the dominant bonds in the stiffest *MC*, which are WC in the WC-type structure and ReC in the NiAs-type structure, we use the calculated ν^H values. The calculated ν^H values of WC-type WC and NiAs-type ReC are lower than 0.23. We may find out that the dominant bonds in them are covalent. The results of ν^H are in good agreement with those of G^H and Y^H . Regarding ν^H of *MC* except for TaC and IrC in the ZnS-type structure, we may find out that they are ionic and metallic. However, ν^H of TaC and IrC in the ZnS-type structure are lower than 0.3. These trends of ν^H in ZnS-type TaC and IrC seem to be slightly different from those of G^H and Y^H in them.

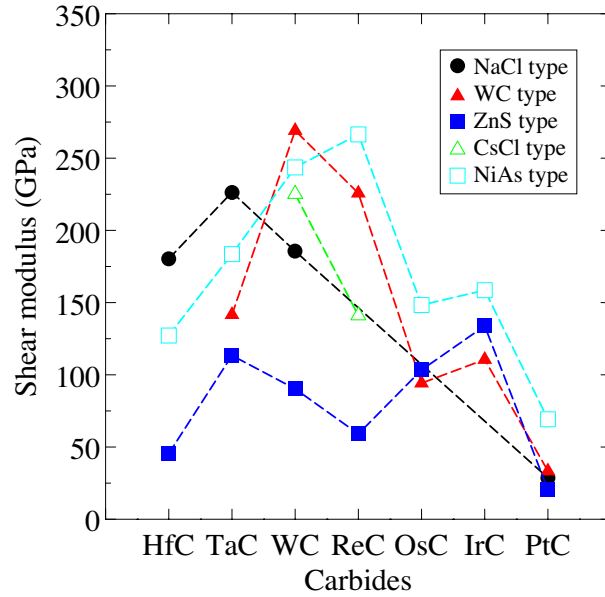


Figure 5.5: Shear moduli G^H (GPa), which are obtained from elastic constants, of *MC* (M = Hf, Ta, W, Re, Os, Ir, and Pt). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively at ambient pressure (0 GPa) and zero temperature (0 K).

5.2.4 Debye Temperature

Mechanical properties such as hardness are related to thermodynamical parameters such as the Debye temperature [64], thermal expansion, melting temperature, and specific heat [65]. The Debye temperature is one of the important parameters for obtaining some information on thermodynamical properties for a material. In addition, the Debye temperature is used to estimate hardness of a solid [6, 55, 75, 76].

Hardness is related to bulk modulus and shear modulus, and they are related to the acoustic propagation velocities in a material. The Debye temperature, which is related to the propagation velocities, is a criterion for estimating the contribution of bulk modulus and shear modulus to hardness. If the propagation velocities in a material are high, then the material is hard and its Debye temperature is also high.

Transverse and longitudinal acoustic velocities (V_t and V_l) are calculated as

$$\begin{aligned} V_t &= \sqrt{\frac{G}{\rho}}, \\ V_l &= \sqrt{\frac{3B + 4G}{3\rho}}, \end{aligned} \tag{5.1}$$

where ρ , B , and G are the mass density, the bulk modulus, and the shear modulus of a material, respectively. The averaged acoustic velocity V_m is described as

$$\frac{1}{V_m^3} = \frac{1}{3} \left(\frac{2}{V_t^3} + \frac{1}{V_l^3} \right). \tag{5.2}$$

The Debye temperature Θ_D [66] is estimated as

$$\Theta_D = \left(\frac{hV_m}{k_B} \right) \left(\frac{3N}{4\pi V} \right)^{1/3}. \tag{5.3}$$

Here, N is the number of atoms in the volume V of a material, h is Plank's constant, and k_B is Boltzmann's constant. The Debye temperature depends on the averaged acoustic velocity.

Bulk modulus B represents resistance of volume dilatation, and shear modulus G expresses resistance of shear flow. Pugh's modulus ratio B/G [23] of a hard material is an important criterion for estimating brittleness and ductility of the hard material. Low and high Pugh's modulus ratios B/G of materials typically indicate brittleness and ductility, respectively. The well-known and useful critical value B/G is around 1.75 [55, 56, 57, 58, 59, 60, 61, 62, 63]. Pugh's criterion B/G can be a good measurement for the brittleness and ductility of a material.

The calculated Θ_D of stable *MC* is shown in Fig. 5.6. Here, we classify the calculated materials into the ductile and brittle material groups according to the calculated B/G ratio, and the results are also plotted in Fig. 5.6 as solid circles and open circles for ductile and brittle materials, respectively. The results indicate that Θ_D of the brittle materials are relatively higher than those of the ductile materials. Figures 5.3 and 5.6 show that the

formation enthalpies of the brittle MC are qualitatively lower than those of the ductile MC . Therefore the results may indicate that the brittle materials are relatively more stable than the ductile materials. Focusing on the highest Θ_D of each MC , we find out that MC within the ranges of less than and more than half filled $5d$ shells are brittle and ductile, respectively. This result might indicate that bonding and anti-bonding states contribute to brittleness and ductility, respectively. In addition, shear modulus may be a dominant factor in the trends of the Debye temperature, because the trends of the calculated G^H and Θ_D are highly similar in Figs. 5.5 and 5.6. Figure 5.6 indicates that Θ_D at the range of half filled $5d$ shell are roughly the highest. This result might suggest that WC in the WC-type structure and ReC in the NiAs-type structure have the highest hardness.

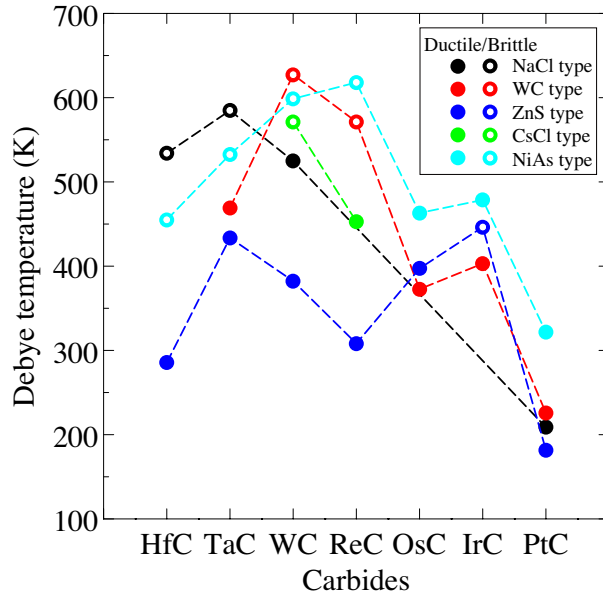


Figure 5.6: Debye temperature Θ_D (K) of MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$). Black, red, blue, green, and cyan colors represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively. The open circles represent brittleness and the solid circles represent ductility.

5.2.5 Electronic Structures

Analyzing electronic structure is important to understand the origin of physical properties for a material, revealing its electronic structure and states. The total densities of states (TDOSs) of MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$) in the NaCl-type and WC-type structures are calculated and shown in Figs. 5.7 and 5.8. Our calculated TDOSs are consistent with the previous DFT researches [17, 18, 19, 20, 21, 22].

Figures 5.7 and 5.8 would suggest that the TDOSs at the Fermi levels in the NaCl-type HfC and the WC-type WC are local minimums. All of the $5d$ transition metal carbides in the NaCl-type and WC-type have metal-bond features at the Fermi levels, as shown in Figs. 5.7 and 5.8. The previous researches [17, 18, 19, 20, 21, 22] mention that the contribution of $5d$ states to the hybridization between $5d$ transition metal and carbon is a dominant factor for hardness. Therefore bonding between metal and carbon may be anisotropic because carbon has anisotropic bonds. Metal-metal bonding may reduce the hardness or brittleness of $5d$ transition metal carbides. It would be said that covalent and metallic bonds increase and decrease anisotropic mechanical properties, respectively. Furthermore, covalent bonds may increase hardness, and metallic bonds may decrease hardness and elastic and structural stabilities.

Figures 5.7 and 5.8 might indicate that the local minimum TDOSs in the NaCl-type and WC-type structures divide TDOSs into bonding states and anti-bonding states. The chemical bonds in the WC-type structure may be considered as a mixture of the primarily metallic and covalent contributions with some of the ionic contributions. Figure 5.8 would indicate that the Fermi level is close to the local minimum TDOS without band gaps in WC-type WC. This may derive stability and high bulk modulus.

Parabolic behavior seen in Figs. 5.2 and 5.4 supports the dominant contribution of the dd bonding to the cohesion. An enhancement of the bulk modulus of the transition metal carbides compared with those of the transition metals may be evidence of important dp bonding between transition metal M and carbon C atoms. The latter bonding may be of covalent nature, increasing the hardness and enhancing the brittleness simultaneously. Figures 5.7 and 5.8 reveal that the local minima divide TDOS into bonding and anti-bonding states in the NaCl-type and WC-type structures. The chemical bonds in the WC-type structure may be considered as a mixture of the primarily metallic and covalent contributions with some of the ionic contribution. The existence of the local minimum in WC with the WC-type structure may lead to the structure stability with the high bulk modulus shown in Fig. 5.4 and Table 5.2.

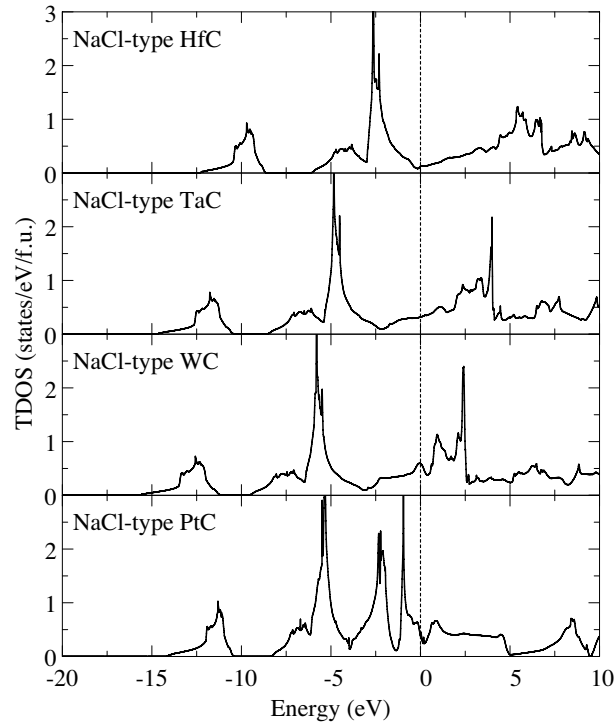


Figure 5.7: Total densities of states for NaCl-type HfC, TaC, WC, and PtC. The dotted line is the Fermi energy.

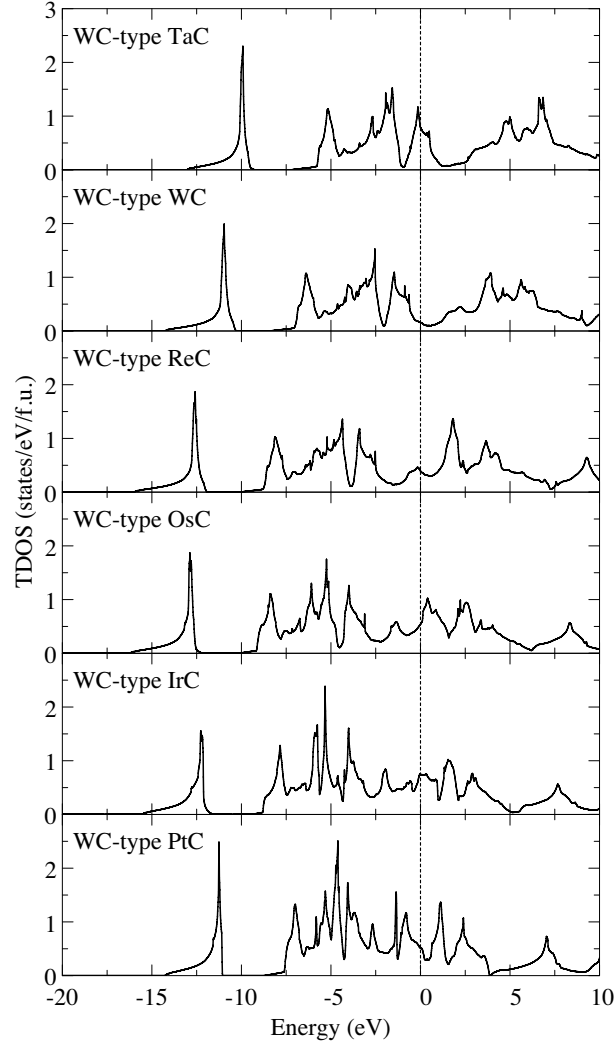


Figure 5.8: Total densities of states for WC-type TaC, WC, ReC, OsC, IrC, and PtC. The dotted line is the Fermi energy.

Chapter 6

3d Transition Metal Monocarbides

In the previous chapter, the effects of spin-orbit coupling (SOC) on bulk modulus are examined in order to check the calculation conditions for the heavy-element materials. Our calculated results show that the bulk modulus difference of WC (tungsten monocarbides) in the WC-type structure with and without SOC is approximately less than 1%, suggesting negligible effects of SOC on bulk modulus. WC in the WC-type structure is a non-magnetic material. In order to compare the tungsten carbide with other materials such as 3d, 4d, and 5d transition metal monocarbides, the effects of SOC and magnetic properties are ignored in the present study. The calculations of the 3d and 4d transition metal monocarbides are only additional information. Important and useful discussions on mechanical properties such as hardness are mainly conducted in Chapter 5.

6.1 Equilibrium Volume, Formation Enthalpy, and Bulk Modulus

We show three fundamental properties of the calculated 3d transition metal monocarbides MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) in the five crystal structures (the NaCl-type, WC-type, ZnS-type, CsCl-type, and NiAs-type structures): the equilibrium volumes V_0 , bulk moduli B_0 , and formation enthalpies ΔH calculated at ambient pressure (0 GPa) and zero temperature (0 K).

Figure 6.1 clearly shows the smooth downward convex curves of V_0 versus MC for each crystal structure. Comparing the 5d transition metal monocarbides shown in Fig. 5.2 with the 3d transition metal monocarbides shown in Fig. 6.1, we find out that under the non-magnetic and non-SOC conditions, the trends and crystal structure order of the 3d transition metal monocarbides are highly similar to those of the 5d transition metal monocarbides. In addition, Figs. 5.2 and 6.1 would indicate that the equilibrium volume V_0 of a 3d transition metal monocarbide in each crystal structure is approximately $5 \text{ \AA}^3/\text{f.u.}$ lower than that of the 5d transition metal monocarbide corresponding to the group element of the 3d transition metal. This is because the atomic sphere radius of a 3d transition metal is shorter than that of the 5d transition metal corresponding to the group element of the 3d transition metal.

Figure 6.1 shows that FeC has the minimum V_0 in all the crystal structures. Therefore, in particular, MnC, FeC, and CoC can be relatively dense materials independent of the crystal structures. This result would indicate that the element combinations of M and C are a very important factor to synthesize high-density materials. This parabolic behavior as a function of the number of valence electrons is a typical feature seen in the cohesive properties of elemental transition metals, indicating that the cohesion in the transition metal monocarbides in the present study is also dominated by the dd bonding of the transition metal atoms. Figure 6.1 would indicate that there is a correlation between the structure trends in V_0 and the coordination numbers (CN) in the crystal structures. Here, note that CN is four in the ZnS-type structure, six in the WC-type, NaCl-type, and NiAs-type structures, and eight in the CsCl-type structure. Figure 6.1 might indicate that as the coordination number in a structure becomes higher and lower, V_0 becomes lower and higher, respectively.

In order to clarify thermodynamical stabilities among the crystal structures, the calculated formation enthalpies $\Delta H(MC)$ with respect to the elemental M and C crystals are plotted in Fig. 6.2. We adopt hcp-Ti, bcc-V, bcc-Cr, fcc-Mn, bcc-Fe, hcp-Co, fcc-Ni, and diamond-C for the reference energies of M and C. Here, note that in order to reduce the calculation cost of Mn, the previous research [77] and the present study adopt fcc-Mn because the crystal structure of Mn shows very complicated configurations at ambient conditions. Mn has two kinds of structures: α -Mn and β -Mn. At zero temperature (0 K), α -Mn is the ground state of Mn: the conventional cell of α -Mn contains 58 atoms.

Figure 6.2 shows that the minimum formation enthalpies $\Delta H(MC)$ in all the crystal structures are as follows: TiC and VC (NaCl-type), CrC, MnC, and FeC (WC-type or NiAs-type), CoC (ZnS-type or NiAs-type), and NiC (NiAs-type). The negative formation enthalpy $\Delta H(MC)$ indicates that the MC phase is stable against segregation into elemental M and C phases. TiC, VC, CrC, and MnC in the most stable phases have the negative formation enthalpies. Therefore our results would indicate that it is difficult to synthesize non-magnetic FeC, CoC, and NiC in the thermodynamically stable phases at ambient pressure (0 GPa) and zero temperature (0 K), though only $\Delta H(\text{FeC})$ in the NiAs-type structure is slightly higher than 0 eV. Comparing the $5d$ transition metal monocarbides shown in Fig. 5.3 with the $3d$ transition metal monocarbides shown in Fig. 6.2, we find out that the trends and crystal structure order of the $3d$ transition metal monocarbides are similar to those of the $5d$ transition metal monocarbides. This would suggest that there is a correlation between $5d$ and $3d$ transition metal monocarbides in the formation enthalpies.

Figure 6.3 shows that the bulk moduli B_0 of all the calculated $3d$ transition metal monocarbides are higher than 150 GPa. As shown in Fig. 6.3, MnC in the NiAs-type and WC-type structures have the highest and second highest B_0 among the calculated $3d$ transition metal monocarbides, respectively. The trends and crystal structure order of the $3d$ transition metal monocarbides are similar to those of the $5d$ transition metal monocarbides because ReC in the NiAs-type and WC-type structures have the highest and second highest bulk moduli among the $5d$ transition metal monocarbides, as shown in Fig. 5.4. Here, note that the group element of Mn is the same as that of Re.

The calculated B_0 versus MC curves shown in Fig. 6.3 show the upward convex curves with the maximum B_0 of MnC in all the crystal structures except for the ZnS-type and CsCl-

type structures. In the ZnS-type and CsCl-type structures, FeC has the highest B_0 among the calculated 3d transition metal monocarbides. Comparing Fig. 6.1 with Fig. 6.3, we find out that FeC, which has the minimum V_0 in the calculated 3d transition metal monocarbides, does not correspond to MnC, which has the maximum B_0 in the calculated 3d transition metal monocarbides. The common parabolic behavior as a function of the number of valence electrons shown in Figs. 6.1 and 6.3 would indicate the dominance of the dd bonding in the cohesive properties just like those in the non-magnetic and non-SOC transition metals.

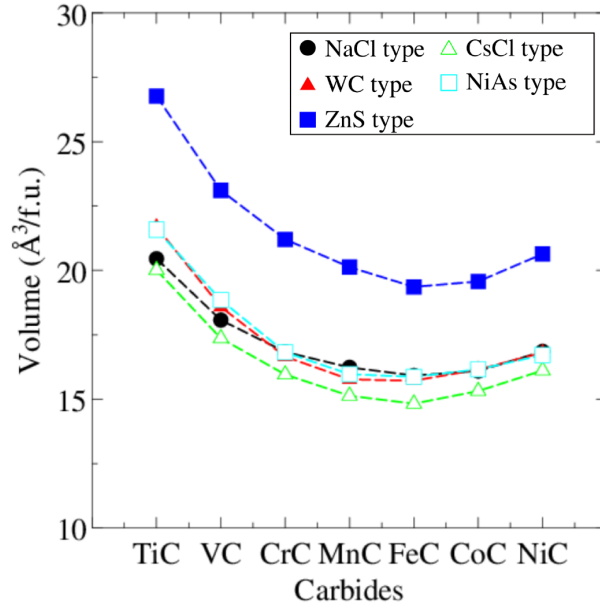


Figure 6.1: Equilibrium volume V_0 (Å³/f.u.) of MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures.

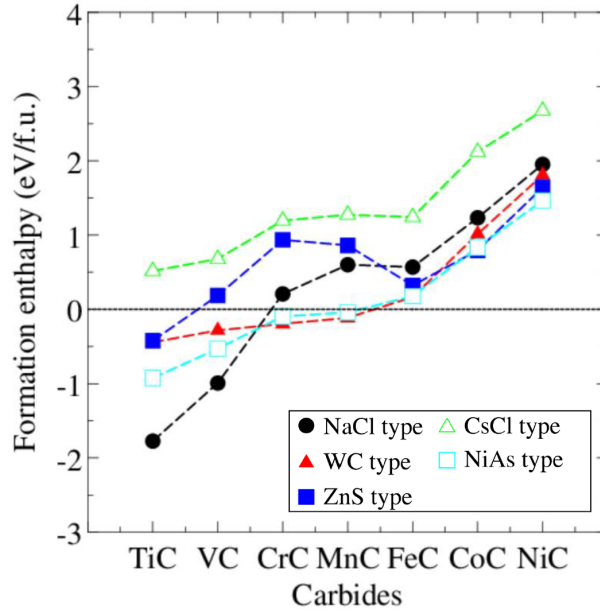


Figure 6.2: Formation enthalpies ΔH (eV/f.u.) of MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively at ambient pressure (0 GPa) and zero temperature (0 K).

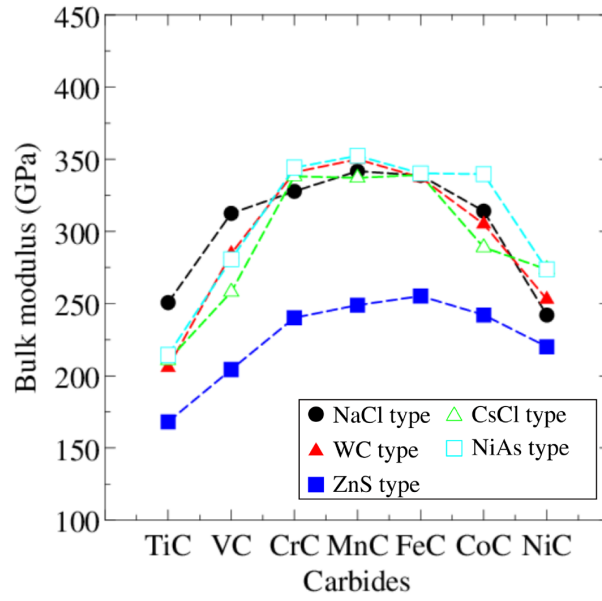


Figure 6.3: Bulk moduli B_0 (GPa), evaluated from Murnaghan's equation of state, of MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures.

6.2 Elastic Constants

The total energies $E(\boldsymbol{\varepsilon})$ of the $3d$ and $4d$ transition metal monocarbides as functions of the six strains $\boldsymbol{\varepsilon} = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$ per formula unit are calculated and fitted to quadratic functions. An asterisk symbol $*$ indicates that a total-energy $E(\boldsymbol{\varepsilon})$ curve is significantly different from the curve of a quadratic function of the six strains. (*e.g.*, the total-energy curve is any one of the M-like, W-like, N-like, and V-like curves). A transition metal monocarbide with an asterisk $*$ is mechanically unstable with respect to the six strains because in the region of the six strains ($\varepsilon \in [-0.03, 0.03]$), the total energy of the transition metal monocarbide with the asterisk $*$ can decrease from the total energy at the equilibrium state ($\boldsymbol{\varepsilon} = 0$) evaluated from Murnaghan's equation of state with its space group fixed. Here, note that ε is any one of the six strains.

Comparing the elastic constants of $5d$ transition metal monocarbides with those of $3d$ transition metal monocarbides enables us to obtain and understand basic information on mechanical properties and to know effects of the difference or correlation between $5d$ and $3d$ orbits. The calculated elastic constants C_{ij} of $3d$ transition metal monocarbides MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) are listed in Tables 6.1 (NaCl-type), 6.2 (WC-type), 6.3 (ZnS-type), 6.4 (CsCl-type), and 6.5 (NiAs-type). Because of the crystal symmetries, only three components (C_{11} , C_{12} , and C_{44}) in the cubic systems and only five components (C_{11} , C_{12} , C_{13} , C_{33} , and C_{44}) in the hexagonal systems are non-zero values.

Because elastic constants show total-energy curves of elastic strains, Tables 6.1–6.5 indicate mechanical stability or instability with respect to the six strains. We find out that TiC in the WC-type structure (Table 6.2), NiC in the ZnS-type structure (Table 6.3), TiC, VC, MnC, FeC, CoC, and NiC in the CsCl-type structure (Table 6.4) are mechanically unstable. We actually confirm that each total energy of $*MC$ ($M = \text{Ti, V, Mn, Co, and Ni}$) in the WC-type, ZnS-type, and CsCl-type structures decreases by applying strains. The other $3d$ transition metal monocarbides listed in Tables 6.1–6.5 are mechanically stable with respect to the six strains. We can predict that it is difficult to synthesize the mechanically unstable materials even in the thermodynamically stable and metastable phases.

In the mechanically stable materials listed in Tables 6.1–6.5, MnC in the NaCl-type structure has the lowest C_{44} (7 GPa) in the calculated $3d$ transition metal monocarbides. This result might indicate that NaCl-type MnC has another thermodynamically or mechanically more stable structure (*e.g.*, a magnetic structure or a crystal structure) because the elastic constant C_{44} (7 GPa) of NaCl-type MnC is too low.

We consider the mechanically stable materials. Comparing the $5d$ transition metal monocarbides with the $3d$ transition metal monocarbides, we find out the following results. WC and TaC have the highest and second highest C_{11} in Table 5.1 (NaCl-type), respectively. VC and CrC have the highest and second highest C_{11} in Table 6.1 (NaCl-type), respectively. ReC and WC have the highest and second highest C_{11} in Table 5.2 (WC-type), respectively. WC and ReC have the highest and second highest C_{33} , respectively. MnC and CrC have the highest and second highest C_{11} (or C_{33}) in Table 6.2 (WC-type), respectively. ReC and WC have the highest and second highest C_{11} (or C_{33}) in Table 5.5 (NiAs-type), respectively. MnC and CrC have the highest and second highest C_{11} in Table 6.5 (NiAs-type), respec-

tively. CrC and MnC have the highest and second highest C_{33} in Table 6.5 (NiAs-type), respectively. These results of C_{11} and C_{33} would indicate the group-element correlation between the $5d$ transition metal monocarbides and $3d$ transition metal monocarbides in any one of the NaCl-type, WC-type, and NiAs-type structures. Here, note the following results. TaC and WC have the highest and second highest C_{11} in Table 5.3 (ZnS-type), respectively. FeC and CoC have the highest and second highest C_{11} in Table 6.3 (ZnS-type), respectively. In the ZnS-type structure, however, the relation of C_{11} between the $5d$ transition metal monocarbides and $3d$ transition metal monocarbides cannot be found out. Here, we do not discuss the CsCl-type structure because the amount of information on the elastic constants in the CsCl-type structure is not sufficient. The same goes for the elastic constant C_{44} . Tables 6.1–6.5 would indicate the group-element rough correlation of C_{44} between the $5d$ transition metal monocarbides and $3d$ transition metal monocarbides.

Table 6.1: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NaCl-type MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$).

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
TiC	520	123	157	255	1.48	422	0.22
VC	687	126	202	313	1.36	556	0.20
CrC	644	183	121	336	2.14	408	0.30
MnC	626	209	7	348	6.97	143	0.43
FeC	623	196	83	338	2.76	328	0.34
CoC	572	192	36	318	4.23	209	0.39
NiC	320	223	43	255	5.68	127	0.42

Table 6.2: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of WC-type MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\epsilon})$ in the region ($\boldsymbol{\epsilon} \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
*TiC	359	65	168	394	-72	-	-	-	-
VC	490	155	181	670	94	294	2.12	360	0.30
CrC	612	156	207	791	294	347	1.35	619	0.20
MnC	639	172	201	860	221	361	1.52	585	0.23
FeC	460	262	236	758	163	343	2.43	372	0.32
CoC	456	207	240	594	135	316	2.38	349	0.32
NiC	341	166	237	425	132	259	2.66	260	0.33

Table 6.3: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of ZnS-type MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). $*MC$ indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of $*MC$ fixed. The total-energy curve of $*MC$ is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
TiC	195	155	104	168	3.07	148	0.35
VC	270	170	123	203	2.37	226	0.31
CrC	314	202	157	239	2.30	273	0.31
MnC	290	227	138	248	3.22	210	0.36
FeC	345	212	178	256	2.13	312	0.30
CoC	319	211	152	247	2.46	265	0.32
*NiC	226	222	59	-	-	-	-

Table 6.4: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of CsCl-type MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). $*MC$ indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of $*MC$ fixed. The total-energy curve of $*MC$ is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
*TiC	-89	380	-333	-	-	-	-
*VC	398	192	-89	-	-	-	-
CrC	678	161	115	333	2.08	414	0.29
*MnC	693	169	34	-	-	-	-
FeC	747	157	-25	354	-	-	-
*CoC	340	273	-25	-	-	-	-
NiC	436	185	-16	269	-	-	-

Table 6.5: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NiAs-type MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
TiC	381	161	84	599	117	223	1.69	330	0.25
VC	490	132	195	638	190	292	1.58	457	0.24
CrC	577	162	223	799	329	346	1.35	616	0.20
MnC	631	119	222	791	296	348	1.30	638	0.19
FeC	462	263	222	737	229	337	2.08	419	0.29
CoC	540	184	194	709	200	323	1.65	489	0.25
NiC	434	142	202	532	165	274	1.81	384	0.27

6.3 Shear Modulus and Debye Temperature

A hard material has both high bulk modulus and high shear modulus. Therefore bulk modulus and shear modulus are one set of the most important values to estimate the hardness of a material. Using the calculated single-crystal elastic constant values, we estimate the bulk moduli B^H and the shear moduli G^H of all the $3d$ transition metal monocarbides MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) in the Voigt-Reuss-Hill approximations. The calculated shear moduli G^H values of the stable $3d$ transition metal monocarbides determine their resistance of the averaged shear strains.

The calculated G^H are plotted in Fig. 6.4. Figure 6.4 shows that MnC in the NiAs-type structure and CrC in the WC-type or NiAs-type structure have the highest and second highest shear moduli, respectively. Because high shear modulus indicates anisotropic chemical bonds in materials, this result may suggest that the dominant bonds in NiAs-type MnC and WC-type (or NiAs-type) CrC are covalent. On the other hand, this result may indicate that the key bonds of TiC, VC, CrC, MnC, FeC, and CoC in the ZnS-type structure and those of MnC, FeC, CoC, and NiC in the NaCl-type structure are metallic and ionic.

Comparing the $5d$ transition metal monocarbides shown in Fig. 5.5 with the $3d$ transition metal monocarbides shown in Fig. 6.4, we find out that the G^H trends of the $3d$ transition metal monocarbides are roughly similar to those of the $5d$ transition metal monocarbides. In addition, we find out that the highest shear modulus G^H with respect to the $3d$ transition metal monocarbides is almost the same as that with respect to the $5d$ transition metal monocarbides. On the other hand, the minimum shear modulus G^H with respect to the $3d$ transition metal monocarbides is almost the same as that with respect to the $5d$ transition metal monocarbides.

Mechanical properties such as hardness are related to thermodynamical parameters such as the Debye temperature, thermal expansion, melting temperature, and specific heat. The Debye temperature is a criterion for estimating the contribution of bulk modulus and shear modulus to hardness. The calculated Debye temperatures Θ^H of the stable $3d$ transition metal monocarbides are plotted in Fig. 6.5 as solid circles and open circles for ductile and brittle materials, respectively. Figure 6.5 shows that CrC in the WC-type (or NiAs-type) structure and MnC in the NiAs-type structure have the highest and second highest Debye temperatures Θ^H in the $3d$ transition metal monocarbides, respectively. Comparing Fig. 6.4 with Fig. 6.5, we find out that the trends of the calculated G^H and Θ^H are highly similar. This result would indicate that shear modulus is a dominant factor in the trends of the Debye temperature.

Comparing the $5d$ transition metal monocarbides shown in Fig. 5.6 with the $3d$ transition metal monocarbides shown in Fig. 6.5, we find out the following relation: The maximum and minimum Debye temperatures with respect to the $3d$ transition metal monocarbides are higher than those with respect to the $5d$ transition metal monocarbides. This is because the mass of a $3d$ transition metal monocarbide is lower than that of a $5d$ transition metal monocarbide. In addition, we find out that the trends and crystal structure order of the Debye temperatures shown in Figs. 5.6 and 6.5 are roughly similar.

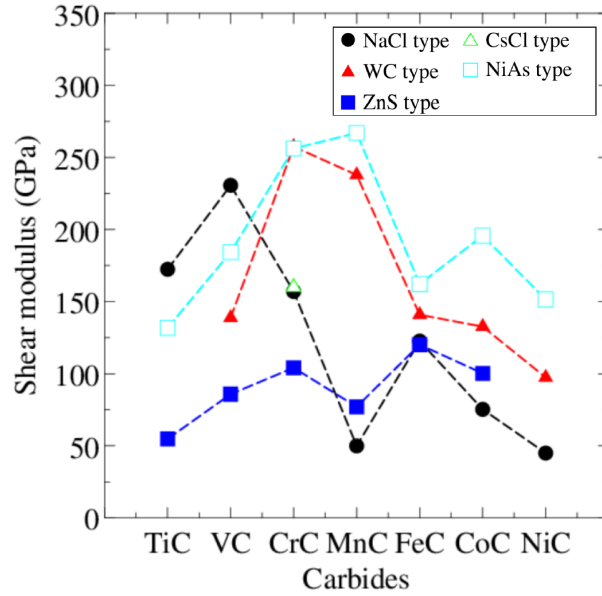


Figure 6.4: Shear moduli G^H (GPa), which are obtained from elastic constants, of MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively, at ambient pressure (0 GPa) and zero temperature (0 K).

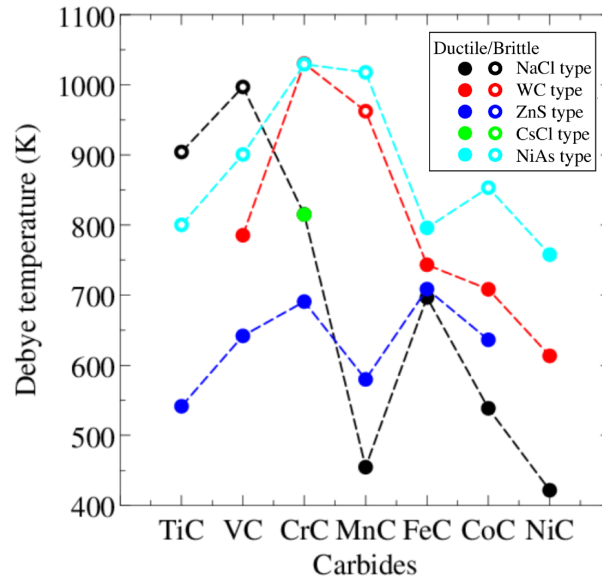


Figure 6.5: Debye temperature Θ_D (K) of MC ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$). Black, red, blue, green, and cyan colors represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively. The open circles represent brittleness and the solid circles represent ductility.

Chapter 7

4*d* Transition Metal Monocarbides

In Chapter 5, the effects of spin-orbit coupling (SOC) on bulk modulus are examined in order to check the calculation conditions for the heavy-element materials. Our calculated results show that the bulk modulus difference of WC (tungsten monocarbides) in the WC-type structure with and without SOC is approximately less than 1%, suggesting negligible effects of SOC on bulk modulus. WC in the WC-type structure is a non-magnetic material. In order to compare the tungsten carbide with other materials such as 3*d*, 4*d*, and 5*d* transition metal monocarbides, the effects of SOC and magnetic properties are ignored in the present study. The calculations of the 3*d* and 4*d* transition metal monocarbides are only additional information. Important and useful discussions on mechanical properties such as hardness are mainly conducted in Chapter 5.

7.1 Equilibrium Volume, Formation Enthalpy, and Bulk Modulus

We show three fundamental properties of the calculated 4*d* transition metal monocarbides *MC* (*M* = Zr, Nb, Mo, Tc, Ru, Rh, and Pd) in the five crystal structures (the NaCl-type, WC-type, ZnS-type, CsCl-type, and NiAs-type structures): the equilibrium volumes V_0 , bulk moduli B_0 , and formation enthalpies ΔH calculated at ambient pressure (0 GPa) and zero temperature (0 K).

Figure 7.1 clearly shows the smooth downward convex curves of V_0 versus *MC* for each crystal structure. Comparing the 5*d* transition metal monocarbides shown in Fig. 5.2 with the 4*d* transition metal monocarbides shown in Fig. 7.1, we find out that under the non-magnetic and non-SOC conditions, the trends and crystal structure order of the 4*d* transition metal monocarbides are highly similar to those of the 5*d* transition metal monocarbides. In addition, Figs. 5.2 and 7.1 would indicate that the equilibrium volume V_0 of a 4*d* transition metal monocarbide in each crystal structure is almost the same as that of the 5*d* transition metal monocarbide corresponding to the group element of the 4*d* transition metal. This is because the atomic sphere radius of a 4*d* transition metal is almost the same as that of the 5*d* transition metal corresponding to the group element of the 4*d* transition metal.

Figure 7.1 shows that TcC and RuC have the lowest and second lowest V_0 in all the crystal structures except for the ZnS-type structure, respectively. In the ZnS-type structure, as shown in Fig. 7.1, RuC and TcC have the lowest and second lowest V_0 , respectively. Therefore, in particular, TcC and RuC can be relatively dense materials independent of the crystal structures. This result would indicate that the element combinations of M and C are a very important factor to synthesize high-density materials. This parabolic behavior as a function of the number of valence electrons is a typical feature seen in the cohesive properties of elemental transition metals, indicating that the cohesion in the transition metal monocarbides in the present study is also dominated by the dd bonding of the transition metal atoms. Figure 7.1 would indicate that there is a correlation between the structure trends in V_0 and the coordination numbers (CN) in the crystal structures. Here, note that CN is four in the ZnS-type structure, six in the WC-type, NaCl-type, and NiAs-type structures, and eight in the CsCl-type structure. Figure 7.1 might indicate that as the coordination number in a structure becomes higher and lower, V_0 becomes lower and higher, respectively.

In order to clarify thermodynamical stabilities among the crystal structures, the calculated formation enthalpies $\Delta H(MC)$ with respect to the elemental M and C crystals are plotted in Fig. 7.2. We adopt hcp-Zr, bcc-Nb, bcc-Mo, hcp-Tc, hcp-Ru, fcc-Rh, fcc-Pd, and diamond-C for the reference energies of M and C .

Figure 7.2 shows that the minimum formation enthalpies $\Delta H(MC)$ in all the crystal structures are as follows: ZrC and NbC (NaCl-type), MoC and TcC (WC-type), RuC, RhC, and PdC (ZnS-type). The negative formation enthalpy $\Delta H(MC)$ indicates that the MC phase is stable against segregation into elemental M and C phases. ZrC, NbC, and MoC in the most stable phases have the negative formation enthalpies. Therefore our results would indicate that it is difficult to synthesize non-magnetic TcC, RuC, RhC, and PdC in the thermodynamically stable phases at ambient pressure (0 GPa) and zero temperature (0 K), though only $\Delta H(\text{TcC})$ in the WC-type structure is slightly higher than 0 eV. Comparing the $5d$ transition metal monocarbides shown in Fig. 5.3 with the $4d$ transition metal monocarbides shown in Fig. 7.2, we find out that the trends and crystal structure order of the $4d$ transition metal monocarbides are similar to those of the $5d$ transition metal monocarbides. This would suggest that there is a correlation between $5d$ and $4d$ transition metal monocarbides in the formation enthalpies.

Figure 7.3 shows that the bulk moduli B_0 of all the calculated $4d$ transition metal monocarbides are higher than approximately 150 GPa. As shown in Fig. 7.3, TcC in the WC-type and NiAs-type structures have the highest and second highest B_0 among the calculated $4d$ transition metal monocarbides, respectively. The trends and crystal structure order of the $4d$ transition metal monocarbides are similar to those of the $5d$ transition metal monocarbides because ReC in the NiAs-type and WC-type structures have the highest and second highest bulk moduli among the $5d$ transition metal monocarbides, as shown in Fig. 5.4. Here, note that the group element of Tc is the same as that of Re.

The calculated B_0 versus MC curves shown in Fig. 7.3 show the upward convex curves with the maximum B_0 of TcC in all the crystal structures. Comparing Fig. 7.1 with Fig. 7.3, we find out that in all the crystal structures except for the ZnS-type structure, TcC, which has the minimum V_0 in the calculated $4d$ transition metal monocarbides, corresponds to

TcC, which has the maximum B_0 in the calculated $4d$ transition metal monocarbides. In the ZnS-type structure, RuC, which has the minimum V_0 in the calculated $4d$ transition metal monocarbides, shifts to TcC, which has the maximum B_0 in the calculated $4d$ transition metal monocarbides. The common parabolic behavior as a function of the number of valence electrons shown in Figs. 7.1 and 7.3 would indicate the dominance of the dd bonding in the cohesive properties just like those in the non-magnetic and non-SOC transition metals.

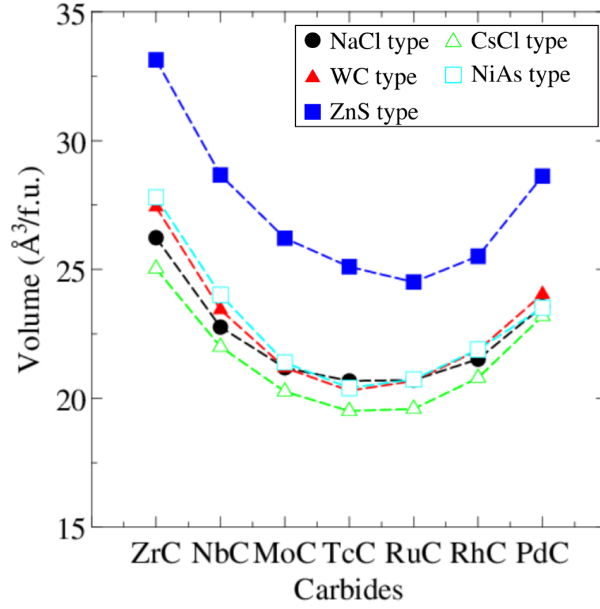


Figure 7.1: Equilibrium volume V_0 (Å³/f.u.) of MC ($M = \text{Zr}, \text{Nb}, \text{Mo}, \text{Tc}, \text{Ru}, \text{Rh}, \text{and Pd}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures.

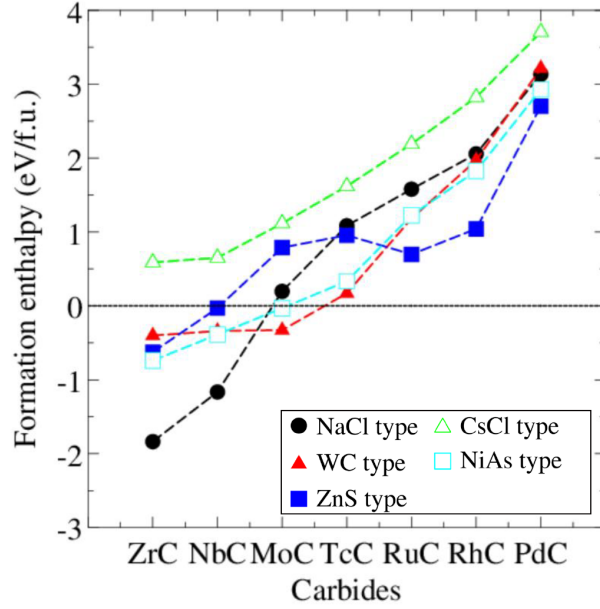


Figure 7.2: Formation enthalpies ΔH (eV/f.u.) of MC ($M = \text{Zr}, \text{Nb}, \text{Mo}, \text{Tc}, \text{Ru}, \text{Rh}, \text{and Pd}$). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively at ambient pressure (0 GPa) and zero temperature (0 K).

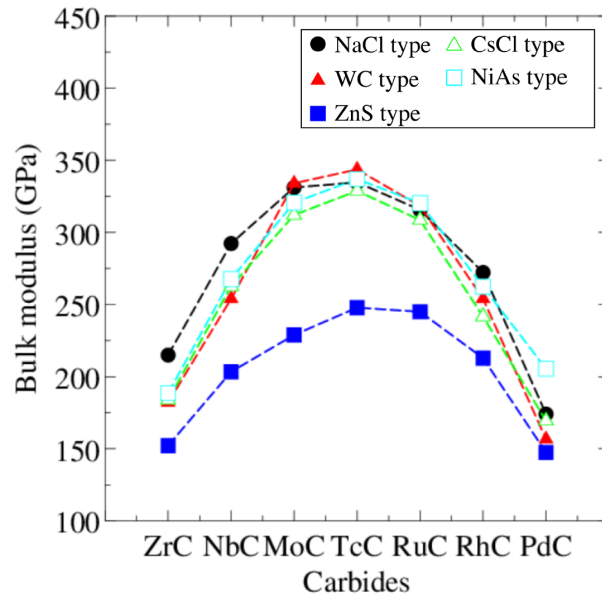


Figure 7.3: Bulk moduli B_0 (GPa), evaluated from Murnaghan's equation of state, of MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$) in the NaCl type (black solid circle), WC type (red solid triangle), ZnS type (blue solid square), CsCl type (green open triangle), and NiAs type (cyan open square) structures.

7.2 Elastic Constants

The total energies $E(\boldsymbol{\varepsilon})$ of the $3d$ and $4d$ transition metal monocarbides as functions of the six strains $\boldsymbol{\varepsilon} = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$ per formula unit are calculated and fitted to quadratic functions. An asterisk symbol $*$ indicates that a total-energy $E(\boldsymbol{\varepsilon})$ curve is significantly different from the curve of a quadratic function of the six strains. (*e.g.*, the total-energy curve is any one of the M-like, W-like, N-like, and V-like curves). A transition metal monocarbide with an asterisk $*$ is mechanically unstable with respect to the six strains because in the region of the six strains ($\varepsilon \in [-0.03, 0.03]$), the total energy of the transition metal monocarbide with the asterisk $*$ can decrease from the total energy at the equilibrium state ($\boldsymbol{\varepsilon} = 0$) evaluated from Murnaghan's equation of state with its space group fixed. Here, note that ε is any one of the six strains.

Comparing the elastic constants of $5d$ transition metal monocarbides with those of $4d$ transition metal monocarbides enables us to obtain and understand basic information on mechanical properties and to know effects of the difference or correlation between $5d$ and $4d$ orbitals. The calculated elastic constants C_{ij} of $4d$ transition metal monocarbides MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$) are listed in Tables 7.1 (NaCl-type), 7.2 (WC-type), 7.3 (ZnS-type), 7.4 (CsCl-type), and 7.5 (NiAs-type). Because of the crystal symmetries, only three components (C_{11} , C_{12} , and C_{44}) in the cubic systems and only five components (C_{11} , C_{12} , C_{13} , C_{33} , and C_{44}) in the hexagonal systems are non-zero values.

Because elastic constants show total-energy curves of elastic strains, Tables 7.1–7.5 indicate mechanical stability or instability with respect to the six strains. We find out that TcC and RhC in the NaCl-type structure (Table 7.1), ZrC in the WC-type structure (Table 7.2), PdC in the ZnS-type structure (Table 7.3), ZrC, NbC, TcC, RuC, RhC, and PdC in the CsCl-type structure (Table 7.4) are mechanically unstable. We actually confirm that each total energy of $*MC$ ($M = \text{Zr, Nb, Tc, Ru, Rh, and Pd}$) in the NaCl-type, WC-type, ZnS-type, and CsCl-type structures decreases by applying strains. The other $4d$ transition metal monocarbides listed in Tables 7.1–7.5 are mechanically stable with respect to the six strains. We can predict that it is difficult to synthesize the mechanically unstable materials even in the thermodynamically stable and metastable phases.

We consider the mechanically stable materials. Comparing the $5d$ transition metal monocarbides with the $4d$ transition metal monocarbides, we find out the following results. WC and TaC have the highest and second highest C_{11} in Table 5.1 (NaCl-type), respectively. MoC and NbC have the highest and second highest C_{11} in Table 7.1 (NaCl-type), respectively. ReC and WC have the highest and second highest C_{11} in Table 5.2 (WC-type), respectively. WC and ReC have the highest and second highest C_{33} , respectively. TcC and MoC have the highest and second highest C_{11} (or C_{33}) in Table 7.2 (WC-type), respectively. ReC and WC have the highest and second highest C_{11} (or C_{33}) in Table 5.5 (NiAs-type), respectively. TcC and MoC have the highest and second highest C_{11} (or C_{33}) in Table 7.5 (NiAs-type), respectively. These results of C_{11} and C_{33} would indicate the group-element correlation between the $5d$ transition metal monocarbides and $4d$ transition metal monocarbides in any one of the NaCl-type, WC-type, and NiAs-type structures. Here, note the following results. TaC and WC have the highest and second highest C_{11} in Table 5.3 (ZnS-type), respectively. RuC

and NbC have the highest and second highest C_{11} in Table 7.3 (ZnS-type), respectively. FeC and CoC have the highest and second highest C_{11} in Table 6.3 (ZnS-type), respectively. In the ZnS-type structure, the rough relation of C_{11} between the $5d$ transition metal monocarbides and $4d$ transition metal monocarbides can be found out. In the ZnS-type structure, the rough correlation between the $3d$ transition metal monocarbides and $4d$ transition metal monocarbides can also be found out. This result would indicate that $4d$ transition metal monocarbides are like the intermediate state between $3d$ and $5d$ transition metal monocarbides. Here, we do not discuss the CsCl-type structure because the amount of information on the elastic constants in the CsCl-type structure is not sufficient. The same goes for the elastic constant C_{44} . Tables 7.1–7.5 would indicate the group-element rough correlation of C_{44} between the $5d$ transition metal monocarbides and $4d$ transition metal monocarbides.

Table 7.1: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NaCl-type MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
ZrC	447	103	150	217	1.38	382	0.21
NbC	661	101	173	288	1.37	507	0.21
MoC	695	154	123	334	1.97	436	0.28
*TcC	578	212	-71	-	-	-	-
RuC	535	205	25	315	5.31	167	0.41
*RhC	427	193	-29	-	-	-	-
PdC	226	148	33	174	4.90	100	0.40

Table 7.2: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of WC-type MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
*ZrC	330	100	86	478	-63	-	-	-	-
NbC	448	155	135	655	31	264	2.99	238	0.35
MoC	602	196	162	836	233	340	1.46	568	0.22
TcC	621	202	154	921	153	350	1.71	514	0.26
RuC	429	284	195	723	93	322	3.13	279	0.36
RhC	363	192	176	559	82	260	2.71	256	0.34
PdC	200	137	142	304	41	168	4.19	112	0.39

Table 7.3: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of ZnS-type MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$).

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
ZrC	188	135	93	152	2.68	152	0.33
NbC	293	163	135	206	2.05	259	0.29
MoC	280	210	128	233	3.05	207	0.35
TcC	267	237	123	247	4.44	155	0.40
RuC	333	209	146	250	2.42	273	0.32
RhC	281	180	128	214	2.43	232	0.32
PdC	151	153	38	152	-	-	-

Table 7.4: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of CsCl-type MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$). * MC indicates mechanical unstability with respect to the six strains because $E(\boldsymbol{\varepsilon})$ in the region ($\varepsilon \in [-0.03, 0.03]$) can decrease from $E(\mathbf{0})$ at the equilibrium state evaluated from Murnaghan's equation of state with the space group of * MC fixed. The total-energy curve of * MC is significantly different from the curve of a quadratic function of the six strains.

	C_{11}	C_{12}	C_{44}	B	B/G	Y	ν
ZrC	95	246	-213	196	-	-	-
*NbC	479	167	-17	-	-	-	-
MoC	768	96	134	320	1.64	487	0.25
*TcC	794	92	35	-	-	-	-
RuC	741	84	-46	303	-	-	-
*RhC	403	165	1	-	-	-	-
*PdC	337	93	0	-	-	-	-

Table 7.5: Calculated elastic constants C_{ij} ($i, j = 1, 2, 3, 4, 5$, and 6) (GPa), bulk moduli B (GPa), shear moduli G (GPa), Young's moduli Y (GPa), and Poisson's ratios ν of NiAs-type MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	B/G	Y	ν
ZrC	353	134	60	514	76	191	1.76	274	0.26
NbC	473	113	158	610	116	265	1.73	385	0.26
MoC	532	192	211	754	274	334	1.53	538	0.23
TcC	612	170	187	846	239	347	1.45	585	0.22
RuC	431	261	193	742	159	317	2.37	352	0.32
RhC	409	168	160	607	106	263	2.09	325	0.29
PdC	286	122	132	417	77	192	2.23	225	0.31

7.3 Shear Modulus and Debye Temperature

A hard material has both high bulk modulus and high shear modulus. Therefore bulk modulus and shear modulus are one set of the most important values to estimate the hardness of a material. Using the calculated single-crystal elastic constant values, we estimate the bulk moduli B^H and the shear moduli G^H of all the $4d$ transition metal monocarbides MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$) in the Voigt-Reuss-Hill approximations. The calculated shear moduli G^H values of the stable $4d$ transition metal monocarbides determine their resistance of the averaged shear strains.

The calculated G^H are plotted in Fig. 7.4. Figure 7.4 shows that TcC in the NiAs-type structure and MoC in the WC-type structure have the highest and second highest shear moduli, respectively. Because high shear modulus indicates anisotropic chemical bonds in materials, this result may suggest that the dominant bonds in NiAs-type TcC and WC-type MoC are covalent. On the other hand, this result may indicate that the key bonds of the $4d$ transition metal monocarbides with low shear moduli are metallic and ionic.

Comparing the $5d$ transition metal monocarbides shown in Fig. 5.5 with the $4d$ transition metal monocarbides shown in Fig. 7.4, we find out that the G^H trends of the $4d$ transition metal monocarbides are roughly similar to those of the $5d$ transition metal monocarbides. In addition, we find out that the highest shear modulus G^H with respect to the $4d$ transition metal monocarbides is lower than that with respect to the $5d$ transition metal monocarbides. On the other hand, the minimum shear modulus G^H with respect to the $4d$ transition metal monocarbides is almost the same as that with respect to the $5d$ transition metal monocarbides.

Mechanical properties such as hardness are related to thermodynamical parameters such as the Debye temperature, thermal expansion, melting temperature, and specific heat. The Debye temperature is a criterion for estimating the contribution of bulk modulus and shear modulus to hardness. The calculated Debye temperatures Θ^H of the stable $4d$ transition metal monocarbides are plotted in Fig. 7.5 as solid circles and open circles for ductile and brittle materials, respectively. Figure 7.5 shows that MoC in the WC-type structure and TcC in the NiAs-type structure have the highest and second highest Debye temperatures Θ^H in the $4d$ transition metal monocarbides, respectively. Comparing Fig. 7.4 with Fig. 7.5, we find out that the trends of the calculated G^H and Θ^H are highly similar. This result would indicate that shear modulus may be a dominant factor in the trends of the Debye temperature.

Comparing the $5d$ transition metal monocarbides shown in Fig. 5.6 with the $4d$ transition metal monocarbides shown in Fig. 7.5, we find out the following relation: The maximum and minimum Debye temperatures with respect to the $4d$ transition metal monocarbides are higher than those with respect to the $5d$ transition metal monocarbides. This is because the mass of a $4d$ transition metal monocarbide is lower than that of a $5d$ transition metal monocarbide. In addition, we find out that the trends and crystal structure order of the Debye temperatures shown in Figs. 5.6 and 7.5 are roughly similar.

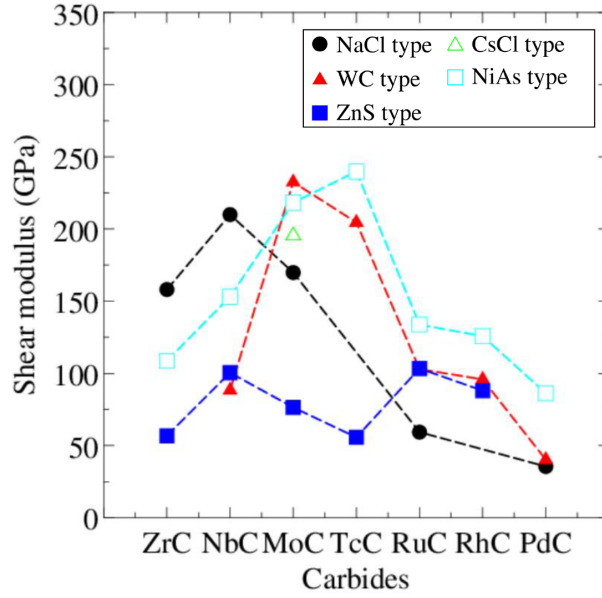


Figure 7.4: Shear moduli G^H (GPa), which are obtained from elastic constants, of MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$). Black solid circle, red solid triangle, blue solid square, green open triangle, and cyan open square symbols represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively at ambient pressure (0 GPa) and zero temperature (0 K).

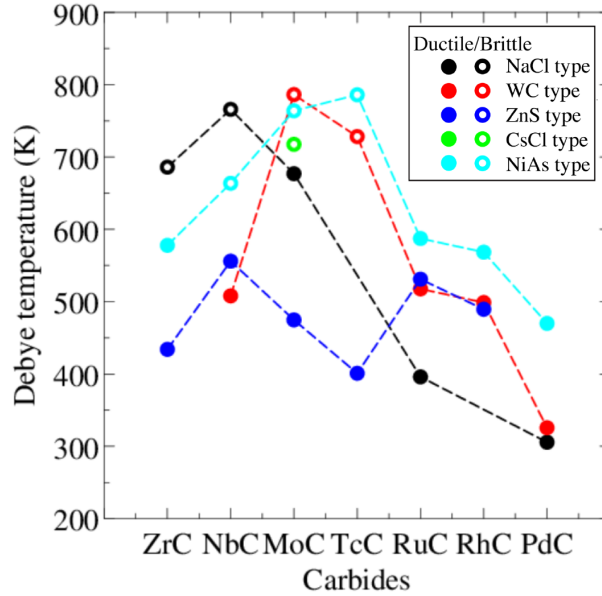


Figure 7.5: Debye temperature Θ_D (K) of MC ($M = \text{Zr, Nb, Mo, Tc, Ru, Rh, and Pd}$). Black, red, blue, green, and cyan colors represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively. The open circles represent brittleness and the solid circles represent ductility.

Chapter 8

Relation between Bulk Modulus and Interstitial Electron Density in 5d Transition Metal Monocarbides

We consider a homogeneous positive charge potential as an external potential for electrons. We assume an electrically neutral case of the system. This model is called the Jellium model or the homogeneous electron gas model (for further proof of the Jellium model see Appendix C). According to the homogeneous electron gas model, there is a strong correlation between electron densities and bulk moduli. To confirm the relation between the valence (interstitial) electron densities ρ_i and the bulk moduli B_0 in the 5d transition metal monocarbides, we define the electron density in the interstitial region as

$$\rho_i = \frac{N - \sum_{\alpha} N_{\alpha}}{V_0 - \sum_{\alpha} V_{\alpha}}, \quad (8.1)$$

where N is the number of electrons in the volume V_0 of MC , and N_{α} is the number of electrons inside the muffin-tin sphere with the volume V_{α} of atom α ($\alpha = M$ or C). We also define the radius r_s of the averaged spherical volume occupied by an interstitial electron as

$$r_s = \left(\frac{3}{4\pi\rho_i} \right)^{1/3}. \quad (8.2)$$

Figure 8.1 shows the calculated relation between B_0 and r_s . We also plot the bulk modulus calculated using the homogeneous electron gas model by the Hedin-Lundqvist expression [78] for the correlation energy.

Our DFT calculations and the values calculated by Moruzzi *et al.* [79] are in good agreement with the theoretical curve in Fig. 8.1. Figure 8.1 shows that as r_s becomes smaller, B_0 of the calculated MC becomes higher, being almost similar to that of the homogeneous electron gas model. This result indicates that a key factor describing B_0 is the interstitial electron density for MC . The trends of B_0 shown in Figs. 5.4 and 8.1 may be related to the compression of the interstitial regions, compared with Fig. 5.2.

The good agreement with the homogeneous electron gas result suggests that most of the contributions to bulk modulus might arise from the electrons in the interstitial region per unit cell. Interestingly, despite the fact that the correlation between the calculated bulk moduli and those of the homogeneous electron gas is less than perfect, this correlation is a fine enough agreement to indicate that interstitial electron density is a more dominant factor than electron density within the muffin tins for bulk modulus. This result might indicate that the electronic structure within the muffin tins is considered rigid. Interstitial electron density would be the most important for bulk modulus.

The calculated $5d$ TM carbides would universally follow the homogeneous electron gas model for bulk modulus, depending on the interstitial electron densities. This result would indicate that the origin of bulk modulus is interstitial electron density. It might be said that interstitial electron density is regarded as sp electron density because d orbital is localized and the hybridization between d orbital and carbon can exist. This might suggest that interstitial electron density (sp electron density) is the origin of mechanical properties.

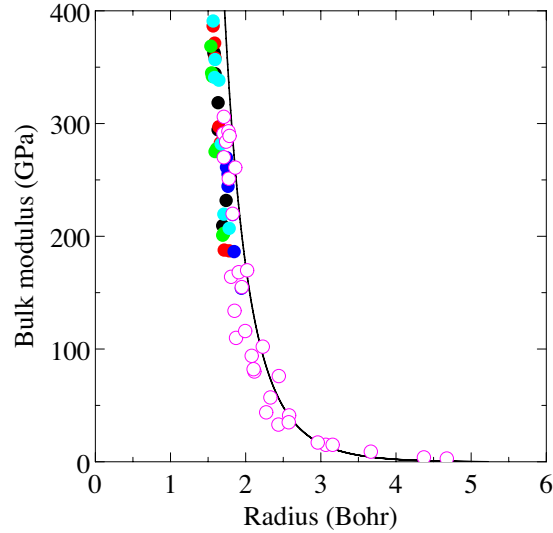


Figure 8.1: Bulk moduli B_0 (GPa), which are obtained by Murnaghan's equation of state, of MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$). Radius (Bohr) represents the radius of the averaged spherical volume occupied by an interstitial electron in the interstitial region. Black, red, blue, green, and cyan solid circles represent the NaCl, WC, ZnS, CsCl, and NiAs type structures, respectively. The pink open circles are the previous calculations [79].

Chapter 9

Conclusion

We have systematically analyzed $5d$ transition metal monocarbides MC ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$), using first-principles electronic structure methods based on the density functional theory. In the present study, since the results of the $3d$ and $4d$ transition metal monocarbides turned out to be no more than additional information, the conclusion does not touch upon them. We have considered five different structures: NaCl-type, WC-type, ZnS-type, CsCl-type, and NiAs-type structures. We have evaluated equilibrium volume, formation enthalpy, elastic constants, bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Pugh's modulus ratio, the Debye temperature, and TDOS. Figure 5.2 shows that as the coordination number in a structure becomes larger and smaller, V_0 becomes lower and higher, respectively. Comparing the diagonal components except for C_{44} with the off-diagonal components, we may find out that the diagonal components are a more dominant factor for bulk modulus than the off-diagonal components. The relation between the calculated bulk moduli and the valence electrons would indicate that a $5d$ shell is half filled between WC and ReC. Our calculations show that incompressibilities are higher along the c axis than along the a axis in the WC-type and NiAs-type structures. The Debye temperature may suggest that bonding and anti-bonding states contribute to brittleness and ductility, respectively. In addition, shear modulus may be a dominant factor in the trends of the Debye temperature. The Debye temperature would indicate that WC-type WC and NiAs-type ReC have the highest hardness. Our analyses might indicate that the origin of hardness is qualitatively related to bonding and anti-bonding states. Our analyses might indicate that the origin of hardness in WC is explained by the dp bonding between transition metal M and carbon C atoms in addition to the dd bonding between the transition metal atoms.

Appendix A

Supplements to Chapter 2

Although the relation between the Hohenberg-Kohn theorems and the Kohn-Sham equation has already been described in Chapter 2, the detailed proof of the Hohenberg-Kohn theorems has not been provided yet. For the sake of completeness, we give here mathematical proof of the Hohenberg-Kohn theorems.

A.1 Hohenberg-Kohn Theorems

The density functional theory (DFT) is a computational quantum mechanical method or a first-principles electronic structure calculation in physics, chemistry, and materials science of many-body systems. The density functional theory is based on two kinds of accomplishments: two theorems proved by Hohenberg and Kohn and an eigenequation derived by Kohn and Sham.

In 1964, Hohenberg and Kohn established the basis of the density functional theory, where the ground-state total energy $E[\rho(\cdot)]$ of a system is described by its electron density $\rho(\mathbf{r})$. They proved two theorems:

1. The electron density $\rho(\mathbf{r})$ determines the unique ground-state wave function and the unique external potential. Here, note that $\mathbf{r}$ is a position vector.
2. The energy-functional variational principle always holds for any electron density

These two theorems are called the Hohenberg-Kohn theorems.

We will consider the first Hohenberg-Kohn theorem. The density functional theory is formalized by solving the ground state of the eigenequation which is written as

$$\mathcal{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots), \quad (\text{A.1})$$

where the Hamiltonian $\mathcal{H}$, kinetic energy T , external potential energy U_{ext} , and electron-

electron interaction potential energy $U_{\text{e-e}}$ are defined as

$$\mathcal{H} = T + U_{\text{e-e}} + U_{\text{ext}}, \quad (\text{A.2})$$

$$T(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) = \sum_i \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \right], \quad (\text{A.3})$$

$$U_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_i v(\mathbf{r}_i), \quad (\text{A.4})$$

$$U_{\text{e-e}}(\mathbf{r}_1, \mathbf{r}_2, \dots) = \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (\text{A.5})$$

Here, the i th electronic position vector is $\mathbf{r}_i = (x_i \ y_i \ z_i)$ and $v(\mathbf{r}_i)$ is the i th electronic external potential energy. In the eigenequation (Eq. A.1), $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$ is the wave function of an electronic subsystem and E is the eigenvalue.

We will define the bra-ket notation of the wave function in the eigenequation (Eq. A.1). The bra-ket notation of the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$ is defined as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = \langle \mathbf{r}_1, \mathbf{r}_2, \dots | \Psi \rangle. \quad (\text{A.6})$$

The complex conjugate of the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$ is defined as

$$\Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots) = \langle \Psi | \mathbf{r}_1, \mathbf{r}_2, \dots \rangle. \quad (\text{A.7})$$

Here, note that the bra-ket notation $\langle \mathbf{r}_1, \mathbf{r}_2, \dots |$ and $|\mathbf{r}_1, \mathbf{r}_2, \dots \rangle$ of the position vectors indicates the relation written as

$$\int \dots \int \prod_i d\mathbf{r}_i |\mathbf{r}_1, \mathbf{r}_2, \dots \rangle \langle \mathbf{r}_1, \mathbf{r}_2, \dots | = \hat{1}, \quad (\text{A.8})$$

where $\hat{1}$ is the identity operator.

The density operator $\hat{n}$ of the system is defined as

$$\hat{n}(\mathbf{r}) = \int \dots \int \prod_i d\mathbf{r}_i |\mathbf{r}_1, \mathbf{r}_2, \dots \rangle n(\mathbf{r}) \langle \mathbf{r}_1, \mathbf{r}_2, \dots |, \quad (\text{A.9})$$

where $n(\mathbf{r})$ is a function of a position vector $\mathbf{r}$ described as

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (\text{A.10})$$

Here, note that $\delta(\mathbf{r} - \mathbf{r}_i)$ is the Dirac delta function. By using the density operator $\hat{n}$, we obtain the expectation value $\rho(\mathbf{r})$ of the electron density of the system at the position $\mathbf{r}$

described as

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \\
&= \langle \Psi | \left(\int \cdots \int \prod_i d\mathbf{r}_i |\mathbf{r}_1, \mathbf{r}_2, \cdots\rangle n(\mathbf{r}) \langle \mathbf{r}_1, \mathbf{r}_2, \cdots| \right) | \Psi \rangle \\
&= \int \cdots \int \prod_i d\mathbf{r}_i \langle \Psi | \mathbf{r}_1, \mathbf{r}_2, \cdots \rangle n(\mathbf{r}) \langle \mathbf{r}_1, \mathbf{r}_2, \cdots | \Psi \rangle \\
&= \int \cdots \int \prod_j d\mathbf{r}_j \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \\
&= \int \cdots \int \sum_i \prod_{j \neq i} d\mathbf{r}_j \Psi^*(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots) \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots) \\
&= \int \cdots \int \sum_i \prod_{j \neq i} d\mathbf{r}_j |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots)|^2 \\
&= \int \cdots \int \prod_{j \neq 1} d\mathbf{r}_j |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \cdots)|^2 \\
&\quad + \int \cdots \int \prod_{j \neq 2} d\mathbf{r}_j |\Psi(\mathbf{r}_1, \mathbf{r}, \cdots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \cdots)|^2 + \cdots \\
&\quad + \int \cdots \int \prod_{j \neq i} d\mathbf{r}_j |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots)|^2 + \cdots \\
&= \sum_i |\psi_i(\mathbf{r})|^2,
\end{aligned} \tag{A.11}$$

where $\psi_i(\mathbf{r})$ is defined as

$$|\psi_i(\mathbf{r})|^2 = \int \cdots \int \prod_{j \neq i} d\mathbf{r}_j |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots)|^2. \tag{A.12}$$

$\psi_i(\mathbf{r})$ indicates the i th electronic wave function in the one-electron approximation. Here, note that since the number of all the electrons is finite, we can exchange the integration and summation written as

$$\begin{aligned}
\sum_i \int d\mathbf{r}_j &= \int d\mathbf{r}_j \sum_i, \\
\sum_i \int d\mathbf{r} &= \int d\mathbf{r} \sum_i.
\end{aligned} \tag{A.13}$$

The expectation value $\langle U_{\text{ext}} \rangle$ of the external potential energy $U_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \cdots)$ is written

as

$$\begin{aligned}
\langle U_{\text{ext}} \rangle &= \langle \Psi | \hat{U}_{\text{ext}} | \Psi \rangle \\
&= \langle \Psi | \left(\int \cdots \int \prod_i d\mathbf{r}_i |\mathbf{r}_1, \mathbf{r}_2, \cdots\rangle U_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \cdots) \langle \mathbf{r}_1, \mathbf{r}_2, \cdots| \right) | \Psi \rangle \\
&= \int \cdots \int \prod_i d\mathbf{r}_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) U_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \cdots) \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \\
&= \int \cdots \int \prod_i d\mathbf{r}_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) \left(\sum_i v(\mathbf{r}_i) \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \\
&= \int \cdots \int \prod_i d\mathbf{r}_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) \left[\sum_i \left(\int d\mathbf{r} v(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) \right) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \tag{A.14} \\
&= \int d\mathbf{r} v(\mathbf{r}) \int \cdots \int \prod_i d\mathbf{r}_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) \sum_j \delta(\mathbf{r} - \mathbf{r}_j) \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \\
&= \int d\mathbf{r} v(\mathbf{r}) \int \cdots \int \prod_i d\mathbf{r}_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \cdots) n(\mathbf{r}) \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots) \\
&= \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}),
\end{aligned}$$

where the external potential energy operator $\hat{U}_{\text{ext}}$ is defined as

$$\hat{U}_{\text{ext}} = \int \cdots \int \prod_i d\mathbf{r}_i |\mathbf{r}_1, \mathbf{r}_2, \cdots\rangle U_{\text{ext}}(\mathbf{r}_1, \mathbf{r}_2, \cdots) \langle \mathbf{r}_1, \mathbf{r}_2, \cdots|. \tag{A.15}$$

In stead of the number N of all the electrons and the external potential $v(\mathbf{r})$, the electron density $\rho(\mathbf{r})$ is regarded as a fundamental parameter in the first Hohenberg-Kohn theorem. Namely, the electron density $\rho(\mathbf{r})$ determines the external potential energy $v(\mathbf{r})$ and the number N of all the electrons. In this case, the difference of a constant energy is not considered. With the electron density $\rho(\mathbf{r})$, the number N of all the electrons is defined as

$$N = \int_V d\mathbf{r} \rho(\mathbf{r}) = \int_{x_s}^{x_f} dx \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \rho(x, y, z), \tag{A.16}$$

where the volume V of the system is calculated as follows:

$$\begin{aligned}
V &= \int_V d\mathbf{r} \\
&= \int_{z_s}^{z_f} \int_{y_s}^{y_f} \int_{x_s}^{x_f} dx dy dz \\
&= (x_f - x_s)(y_f - y_s)(z_f - z_s).
\end{aligned} \tag{A.17}$$

Here, in the Cartesian coordinates, $[x_s : x_f]$ is the x-axis range, $[y_s : y_f]$ is the y-axis range, and $[z_s : z_f]$ is the z-axis range. Therefore the electron density $\rho(\mathbf{r})$ provides the ground-state wave function and electronic properties of materials. Note that $v(\mathbf{r})$ is a general function. $v(\mathbf{r})$ is not limited to the Coulomb potential energy.

A.1.1 Non-Degenerate Ground State

The original proof of the first Hohenberg-Kohn theorem is surprisingly simple. Only the least-energy principle of the ground state is needed in the first Hohenberg-Kohn theorem. We will assume a non-degenerate ground state of the system. We consider a case where we could have two kinds of ground-state wave functions Ψ_1 and Ψ_2 which are derived from two different Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. We assume that the two ground-state wave functions Ψ_1 and Ψ_2 correspond to the same electron density $\rho(\mathbf{r})$. If the ground-state anti-symmetric wave function Ψ which is derived from a Hamiltonian $\mathcal{H}$ in the eigenequation (Eq. A.1) leads to the electron density $\rho(\mathbf{r})$, this is called V -representability. We assume that all of the functionals are constructed by V -representable electron density $\rho(\mathbf{r})$. Here, note that because the two Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ are different, the external potential energy $v_1(\mathbf{r})$ of the Hamiltonian $\mathcal{H}_1$ is different from the external potential energy $v_2(\mathbf{r})$ of the Hamiltonian $\mathcal{H}_2$.

We will consider the least-energy principle. In order to solve a minimization problem of the Hamiltonian $\mathcal{H}_1$, we regard the wave function Ψ_2 as a trial function. By using (Eq. A.14) and noting that the trial function Ψ_2 is not the true ground-state eigenfunction, we obtain the relation written as

$$\begin{aligned} E_1 &= \langle \Psi_1 | \hat{\mathcal{H}}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{\mathcal{H}}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{\mathcal{H}}_1 - \hat{\mathcal{H}}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{\mathcal{H}}_2 | \Psi_2 \rangle \\ &= \langle \Psi_2 | \hat{\mathcal{H}}_1 - \hat{\mathcal{H}}_2 | \Psi_2 \rangle + E_2 \\ &= \int d\mathbf{r} (v_1(\mathbf{r}) - v_2(\mathbf{r})) \rho(\mathbf{r}) + E_2, \end{aligned} \tag{A.18}$$

where the wave function Ψ_1 is the true ground-state eigenfunction of the Hamiltonian $\mathcal{H}_1$. Here, E_1 and E_2 are the ground-state energies of the Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. $\hat{\mathcal{H}}_1$ and $\hat{\mathcal{H}}_2$ are the Hamiltonian operators of the Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. Likewise, when we regard the wave function Ψ_1 as a trial function for the minimization problem of the Hamiltonian $\mathcal{H}_2$, we obtain the relation described as

$$\begin{aligned} E_2 &= \langle \Psi_2 | \hat{\mathcal{H}}_2 | \Psi_2 \rangle < \langle \Psi_1 | \hat{\mathcal{H}}_2 | \Psi_1 \rangle = \langle \Psi_1 | \hat{\mathcal{H}}_2 - \hat{\mathcal{H}}_1 | \Psi_1 \rangle + \langle \Psi_1 | \hat{\mathcal{H}}_1 | \Psi_1 \rangle \\ &= \langle \Psi_1 | \hat{\mathcal{H}}_2 - \hat{\mathcal{H}}_1 | \Psi_1 \rangle + E_1 \\ &= \int d\mathbf{r} (v_2(\mathbf{r}) - v_1(\mathbf{r})) \rho(\mathbf{r}) + E_1 \\ &= - \int d\mathbf{r} (v_1(\mathbf{r}) - v_2(\mathbf{r})) \rho(\mathbf{r}) + E_1. \end{aligned} \tag{A.19}$$

By adding (Eq. A.18) to (Eq. A.19), we obtain the relation described as

$$E_1 + E_2 < E_1 + E_2. \tag{A.20}$$

This is not consistent. Therefore under the assumption of the V -representability, the wave function Ψ corresponding to the electron density $\rho(\mathbf{r})$ is unique. Likewise, the external potential $v(\mathbf{r})$ is unique. Here, note that the unique external potential $v(\mathbf{r})$ uniquely produces the ground-state wave function Ψ by solving the stationary Schrödinger equation. Namely, the ground-state physical properties of materials are unique and universal functionals of the electron density $\rho(\mathbf{r})$.

The original proof of the second Hohenberg-Kohn theorem is also simple. By using the first Hohenberg-Kohn theorem and the least-energy principle of the wave function Ψ , we obtain the relation written as

$$\begin{aligned}\langle \Psi_2 | \hat{\mathcal{H}}_1 | \Psi_2 \rangle &= \int d\mathbf{r} v_1(\mathbf{r}) \rho_2(\mathbf{r}) + F[\rho_2(\cdot)] \\ &> \langle \Psi_1 | \hat{\mathcal{H}}_1 | \Psi_1 \rangle = \int d\mathbf{r} v_1(\mathbf{r}) \rho_1(\mathbf{r}) + F[\rho_1(\cdot)],\end{aligned}\tag{A.21}$$

where the trial function Ψ_2 corresponding to the electron density $\rho_2(\mathbf{r})$ is not the true ground-state eigenfunction Ψ_1 corresponding to the electron density $\rho_1(\mathbf{r})$ of the Hamiltonian $\hat{\mathcal{H}}_1$. The Hohenberg-Kohn functional $E_{\text{HK}}[\rho(\cdot)]$ is defined as

$$\begin{aligned}E_{\text{HK}}[\rho(\cdot)] &= \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle \\ &= \langle \Psi | \left(\hat{T} + \hat{U}_{\text{e-e}} + \hat{U}_{\text{ext}} \right) | \Psi \rangle \\ &= \langle \Psi | \hat{U}_{\text{ext}} | \Psi \rangle + \langle \Psi | \left(\hat{T} + \hat{U}_{\text{e-e}} \right) | \Psi \rangle \\ &= \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) + F[\rho(\cdot)], \\ F[\rho(\cdot)] &= \langle \Psi | \left(\hat{T} + \hat{U}_{\text{e-e}} \right) | \Psi \rangle,\end{aligned}\tag{A.22}$$

where Ψ corresponding to the electron density $\rho(\mathbf{r})$ is a trial function, and $\hat{\mathcal{H}}$, $\hat{T}$, $\hat{U}_{\text{e-e}}$, and $\hat{U}_{\text{ext}}$ are the operators of $\mathcal{H}$, T , $U_{\text{e-e}}$, and U_{ext} , respectively, in (Eq. A.2)–(Eq. A.5). Therefore the second Hohenberg-Kohn theorem insists that the Hohenberg-Kohn functional $E_{\text{HK}}[\rho(\cdot)]$ with the exact ground-state electron density $\rho(\mathbf{r})$ of the Hamiltonian $\mathcal{H}$ be the minimum over all of the functions Ψ corresponding to the electron density $\rho(\mathbf{r})$.

A.1.2 Degenerate Ground State

We assume a degenerate ground state of the system. If the definition of the Hohenberg-Kohn functional $E_{\text{HK}}[\rho(\cdot)]$ is extended, the first Hohenberg-Kohn theorem is applied to the degenerate ground state of the system. The proof of the first Hohenberg-Kohn theorem with the degenerate ground state is given below. Orthonormal degenerate ground states concerning the external potential energy $v(\mathbf{r})$ are defined as

$$|\Psi_{0,1}\rangle, |\Psi_{0,2}\rangle, \dots, |\Psi_{0,q}\rangle,\tag{A.23}$$

where q is the number of the orthonormal ground states. We will define a statistical density matrix $\hat{D}$ by using these states. The statistical density matrix $\hat{D}$ is defined as

$$\begin{aligned}\hat{D} &= \sum_{i=1}^q c_i |\Psi_{0,i}\rangle \langle \Psi_{0,i}|, \\ c_i^* &= c_i \geq 0, \quad \sum_{i=1}^q c_i = 1.\end{aligned}\tag{A.24}$$

The corresponding ensemble density $\rho_D(\mathbf{r})$ is written as

$$\begin{aligned}\rho_D(\mathbf{r}) &= \text{Tr}(\hat{D} \hat{n}(\mathbf{r})) \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,i} \rangle \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \left(\int \cdots \int \prod_{j=1}^N d\mathbf{r}_j |\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\rangle n(\mathbf{r}) \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N| \right) | \Psi_{0,i} \rangle \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \left[\int \cdots \int \prod_{j=1}^N d\mathbf{r}_j |\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\rangle \left(\sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) \right) \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N| \right] | \Psi_{0,i} \rangle,\end{aligned}\tag{A.25}$$

where N is the number of all the electrons. Here, note that the ensemble density $\rho_D(\mathbf{r})$ cannot be obtained from a single ground state $|\Psi_0\rangle$.

We will explicitly describe pure state and ensemble-state V -representability. The general ground state of the degenerate system is written as

$$\begin{aligned}|\Psi_0\rangle &= \sum_{i=1}^q d_i |\Psi_{0,i}\rangle, \quad \langle \Psi_0 | \Psi_0 \rangle = 1, \\ \sum_{i=1}^q d_i^* d_i &= \sum_{i=1}^q |d_i|^2 = 1.\end{aligned}\tag{A.26}$$

Here, note that the fundamental idea of the above statement is the Gram-Schmidt orthogonalization. Therefore we obtain the corresponding density $\rho_0(\mathbf{r})$ written as

$$\begin{aligned}\rho_0(\mathbf{r}) &= \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \\ &= \left(\sum_{i=1}^q d_i^* \langle \Psi_{0,i} | \right) \hat{n}(\mathbf{r}) \left(\sum_{j=1}^q d_j |\Psi_{0,j}\rangle \right) \\ &= \sum_{i,j=1}^q d_i^* d_j \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle.\end{aligned}\tag{A.27}$$

Because the density $\rho_D(\mathbf{r})$ is exactly the same as the density $\rho_0(\mathbf{r})$, we obtain the relation described as

$$\sum_{i,j=1}^q (c_i \delta_{i,j} - d_i^* d_j) \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle = 0. \quad (\text{A.28})$$

Because the term $\langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle$ does not equal zero, although it could occur accidentally, we obtain the relation written as

$$c_i \delta_{i,j} - d_i^* d_j = 0. \quad (\text{A.29})$$

In short, we can describe pure-state and ensemble-state V -representability as follows:

Pure State: The density $\rho(\mathbf{r})$ directly results from a single state $|\Psi_0\rangle$.

Ensemble State: The density $\rho(\mathbf{r})$ indirectly results from a state $|\Psi_{0,i}\rangle$, although it directly results from a statistical and ensemble density matrix $\hat{D}$. Here, note that we redefine expectation value. The expectation value A of an operator $\hat{A}$ by using the density matrix $\hat{D}$ is described as

$$\begin{aligned} A &= \text{Tr}(\hat{D}\hat{A}) \\ &= \sum_{i=1}^q \langle \Psi_{0,i} | \left(\sum_{j=1}^q c_j |\Psi_{0,j}\rangle \langle \Psi_{0,j}| \hat{A} \right) | \Psi_{0,i} \rangle \\ &= \sum_{i,j=1}^q c_j \delta_{i,j} \langle \Psi_{0,j} | \hat{A} | \Psi_{0,i} \rangle \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{A} | \Psi_{0,i} \rangle, \end{aligned} \quad (\text{A.30})$$

where the relation between $\langle \Psi_{0,i} |$ and $|\Psi_{0,j}\rangle$ is written as

$$\langle \Psi_{0,i} | \Psi_{0,j} \rangle = \delta_{i,j}. \quad (\text{A.31})$$

The original Hohenberg-Kohn energy functional $E_{\text{HK}}[\rho(\cdot)]$ is merely defined for pure-state density $\rho(\mathbf{r})$. The Hohenberg-Kohn energy functional $E_{\text{HK}}[\rho(\cdot)]$ needs to be redefined for ensemble-state density $\rho(\mathbf{r})$. In order to deal with ensemble-state V -representable density successfully, we replace the set B_{pure} of all pure ground states $\{|\Psi_0\rangle\}$ with the set B_{ensemble} of all density matrices of ensemble ground states $\{|\Psi_{0,i}\rangle\}$. By using the external potential energy $v(\mathbf{r})$, the set B_{ensemble} is written as

$$B_{\text{ensemble}} = \left\{ \hat{D} \left| c_i = c_i^* \geq 0, \sum_{i=1}^q c_i = 1, \hat{D} = \sum_{i=1}^q c_i |\Psi_{0,i}\rangle \langle \Psi_{0,i}| \right. \right\}, \quad (\text{A.32})$$

where $|\Psi_{0,i}\rangle$ is the i th degenerate ground state leading to $v(\mathbf{r})$ and q is the number of all the orthonormal degenerate ground states.

A one-to-one correspondence exists between the external potential energy $v(r)$, the ensemble-state set B_{ensemble} , and the ensemble-state density $\rho_D(\mathbf{r})$, as shown in the first Hohenberg-Kohn theorem with ensemble state. The proof of the first Hohenberg-Kohn theorem with ensemble state is similar to that of the original first Hohenberg-Kohn theorem with pure state. Any given ensemble density $\rho_D(\mathbf{r})$ uniquely determines the sets of $v(\mathbf{r})$ and B_{ensemble} . When ensemble-state densities $\rho_D(\mathbf{r})$ and $\rho'_D(\mathbf{r})$ are given, the sets $B_{\text{ensemble}}(\rho_D)$ and $B_{\text{ensemble}}(\rho'_D)$ are disjoint. The ensemble-state Hohenberg-Kohn energy functional $E_{\text{EHK}}[\rho(\cdot)]$ is defined as

$$\begin{aligned} E_{\text{EHK}}[\rho(\cdot)] &= \text{Tr}(\hat{D}(\rho(\cdot))\hat{\mathcal{H}}) = \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{\mathcal{H}} | \Psi_{0,i} \rangle \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \varepsilon_0 | \Psi_{0,i} \rangle = \varepsilon_0 \sum_{i=1}^q c_i \langle \Psi_{0,i} | \Psi_{0,i} \rangle = \varepsilon_0, \\ \rho(\mathbf{r}) &= \text{Tr}(\hat{D}(\rho(\cdot))\hat{n}(\mathbf{r})) = \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,i} \rangle, \end{aligned} \tag{A.33}$$

where $|\Psi_{0,i}\rangle$ is one of the ensemble-orthonormal ground states corresponding to the Hamiltonian $\hat{\mathcal{H}}$ and ε_0 is the ground-state eigenvalue of the Hamiltonian $\hat{\mathcal{H}}$. The ensemble-state Hohenberg-Kohn energy functional $E_{\text{EHK}}[\rho(\cdot)]$ is a unique density functional which generates ε_0 . The first and second Hohenberg-Kohn theorems are applied to the domain ranging from pure state to ensemble state. The least-energy principle is also applied to this functional $E_{\text{EHK}}[\rho(\cdot)]$.

A.2 Concrete Formation of Wave Function Corresponding to Specific Electron Density

We will construct a formation of the ground-state wave function Ψ leading to the electron density $\rho(\mathbf{r})$ as follows:

$$\Psi \rightarrow \rho(\mathbf{r}). \tag{A.34}$$

If we can construct it, the above relation (A.34) and the first Hohenberg-Kohn theorem derive the electron density $\rho(\mathbf{r})$ with the one-to-one correspondence to the ground-state wave function Ψ as follows:

$$\Psi \leftrightarrow \rho(\mathbf{r}). \tag{A.35}$$

We concretely construct an anti-symmetric normalizable N -particle function Ψ with the one-to-one correspondence to the non-negative density $\rho(\mathbf{r})$. We will construct the function Ψ in the one-electron approximation by the Slater determinant. We give an element $\psi_{\mathbf{k}}(\mathbf{r})$ of the Slater determinant. Ignoring spin for simplicity, we construct the $\mathbf{k}$ th electronic wave function $\psi_{\mathbf{k}}(\mathbf{r})$ with the definition of suitable one-electron orbitals defined as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \left(\frac{\rho(\mathbf{r})}{N} \right)^{1/2} \exp [i (\mathbf{k} \cdot \mathbf{f}(\mathbf{r}) + \varphi(\mathbf{r}))]. \tag{A.36}$$

Here, i is the imaginary unit and the number of all the electrons is N defined as

$$N = \int d\mathbf{r} \rho(\mathbf{r}). \quad (\text{A.37})$$

The Cartesian components of $\mathbf{r}$ are defined as

$$\mathbf{r} = (x \ y \ z). \quad (\text{A.38})$$

$\mathbf{k}$ is an integer constant vector and the Cartesian components of the vector $\mathbf{k}$ are defined as

$$\begin{aligned} \mathbf{k} &= (k_1 \ k_2 \ k_3), \\ k_i &\in \mathbb{Z} \ (i = 1, 2, 3). \end{aligned} \quad (\text{A.39})$$

The Cartesian components of the vector field $\mathbf{f}(\mathbf{r})$ are defined as

$$\begin{aligned} \mathbf{f}(\mathbf{r}) &= (f_1 \ f_2 \ f_3), \\ f_1(\mathbf{r}) &= 2\pi \frac{\int_{x_s}^x dx' \rho(x', y, z)}{\int_{x_s}^{x_f} dx' \rho(x', y, z)}, \\ f_2(\mathbf{r}) &= 2\pi \frac{\int_{y_s}^y dy' \int_{x_s}^{x_f} dx' \rho(x', y', z)}{\int_{y_s}^{y_f} dy' \int_{x_s}^{x_f} dx' \rho(x', y', z)}, \\ f_3(\mathbf{r}) &= 2\pi \frac{\int_{z_s}^z dz' \int_{y_s}^{y_f} dy' \int_{x_s}^{x_f} dx' \rho(x', y', z')}{\int_{z_s}^{z_f} dz' \int_{y_s}^{y_f} dy' \int_{x_s}^{x_f} dx' \rho(x', y', z')}. \end{aligned} \quad (\text{A.40})$$

$\varphi(\mathbf{r})$ is an arbitrary scalar field and $\varphi(\mathbf{r})$ is not unique. We can choose a different scalar field $\varphi(\mathbf{r})$. In the Cartesian coordinates, the space of the system is a cuboid whose volume V is described as

$$V = (x_f - x_s)(y_f - y_s)(z_f - z_s). \quad (\text{A.41})$$

Here, note that different choices of the function $\psi_{\mathbf{k}}(\mathbf{r})$ with the one-to-one correspondence to the density $\rho(\mathbf{r})$ are possible. In this description, we select the function $\psi_{\mathbf{k}}(\mathbf{r})$ defined in (Eq. A.36).

We give mathematical proof of the orthonormality between two functions $\psi_{\mathbf{k}_1}(\mathbf{r})$ and $\psi_{\mathbf{k}_2}(\mathbf{r})$. In advance, we see the relation described as

$$\begin{aligned} & d\mathbf{f}(\mathbf{r}) \\ &= df_1(\mathbf{r})df_2(\mathbf{r})df_3(\mathbf{r}) \\ &= \left| \frac{\partial(f_1, f_2, f_3)}{\partial(x, y, z)} \right| d\mathbf{r} \\ &= \left(\frac{\partial}{\partial x} f_1(x, y, z) \right) \left(\frac{\partial}{\partial y} f_2(y, z) \right) \left(\frac{\partial}{\partial z} f_3(z) \right) dx dy dz, \end{aligned} \quad (\text{A.42})$$

where $\left| \frac{\partial(f_1, f_2, f_3)}{\partial(x, y, z)} \right|$ is the Jacobi determinant of the vector field $\mathbf{f}(\mathbf{r})$. We check whether the orthonormality between $\psi_{\mathbf{k}_1}(\mathbf{r})$ and $\psi_{\mathbf{k}_2}(\mathbf{r})$ exists. The inner product $\langle \psi_{\mathbf{k}_2} | \psi_{\mathbf{k}_1} \rangle$ between $\psi_{\mathbf{k}_1}(\mathbf{r})$ and $\psi_{\mathbf{k}_2}(\mathbf{r})$ is written as

$$\begin{aligned}
& \langle \psi_{\mathbf{k}_2} | \psi_{\mathbf{k}_1} \rangle \\
&= \langle \psi_{\mathbf{k}_2} | \left(\int_V d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| \right) | \psi_{\mathbf{k}_1} \rangle \\
&= \int_V d\mathbf{r} \psi_{\mathbf{k}_2}^*(\mathbf{r}) \psi_{\mathbf{k}_1}(\mathbf{r}) \\
&= \int_V d\mathbf{r} \left(\frac{\rho(\mathbf{r})}{N} \right)^{1/2} \exp[-i\mathbf{k}_2 \cdot \mathbf{f}(\mathbf{r}) - i\varphi(\mathbf{r})] \left(\frac{\rho(\mathbf{r})}{N} \right)^{1/2} \exp[i\mathbf{k}_1 \cdot \mathbf{f}(\mathbf{r}) + i\varphi(\mathbf{r})] \quad (\text{A.43}) \\
&= \frac{1}{N} \int_V d\mathbf{r} \rho(\mathbf{r}) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(\mathbf{r})] \\
&= \frac{1}{N} \int_{x_s}^{x_f} dx \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \rho(x, y, z) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(x, y, z)] \\
&= \frac{1}{N} \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \int_{x_s}^{x_f} dx \rho(x, y, z) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(x, y, z)].
\end{aligned}$$

When we substitute f_1 for x , we obtain the relation described as

$$\begin{aligned}
& \langle \psi_{\mathbf{k}_2} | \psi_{\mathbf{k}_1} \rangle \\
&= \frac{1}{N} \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \left(\frac{\partial}{\partial x} f_1(x, y, z) \right)^{-1} \rho(x, y, z) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, y, z)] \\
&= \frac{1}{N} \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \left(\frac{2\pi\rho(x, y, z)}{\int_{x_s}^{x_f} dx' \rho(x', y, z)} \right)^{-1} \rho(x, y, z) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, y, z)] \\
&= \frac{1}{N} \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \left(\frac{\int_{x_s}^{x_f} dx' \rho(x', y, z)}{2\pi\rho(x, y, z)} \right) \rho(x, y, z) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, y, z)] \\
&= \frac{1}{N} \frac{1}{2\pi} \int_{y_s}^{y_f} dy \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \left(\int_{x_s}^{x_f} dx' \rho(x', y, z) \right) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, y, z)] \\
&= \frac{1}{N} \frac{1}{2\pi} \int_{z_s}^{z_f} dz \int_{y_s}^{y_f} dy \int_{f_1(x_s)}^{f_1(x_f)} df_1 \left(\int_{x_s}^{x_f} dx' \rho(x', y, z) \right) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, y, z)].
\end{aligned} \tag{A.44}$$

When we substitute f_2 for y , we obtain the relation written as

$$\begin{aligned}
& \langle \psi_{\mathbf{k}_2} | \psi_{\mathbf{k}_1} \rangle \\
&= \frac{1}{N} \frac{1}{2\pi} \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \left(\int_{x_s}^{x_f} dx' \rho(x', y, z) \right) \left(\frac{\partial}{\partial y} f_2(y, z) \right)^{-1} \\
&\quad \times \exp [i (\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, z)] \\
&= \frac{1}{N} \frac{1}{2\pi} \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \left(\int_{x_s}^{x_f} dx' \rho(x', y, z) \right) \left(\frac{2\pi \int_{x_s}^{x_f} dx'' \rho(x'', y, z)}{\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z)} \right)^{-1} \\
&\quad \times \exp [i (\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, z)] \\
&= \frac{1}{N} \frac{1}{2\pi} \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \left(\int_{x_s}^{x_f} dx' \rho(x', y, z) \right) \left(\frac{\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z)}{2\pi \int_{x_s}^{x_f} dx'' \rho(x'', y, z)} \right) \\
&\quad \times \exp [i (\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, z)] \\
&= \frac{1}{N} \frac{1}{(2\pi)^2} \int_{z_s}^{z_f} dz \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \left(\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z) \right) \\
&\quad \times \exp [i (\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, z)].
\end{aligned} \tag{A.45}$$

When we substitute f_3 for z , we obtain the relation described as

$$\begin{aligned}
& \langle \psi_{\mathbf{k}_2} | \psi_{\mathbf{k}_1} \rangle \\
&= \frac{1}{N} \frac{1}{(2\pi)^2} \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \int_{z_s}^{z_f} dz \left(\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z) \right) \\
&\quad \times \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, z)] \\
&= \frac{1}{N} \frac{1}{(2\pi)^2} \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \int_{f_3(z_s)}^{f_3(z_f)} df_3 \left(\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z) \right) \left(\frac{\partial}{\partial z} f_3(z) \right)^{-1} \\
&\quad \times \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, f_3)] \\
&= \frac{1}{N} \frac{1}{(2\pi)^2} \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \int_{f_3(z_s)}^{f_3(z_f)} df_3 \left(\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z) \right) \\
&\quad \times \left(\frac{2\pi \int_{x_s}^{x_f} dx''' \int_{y_s}^{y_f} dy''' \rho(x''', y''', z)}{\int_{x_s}^{x_f} dx''' \int_{y_s}^{y_f} dy''' \int_{z_s}^{z_f} dz''' \rho(x''', y''', z''')} \right)^{-1} \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, f_3)] \\
&= \frac{1}{N} \frac{1}{(2\pi)^2} \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \int_{f_3(z_s)}^{f_3(z_f)} df_3 \left(\int_{x_s}^{x_f} dx'' \int_{y_s}^{y_f} dy'' \rho(x'', y'', z) \right) \\
&\quad \times \left(\frac{\int_{x_s}^{x_f} dx''' \int_{y_s}^{y_f} dy''' \int_{z_s}^{z_f} dz''' \rho(x''', y''', z''')}{2\pi \int_{x_s}^{x_f} dx''' \int_{y_s}^{y_f} dy''' \rho(x''', y''', z)} \right) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, f_3)] \\
&= \frac{1}{N} \frac{1}{(2\pi)^3} \int_{f_1(x_s)}^{f_1(x_f)} df_1 \int_{f_2(y_s)}^{f_2(y_f)} df_2 \int_{f_3(z_s)}^{f_3(z_f)} df_3 \left(\int_{x_s}^{x_f} dx''' \int_{y_s}^{y_f} dy''' \int_{z_s}^{z_f} dz''' \rho(x''', y''', z''') \right) \\
&\quad \times \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}(f_1, f_2, f_3)] \\
&= \frac{1}{N} \frac{N}{(2\pi)^3} \int_0^{2\pi} df_1 \int_0^{2\pi} df_2 \int_0^{2\pi} df_3 \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{f}] \\
&= \frac{1}{(2\pi)^3} \int_V d\mathbf{f} \exp[i\mathbf{f} \cdot (\mathbf{k}_1 - \mathbf{k}_2)] \\
&= \frac{1}{(2\pi)^3} \int_V d\mathbf{f} \exp[-i\mathbf{f} \cdot (\mathbf{k}_2 - \mathbf{k}_1)] \\
&= \delta_{\mathbf{k}_2, \mathbf{k}_1}.
\end{aligned} \tag{A.46}$$

Here, note the following relations. The Fourier series expansion of the Dirac delta function

$\delta(\mathbf{r})$ and the Kronecker delta $\delta_{\mathbf{k},\mathbf{g}}$ are written as

$$\begin{aligned}
\delta_{\mathbf{k},\mathbf{g}} &= \delta_{k_1,g_1} \delta_{k_2,g_2} \delta_{k_3,g_3} \\
&= \frac{1}{(2\pi)^3} \prod_{j=1}^3 \int_0^{2\pi} df_j \exp[-i(k_j - g_j) \cdot f_j], \\
\delta(\mathbf{r}' - \mathbf{r}) &= \delta(r'_1 - r_1) \delta(r'_2 - r_2) \delta(r'_3 - r_3) \\
&= \frac{1}{(2\pi)^3} \prod_{j=1}^3 \sum_{\mathbf{k} \in \mathbb{Z}} \exp[ik_j \cdot (r'_j - r_j)],
\end{aligned} \tag{A.47}$$

where the Cartesian components of the two constant wave vectors $\mathbf{k}$ and $\mathbf{g}$ are defined as

$$\mathbf{k} = (k_1 \ k_2 \ k_3), \quad \mathbf{g} = (g_1 \ g_2 \ g_3), \tag{A.48}$$

and those of two constant position vectors $\mathbf{r}$ and $\mathbf{r}'$ are defined as

$$\mathbf{r} = (r_1 \ r_2 \ r_3), \quad \mathbf{r}' = (r'_1 \ r'_2 \ r'_3). \tag{A.49}$$

We obtain the orthonormality of two arbitrary functions $\psi_{\mathbf{k}_1}(\mathbf{r})$ and $\psi_{\mathbf{k}_2}(\mathbf{r})$. We also check whether the orthonormality between two position vectors $\mathbf{r}$ and $\mathbf{r}'$ exists. In advance, we see the relation between the Dirac delta function $\delta(x)$ and an arbitrary function $f(x)$:

$$\delta(f(x)) = \sum_{\ell} \frac{1}{\left| \frac{d}{dx} f(x) \right|_{x=a_{\ell}}} \delta(x - a_{\ell}), \tag{A.50}$$

where $x = a_{\ell}$ satisfies the relation described as

$$f(x) = 0. \tag{A.51}$$

Here, note that $x = a_{\ell}$ is not a multiple root.

The orthonormality relation $\langle \mathbf{r} | \mathbf{r}' \rangle$ between position vectors $\mathbf{r}$ and $\mathbf{r}'$ is calculated as

$$\begin{aligned}
& \langle \mathbf{r} | \left(\sum_{\mathbf{k} \in \mathbb{Z}} |\psi_{\mathbf{k}}\rangle \langle \psi_{\mathbf{k}}| \right) | \mathbf{r}' \rangle \\
&= \sum_{\mathbf{k} \in \mathbb{Z}} \langle \mathbf{r} | \psi_{\mathbf{k}} \rangle \langle \psi_{\mathbf{k}} | \mathbf{r}' \rangle \\
&= \sum_{\mathbf{k} \in \mathbb{Z}} \psi_{\mathbf{k}}^*(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}) \\
&= \sum_{\mathbf{k} \in \mathbb{Z}} \left(\frac{\rho(\mathbf{r}')}{N} \right)^{1/2} \exp[-i(\mathbf{k} \cdot \mathbf{f}(\mathbf{r}') + \varphi(\mathbf{r}'))] \left(\frac{\rho(\mathbf{r})}{N} \right)^{1/2} \exp[i(\mathbf{k} \cdot \mathbf{f}(\mathbf{r}) + \varphi(\mathbf{r}))] \\
&= \sum_{\mathbf{k} \in \mathbb{Z}} \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \exp[-i\mathbf{k} \cdot (\mathbf{f}(\mathbf{r}') - \mathbf{f}(\mathbf{r}))] \\
&= \sum_{\mathbf{k} \in \mathbb{Z}} \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \exp[i\mathbf{k} \cdot (\mathbf{f}(\mathbf{r}) - \mathbf{f}(\mathbf{r}'))] \\
&= \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \left(\sum_{\mathbf{k} \in \mathbb{Z}^3} \exp[i\mathbf{k} \cdot (\mathbf{f}(\mathbf{r}) - \mathbf{f}(\mathbf{r}'))] \right) \\
&= \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] ((2\pi)^3 \delta(\mathbf{f}(\mathbf{r}) - \mathbf{f}(\mathbf{r}'))) \\
&= (2\pi)^3 \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \left[\sum_{\ell} \frac{1}{a_{\ell}} \delta(\mathbf{r} - \mathbf{r}') \right] \\
&= (2\pi)^3 \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \left[\left| \frac{\partial(f_1, f_2, f_3)}{\partial(x, y, z)} \right|^{-1} \delta(\mathbf{r} - \mathbf{r}') \right] \\
&= (2\pi)^3 \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \delta(\mathbf{r} - \mathbf{r}') \left(\frac{\partial f_1}{\partial x} \frac{\partial f_2}{\partial y} \frac{\partial f_3}{\partial z} \right)^{-1} \\
&= (2\pi)^3 \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{N} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \delta(\mathbf{r} - \mathbf{r}') \left(\frac{\int_{x_s}^{x_f} dx' \int_{y_s}^{y_f} dy' \int_{z_s}^{z_f} dz' \rho(x', y', z')}{(2\pi)^3 \rho(\mathbf{r})} \right) \\
&= \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{\rho(\mathbf{r})} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] \delta(\mathbf{r} - \mathbf{r}') \\
&= \delta(\mathbf{r} - \mathbf{r}').
\end{aligned} \tag{A.52}$$

Here, note that the vector field $\mathbf{f}$ is a monotonically increasing function of $\mathbf{r}$. Therefore we

obtain the relation described as

$$a_1 = \left| \frac{\partial(f_1, f_2, f_3)}{\partial(x, y, z)} \right|, \quad (A.53)$$

$$\lim_{\mathbf{r} \rightarrow \mathbf{r}'} \frac{\sqrt{\rho(\mathbf{r}')\rho(\mathbf{r})}}{\rho(\mathbf{r})} \exp[i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')] = 1,$$

where ℓ is the only one. In addition, because of the orthonormality relation described as

$$\langle \mathbf{r} | \left(\sum_{\mathbf{k} \in \mathbb{Z}} |\psi_{\mathbf{k}}\rangle \langle \psi_{\mathbf{k}}| \right) | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') = \langle \mathbf{r} | \mathbf{r}' \rangle, \quad (A.54)$$

we obtain the identity operator $\hat{1}$ written as

$$\hat{1} = \sum_{\mathbf{k} \in \mathbb{Z}} |\psi_{\mathbf{k}}\rangle \langle \psi_{\mathbf{k}}|. \quad (A.55)$$

Therefore the set $\{\psi_{\mathbf{k}}(\mathbf{r})\}$ of all the functions $\psi_{\mathbf{k}}(\mathbf{r})$ is an orthonormal and complete basis set.

By using the function $\psi_{\mathbf{k}}$, we can construct an anti-symmetric N -particle state. The wave function Ψ with the Slater determinant is written as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\mathbf{k}_1}(\mathbf{r}_1) & \psi_{\mathbf{k}_1}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_1}(\mathbf{r}_N) \\ \psi_{\mathbf{k}_2}(\mathbf{r}_1) & \psi_{\mathbf{k}_2}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_2}(\mathbf{r}_N) \\ \vdots & \vdots & & \vdots \\ \psi_{\mathbf{k}_N}(\mathbf{r}_1) & \psi_{\mathbf{k}_N}(\mathbf{r}_2) & \cdots & \psi_{\mathbf{k}_N}(\mathbf{r}_N) \end{vmatrix}. \quad (A.56)$$

Because of $\langle \psi_{\mathbf{k}_i} | \psi_{\mathbf{k}_j} \rangle = \delta_{\mathbf{k}_i, \mathbf{k}_j}$ and $\langle \Psi | \Psi \rangle = 1$, the electron density $\rho(\mathbf{r})$ with the one-to-one

correspondence to the wave function Ψ is calculated as

$$\begin{aligned}
& \langle \Psi | \hat{n} | \Psi \rangle \\
&= \int \cdots \int \sum_{i=1}^N \prod_{\substack{j=1 \\ (j \neq i)}}^N d\mathbf{r}_j \Psi^*(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N) \\
&= \int \cdots \int \sum_{i=1}^N \prod_{\substack{j=1 \\ (j \neq i)}}^N d\mathbf{r}_j |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N)|^2 \\
&= \int \cdots \int \prod_{j=2}^N d\mathbf{r}_j |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N)|^2 \\
&\quad + \int \cdots \int \prod_{\substack{j=1 \\ (j \neq 2)}}^N d\mathbf{r}_j |\Psi(\mathbf{r}_1, \mathbf{r}, \cdots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N)|^2 + \cdots \\
&\quad + \int \cdots \int \prod_{\substack{j=1 \\ (j \neq i)}}^N d\mathbf{r}_j |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \cdots, \mathbf{r}_N)|^2 + \cdots \\
&\quad + \int \cdots \int \prod_{j=1}^{N-1} d\mathbf{r}_j |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_{i-1}, \mathbf{r}_i, \mathbf{r}_{i+1}, \cdots, \mathbf{r})|^2 \\
&= \sum_{i=1}^N \left[\left(\frac{1}{\sqrt{N}} \right)^2 (N \times |\psi_{\mathbf{k}_i}(\mathbf{r})|^2) \right] \\
&= \sum_{i=1}^N |\psi_{\mathbf{k}_i}(\mathbf{r})|^2 \\
&= \sum_{i=1}^N \left(\frac{\rho(\mathbf{r})}{N} \right) \\
&= N \times \left(\frac{\rho(\mathbf{r})}{N} \right) \\
&= \rho(\mathbf{r}).
\end{aligned} \tag{A.57}$$

We understand the wave function Ψ with the one-to-one correspondence to the electron density $\rho(\mathbf{r})$. The wave function Ψ is V -representable. Therefore by using the normalized, orthonormal, and complete basis $\psi_{\mathbf{k}_i}$ ($i = 1, 2, \cdots, N$), we always obtain the electron density $\rho(\mathbf{r})$ described as

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_{\mathbf{k}_i}(\mathbf{r})|^2. \tag{A.58}$$

Most density functional calculations are based on the Slater determinant, which is N -representable. We need not pay attention to the problem of N -representability. Here, note that N -representability expresses the satisfaction of the condition described as

$$\rho(\mathbf{r}) \geq 0, \quad \int d\mathbf{r} \rho(\mathbf{r}) = N, \quad \text{and} \quad \int d\mathbf{r} |\nabla \rho(\mathbf{r})^{1/2}|^2 \leq \infty. \quad (\text{A.59})$$

Appendix B

Supplements to Chapter 3

In Chapter 3, we have described elastic mechanics. Here, for a better understanding, we will deal with elastic constants according to crystal systems and provide detailed information about the Voigt, Reuss, and Hill approximations.

B.1 Elastic Constants According to Crystal Systems

Elastic constants according to the seven crystal systems shown in Table 3.1 are described as (B.1)–(B.7). Isotropic elastic constants are written as (B.8).

$$\text{Triclinic : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & \text{Sym.} & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{pmatrix}. \quad (\text{B.1})$$

$$\text{Monoclinic : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{22} & C_{23} & 0 & 0 & C_{26} \\ & & C_{33} & 0 & 0 & C_{36} \\ & \text{Sym.} & & C_{44} & C_{45} & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{pmatrix}. \quad (\text{B.2})$$

$$\text{Orthorhombic : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & \text{Sym.} & & C_{44} & 0 & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{pmatrix}. \quad (\text{B.3})$$

$$\text{Tetragonal : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & \text{Sym.} & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix}. \quad (\text{B.4})$$

$$\text{Trigonal (Rhombohedral) : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & \text{Sym.} & & C_{44} & 0 & 0 \\ & & & & C_{44} & C_{14} \\ & & & & & (C_{11} - C_{12})/2 \end{pmatrix}. \quad (\text{B.5})$$

$$\text{Hexagonal : } \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & \text{Sym.} & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & (C_{11} - C_{12})/2 \end{pmatrix}. \quad (\text{B.6})$$

$$\text{Cubic : } \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ & C_{11} & C_{12} & 0 & 0 & 0 \\ & & C_{11} & 0 & 0 & 0 \\ & \text{Sym.} & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{44} \end{pmatrix}. \quad (\text{B.7})$$

$$\text{Isotropic : } \begin{pmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ & & \lambda + 2\mu & 0 & 0 & 0 \\ & \text{Sym.} & & \mu & 0 & 0 \\ & & & & \mu & 0 \\ & & & & & \mu \end{pmatrix}. \quad (\text{B.8})$$

B.2 Voigt, Reuss, and Hill Approximations

In most cases, a material has anisotropic elastic properties in its unit cell. When the material has random crystal orientations (*i.e.*, the material is polycrystalline), we can regard the elastic properties of the material as isotropic elastic properties. When we convert anisotropic elastic properties to isotropic elastic properties, we use the Euler angles (ϕ, θ, ψ) and the 6×6 rotation matrix M , which has the parameters ϕ , θ , and ψ . By using the Euler angles, the rotated elastic constant matrix $[C_{ij}^{\text{rot}}(C_{ij}, \phi, \theta, \psi)]$ is described as

$$[C_{ij}^{\text{rot}}(C_{ij}, \phi, \theta, \psi)] = M[C_{ij}]M^t, \quad (\text{B.9})$$

where $[C_{ij}]$ is the 6×6 elastic constant matrix before the rotations and M^t is the transposed matrix of the rotation matrix M . The normalization constant Ω_0 is written as

$$\Omega_0 = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^{2\pi} d\psi \sin \theta = (2\pi)^2 [-\cos \theta]_{\theta=0}^\pi = 8\pi^2. \quad (\text{B.10})$$

When we assume the uniform and homogeneous strains, we obtain the averaged ij th elastic constant $\langle C_{ij} \rangle^{\text{Voigt}}$ described as

$$\langle C_{ij} \rangle^{\text{Voigt}} = \frac{1}{\Omega_0} \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^{2\pi} d\psi C_{ij}^{\text{rot}}(C_{ij}, \phi, \theta, \psi) \sin \theta. \quad (\text{B.11})$$

This approximation is called the Voigt approximation [71]. When we assume the uniform and homogeneous stresses, we obtain the averaged ij th compliance constant $\langle s_{ij} \rangle^{\text{Reuss}}$ described as

$$\langle s_{ij} \rangle^{\text{Reuss}} = \frac{1}{\Omega_0} \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^{2\pi} d\psi s_{ij}^{\text{rot}}(s_{ij}, \phi, \theta, \psi) \sin \theta. \quad (\text{B.12})$$

Here, the compliance constant matrix is the inverse matrix of the elastic constant matrix, $s_{ij}^{\text{rot}}(s_{ij}, \phi, \theta, \psi)$ is the rotated ij th compliance constant with the Euler angles, and s_{ij} is the ij th compliance constant before the rotations. This approximation is called the Reuss approximation [72]. Moreover, by using the Voigt and Reuss approximations, we obtain the relation described as

$$\langle C_{ij} \rangle^{\text{Hill}} = \frac{1}{2} \left[\langle C_{ij} \rangle^{\text{Voigt}} + \left(\langle s_{ij} \rangle^{\text{Reuss}} \right)^{-1} \right]. \quad (\text{B.13})$$

This approximation is called the Hill approximation or the Voigt-Reuss-Hill approximation [73].

The Voigt and Reuss approximations are regarded as upper and lower bounds of the true elastic constant, respectively. The Voigt-Reuss-Hill approximation gives averaged values, which are almost the same as true values. In order to calculate the averaged ij th elastic constant under the Voigt and Reuss approximations, we need numerical calculations. In the cubic, hexagonal, tetragonal, and orthorhombic structures, we obtain analytical formulations described as

$$\begin{aligned} 9B^{\text{Voigt}} &= C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{23} + C_{31}), \\ 15G^{\text{Voigt}} &= C_{11} + C_{22} + C_{33} - (C_{12} + C_{23} + C_{31}) \\ &\quad + 3(C_{44} + C_{55} + C_{66}), \end{aligned} \quad (\text{B.14})$$

$$\begin{aligned} 1/B^{\text{Reuss}} &= s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{23} + s_{31}), \\ 15/G^{\text{Reuss}} &= 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) \\ &\quad + 3(s_{44} + s_{55} + s_{66}), \end{aligned} \quad (\text{B.15})$$

where s_{ij} is the ij th compliance constant calculated as $s_{ij} = ([C_{kl}]^{-1})_{ij}$. Here, B^{Voigt} and G^{Voigt} are the bulk modulus and shear modulus under the Voigt approximation, respectively.

In addition, B^{Reuss} and G^{Reuss} are the bulk modulus and shear modulus under the Reuss approximation.

The bulk modulus B^{Hill} and shear modulus G^{Hill} under the Voigt-Reuss-Hill approximation are described as

$$\begin{aligned} B^{\text{Hill}} &= \frac{1}{2} (B^{\text{Voigt}} + B^{\text{Reuss}}), \\ G^{\text{Hill}} &= \frac{1}{2} (G^{\text{Voigt}} + G^{\text{Reuss}}). \end{aligned} \tag{B.16}$$

Hard material samples are usually prepared as polycrystalline forms with random crystal orientations. Therefore, in the present study, we mainly show elastic moduli estimated under the Voigt-Reuss-Hill approximation.

Appendix C

Supplements to Chapter 8

C.1 Jellium Model

In Chapter 8, we have dealt with the Jellium model. Using the Jellium model, we will provide proof that there is a strong correlation between electron density and bulk modulus. For the sake of completeness, we present mathematical proof of the derivation of the Jellium model.

C.1.1 Total Energy

We consider homogeneous positive charge. We assume an electrically neutral case. This model is called the Jellium model or the homogeneous electron gas model. The homogeneous positive charge determines the interaction between electrons and the positive charge. It also decides the interaction between the positive charge and the positive charge. Here, note that the positive charge number density $\rho_p(\mathbf{r})$ is described as

$$\rho_p(\mathbf{r}) = \frac{N}{V}, \quad (\text{C.1})$$

where N is the number of all the electrons and V is the volume of the system.

We use the Hartree-Fock equation in order to solve the Jellium model. The Hartree-Fock equation of the Jellium model is written as

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{ext}}(\mathbf{r}) \right) \psi_{\mathbf{k}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) + V_{\text{Fock}}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}), \quad (\text{C.2})$$

where the Hartree term $V_{\text{Hartree}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})$ and the Fock term E_{Fock} are described as

$$\begin{aligned}
V_{\text{Hartree}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) &= \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}), \\
V_{\text{Fock}}(\mathbf{r}) &= - \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}'), \\
\rho(\mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}'), \\
\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}) &= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} |\psi_{\mathbf{k}}(\mathbf{r})|^2.
\end{aligned} \tag{C.3}$$

Here, $\mathbb{Z}_{\psi}$ includes all the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ and $\mathbf{k}$ is an integer vector. The summation within $\mathbb{Z}_{\psi}$ is described as

$$\sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} 1 = N. \tag{C.4}$$

$\varepsilon_{\mathbf{k}}$ is the $\mathbf{k}$ th eigenvalue and $\psi_{\mathbf{k}}(\mathbf{r})$ is the $\mathbf{k}$ th wave function which is defined as

$$\psi_{\mathbf{k}} = \frac{1}{\sqrt{V}} \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{C.5}$$

because we assume the homogeneous electron gas. $U_{\text{ext}}(\mathbf{r})$ is the external potential energy. The interaction energy $v(\mathbf{r})$ is defined as

$$\begin{aligned}
v(\mathbf{r}) &= \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}|} \\
&= \frac{\alpha\hbar c}{|\mathbf{r}|} \\
&= v(-\mathbf{r}).
\end{aligned} \tag{C.6}$$

The constant α is defined as

$$\begin{aligned}
\alpha &= \frac{e^2}{4\pi\varepsilon_0\hbar c} \\
&\approx \frac{1}{137}.
\end{aligned} \tag{C.7}$$

We consider the external potential energy $U_{\text{ext}}(\mathbf{r})$. The interaction between electrons and the positive charge is related to the external potential energy $U_{\text{ext}}(\mathbf{r})$. The external potential

energy $\mathcal{E}_{\text{e-p}}^{\mathbf{k}}$ of the $\mathbf{k}$ th electron is described as

$$\begin{aligned}
\mathcal{E}_{\text{e-p}}^{\mathbf{k}} &= \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) U_{\text{ext}}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \\
&= \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) \left(- \int d\mathbf{r}' \rho_{\text{p}}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \right) \psi_{\mathbf{k}}(\mathbf{r}) \\
&= -\frac{N}{V} \iint d\mathbf{r} d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') |\psi_{\mathbf{k}}(\mathbf{r})|^2 \\
&= -\frac{N}{V} \iint d\mathbf{r} d\mathbf{Y} v(-\mathbf{Y}) \rho_{\mathbf{k}}(\mathbf{r}) \\
&= -\frac{N}{V} \int d\mathbf{r} \left(\int d\mathbf{Y} v(\mathbf{Y}) \right) \rho_{\mathbf{k}}(\mathbf{r}) \\
&= -\frac{N v_0}{V},
\end{aligned} \tag{C.8}$$

where we substitute $-\mathbf{Y}$ for $\mathbf{r} - \mathbf{r}'$. Here, note the relations described as

$$\begin{aligned}
U_{\text{ext}}(\mathbf{r}) &= - \int d\mathbf{r}' \rho_{\text{p}}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}'), \\
\rho_{\mathbf{k}}(\mathbf{r}) &= |\psi_{\mathbf{k}}(\mathbf{r})|^2, \\
\int d\mathbf{r} \rho_{\mathbf{k}}(\mathbf{r}) &= 1.
\end{aligned} \tag{C.9}$$

v_0 is defined as

$$\begin{aligned}
v_0 &= \int d\mathbf{r} v(\mathbf{r}) \\
&= \lim_{L \rightarrow \infty} \int_{-L}^L dx \int_{-L}^L dy \int_{-L}^L dz v(x, y, z) \\
&= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz v(x, y, z),
\end{aligned} \tag{C.10}$$

where the volume V of the system is defined as

$$V = L^3. \tag{C.11}$$

The interaction energy $\mathcal{E}_{\text{p-p}}$ between the positive charge and the positive charge is described

as

$$\begin{aligned}
\mathcal{E}_{\text{p-p}} &= \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho_{\text{p}}(\mathbf{r}) \rho_{\text{p}}(\mathbf{r}') \\
&= \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \left(\frac{N}{V} \right)^2 \\
&= \left(\frac{N}{V} \right)^2 \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \\
&= \frac{1}{2} \left(\frac{N}{V} \right)^2 \int d\mathbf{r} \left(\int d\mathbf{Y} v(-\mathbf{Y}) \right) \\
&= \frac{1}{2} \left(\frac{N}{V} \right)^2 v_0 \int d\mathbf{r} \\
&= \frac{1}{2} \left(\frac{N}{V} \right)^2 v_0 V \\
&= \frac{1}{2} \frac{N^2 v_0}{V}.
\end{aligned} \tag{C.12}$$

The Hartree term $\mathcal{E}_{\text{Hartree}}^{\mathbf{k}}$ of the $\mathbf{k}$ th wave function is described as

$$\begin{aligned}
\mathcal{E}_{\text{Hartree}}^{\mathbf{k}} &= \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) V_{\text{Hartree}}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \\
&= \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \left(\sum_{\mathbf{k}' \in \mathbb{Z}_\psi} \psi_{\mathbf{k}'}^*(\mathbf{r}') \psi_{\mathbf{k}'}(\mathbf{r}') \right) (\psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r})) \\
&= \frac{N}{V^2} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \\
&= \frac{N}{V^2} \int d\mathbf{r} \int d\mathbf{Y} v(-\mathbf{Y}) \\
&= \frac{N}{V^2} V v_0 \\
&= \frac{N v_0}{V}.
\end{aligned} \tag{C.13}$$

The Fock term $\mathcal{E}_{\text{Fock}}^{\mathbf{k}}$ of the $\mathbf{k}$ th wave function is written as

$$\begin{aligned}
\mathcal{E}_{\text{Fock}}^{\mathbf{k}} &= - \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \psi_{\mathbf{k}'}^*(\mathbf{r}') \psi_{\mathbf{k}'}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}') \\
&= - \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \frac{\exp(-i\mathbf{k} \cdot \mathbf{r})}{\sqrt{V}} \frac{\exp(-i\mathbf{k}' \cdot \mathbf{r}')}{\sqrt{V}} \frac{\exp(i\mathbf{k}' \cdot \mathbf{r})}{\sqrt{V}} \frac{\exp(i\mathbf{k} \cdot \mathbf{r}')}{\sqrt{V}} \\
&= - \frac{1}{V^2} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \exp(i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}') \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}) \\
&= - \frac{1}{V^2} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \exp(-i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{r} - \mathbf{r}')) \\
&= - \frac{1}{V^2} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \int d\mathbf{r}' \int d\mathbf{Y} v(\mathbf{Y}) \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{Y}) \\
&= - \frac{1}{V^2} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} \int d\mathbf{r}' v_{\mathbf{k}-\mathbf{k}'} \\
&= - \frac{1}{V^2} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} V v_{\mathbf{k}-\mathbf{k}'} \\
&= - \frac{1}{V} \sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} v_{\mathbf{k}-\mathbf{k}'},
\end{aligned} \tag{C.14}$$

where we substitute $\mathbf{Y}$ for $\mathbf{r} - \mathbf{r}'$. Here, $v_{\mathbf{k}-\mathbf{k}'}$ and the summation of the $\mathbf{k}'$ are defined as

$$\begin{aligned}
v_{\mathbf{k}-\mathbf{k}'} &= \int d\mathbf{r} v(\mathbf{r}) \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}), \\
\sum_{\mathbf{k}' \in \mathbb{Z}_{\psi}} 1 &= N.
\end{aligned} \tag{C.15}$$

Therefore we obtain the Hartree-Fock total energy E_{HF} described as

$$\begin{aligned}
E_{\text{HF}} &= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \left(\frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{N v_0}{V} \right) + \frac{N^2 v_0}{2V} + \frac{1}{2} \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \frac{N v_0}{V} - \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_{\psi}} v_{\mathbf{k}-\mathbf{k}'} \\
&= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{N^2 v_0}{V} + \frac{N^2 v_0}{2V} + \frac{N^2 v_0}{2V} - \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_{\psi}} v_{\mathbf{k}-\mathbf{k}'} \\
&= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_{\psi}} v_{\mathbf{k}-\mathbf{k}'},
\end{aligned} \tag{C.16}$$

where the above summation of $\mathbf{k}$ and $\mathbf{k}'$ is described as

$$\sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_{\psi}} 1 = N^2. \tag{C.17}$$

We calculate the concrete value of $v_{\mathbf{k}-\mathbf{k}'}$. We will give mathematical proof of $v_{\mathbf{k}}$ described as

$$\begin{aligned}
v_{\mathbf{k}} &= \int d\mathbf{r} v(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \\
&= \alpha \hbar c \int d\mathbf{r} \frac{\exp(-i\mathbf{k} \cdot \mathbf{r})}{|\mathbf{r}|} \\
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz \frac{\exp(-i(k_x x + k_y y + k_z z))}{\sqrt{x^2 + y^2 + z^2}},
\end{aligned} \tag{C.18}$$

where the Cartesian components of the position vector $\mathbf{r}$ and the wave vector $\mathbf{k}$ are described as

$$\begin{aligned}
\mathbf{r} &= (x \ y \ z), \\
\mathbf{k} &= (k_x \ k_y \ k_z), \\
r &= |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}.
\end{aligned} \tag{C.19}$$

When we use a coordinate transformation as follows:

$$\begin{aligned}
x(r, \theta, \phi) &= r \sin \theta \cos \phi, \\
y(r, \theta, \phi) &= r \sin \theta \sin \phi, \\
z(r, \theta, \phi) &= r \cos \theta,
\end{aligned} \tag{C.20}$$

we obtain the relation described as

$$\begin{aligned}
d\mathbf{r} &= dx dy dz \\
&= \left| \frac{\partial(x, y, z)}{\partial(r, \theta, \phi)} \right| dr d\theta d\phi \\
&= \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix} dr d\theta d\phi \\
&= \begin{vmatrix} \sin \theta \cos \phi & r \cos \theta \cos \phi & -r \sin \theta \sin \phi \\ \sin \theta \sin \phi & r \cos \theta \sin \phi & r \sin \theta \cos \phi \\ \cos \theta & -r \sin \theta & 0 \end{vmatrix} dr d\theta d\phi \\
&= r^2 \sin \theta dr d\theta d\phi,
\end{aligned} \tag{C.21}$$

where $\frac{\partial(x, y, z)}{\partial(r, \theta, \phi)}$ is the Jacobi determinant of the position vector $\mathbf{r}$. Because of this transformation, we obtain the relation written as

$$\begin{aligned}
v_{\mathbf{k}} &= \alpha \hbar c \int_0^{\infty} dr \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \frac{1}{r} \exp(-ikr \cos \theta) r^2 \sin \theta \\
&= \alpha \hbar c \int_0^{\infty} dr \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \exp(-ikr \cos \theta) r \sin \theta,
\end{aligned} \tag{C.22}$$

where the wave vector $\mathbf{k}$ is directed to the z axis and the constant absolute value of $\mathbf{k}$ is defined as

$$k = |\mathbf{k}|. \quad (\text{C.23})$$

If we regard t as $\cos \theta$, then we obtain the relations written as

$$\begin{aligned} dt &= -\sin \theta d\theta, \\ v_{\mathbf{k}} &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi \left(- \int_0^\pi d\theta \exp(-ikr \cos \theta) (-r \sin \theta) \right) \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi \left(- \int_1^{-1} dt r \exp(-ikrt) \right) \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi r \int_{-1}^1 dt \exp(-ikrt) \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi r \left[\frac{\exp(-ikrt)}{-ikr} \right]_{t=-1}^1 \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi \frac{1}{ik} (\exp(ikr) - \exp(-ikr)) \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi \frac{2i}{ik} \left(\frac{\exp(ikr) - \exp(-ikr)}{2i} \right) \\ &= \alpha \hbar c \int_0^\infty dr \int_0^{2\pi} d\phi \frac{2}{ik} i \sin(kr) \\ &= \alpha \hbar c \int_0^\infty dr \left(\int_0^{2\pi} d\phi \right) \frac{2}{k} \sin(kr) \\ &= 4\pi \alpha \hbar c \int_0^\infty dr \frac{\sin kr}{k}. \end{aligned} \quad (\text{C.24})$$

If we regard t' as kr , then we obtain the relations described as

$$\begin{aligned} dt' &= k dr, \\ I &= 4\pi \alpha \hbar c \int_0^\infty \frac{dt'}{k} \frac{\sin t'}{k} \\ &= \frac{4\pi \alpha \hbar c}{k^2} \int_0^\infty dt' \sin t' \\ &= \frac{4\pi \alpha \hbar c}{k^2} \int_0^\infty dx \sin x \\ &= \frac{4\pi \alpha \hbar c}{k^2} \int_0^\infty dx f(x). \end{aligned} \quad (\text{C.25})$$

Here, note that t' is replaced by x . A function $f(x)$ is defined as

$$f(x) = \sin x. \quad (\text{C.26})$$

Here, note that the integral $\int_0^\infty dx f(x)$ of the function $f(x)$ is not “absolutely convergent.” It is, however, “conditionally convergent.” We give mathematical proof of it.

We focus on an exponential function $g(x, \varepsilon) = \exp(-\varepsilon x)$. Here, note that ε is a non-negative constant value $\varepsilon > 0$. We check a function written as

$$1 - g(x, \varepsilon) \geq 0, \quad g(x, \varepsilon) = \exp(-\varepsilon x), \quad (\text{C.27})$$

where $1 - g(x, \varepsilon)$ is a monotonically increasing function. Because of the function $1 - g(x, \varepsilon)$, we obtain the relation described as

$$\begin{aligned} (1 - g(a, \varepsilon)) \int_a^b dx f(x) &< \int_a^b dx (1 - g(x, \varepsilon)) f(x) < (1 - g(b, \varepsilon)) \int_a^b dx f(x) \\ \lim_{a \rightarrow +0} (1 - g(a, \varepsilon)) \int_a^b dx f(x) &< \lim_{a \rightarrow +0} \int_a^b dx (1 - g(x, \varepsilon)) f(x) < \lim_{a \rightarrow +0} (1 - g(b, \varepsilon)) \int_a^b dx f(x) \\ \left[\lim_{a \rightarrow +0} (1 - g(a, \varepsilon)) \right] \int_0^b dx f(x) &< \int_0^b dx (1 - g(x, \varepsilon)) f(x) < (1 - g(b, \varepsilon)) \int_0^b dx f(x) \\ 0 \times M = 0 &< \int_0^b dx (1 - g(x, \varepsilon)) f(x) < (1 - g(b, \varepsilon)) \int_0^b dx f(x) \\ \lim_{\varepsilon \rightarrow +0} 0 &< \lim_{\varepsilon \rightarrow +0} \int_0^b dx (1 - g(x, \varepsilon)) f(x) < \lim_{\varepsilon \rightarrow +0} (1 - g(b, \varepsilon)) \int_0^b dx f(x) = \left[\lim_{\varepsilon \rightarrow +0} (1 - g(b, \varepsilon)) \right] M \\ 0 &< \lim_{\varepsilon \rightarrow +0} \int_0^b dx (1 - g(x, \varepsilon)) f(x) < 0. \end{aligned} \quad (\text{C.28})$$

Here, note that the integration of the function $f(x)$ described as

$$M = \int_0^b dx f(x), \quad \sup_{b>0} |M| < \infty \quad (\text{C.29})$$

is finite. Therefore we obtain the relation written as

$$\begin{aligned} \lim_{\varepsilon \rightarrow +0} \int_0^b dx (1 - g(x, \varepsilon)) f(x) &= 0 \\ \int_0^b dx f(x) &= \lim_{\varepsilon \rightarrow +0} \int_0^b dx f(x) = \lim_{\varepsilon \rightarrow +0} \int_0^b dx g(x, \varepsilon) f(x) \\ \int_0^\infty dx f(x) &= \lim_{b \rightarrow +\infty} \int_0^b dx f(x) = \lim_{b \rightarrow +\infty} \lim_{\varepsilon \rightarrow +0} \int_0^b dx f(x) = \lim_{b \rightarrow +\infty} \lim_{\varepsilon \rightarrow +0} \int_0^b dx g(x, \varepsilon) f(x). \end{aligned} \quad (\text{C.30})$$

In advance, we see the indefinite integration of the function $\exp(ax) \sin bx$ (a, b : constant) calculated as

$$\int dx \exp(ax) \sin bx = \frac{\exp(ax) (a \sin bx - b \cos bx)}{a^2 + b^2}, \quad (\text{C.31})$$

by using integration by parts. We obtain the relation written as

$$\begin{aligned}
\lim_{b \rightarrow +\infty} \lim_{\varepsilon \rightarrow +0} \int_0^b dx g(x, \varepsilon) f(x) &= \lim_{b \rightarrow +\infty} \lim_{\varepsilon \rightarrow +0} \int_0^b dx \exp(-\varepsilon x) \sin(x) \\
&= \lim_{\varepsilon \rightarrow +0} \lim_{b \rightarrow +\infty} \int_0^b dx \exp(-\varepsilon x) \sin(x) \\
&= \lim_{\varepsilon \rightarrow +0} \int_0^\infty dx \exp(-\varepsilon x) \sin(x) \\
&= \lim_{\varepsilon \rightarrow +0} \frac{1}{\varepsilon^2 + 1} \\
&= 1.
\end{aligned} \tag{C.32}$$

Here, note that we can exchange $\lim_{\varepsilon \rightarrow +0}$ and $\lim_{b \rightarrow +\infty}$ because the integral $\int_0^\infty dx \exp(-\varepsilon x) \sin(x)$ is an improper integration. We give mathematical proof of it. When we assume $0 < b_1 < b_2 < b_3$, we obtain the relation described as

$$\int_{b_1}^{b_3} dx g(x, \varepsilon) f(x) = g(b_1, \varepsilon) \int_{b_1}^{b_2} dx f(x) + g(b_3, \varepsilon) \int_{b_2}^{b_3} dx f(x), \tag{C.33}$$

where we use the weighted mean-value theorem for integral. We define a function $g'(x, \varepsilon)$ which is very similar to the function $g(x, \varepsilon)$. The function $g'(x, \varepsilon)$ is defined as

$$g'(x, \varepsilon) = \begin{cases} 0 & (x = b_3) \\ g(x, \varepsilon) & (x \neq b_3) \end{cases}. \tag{C.34}$$

Therefore we obtain the integration of the function $g(x, \varepsilon)$ described as

$$\begin{aligned}
\int_{b_1}^{b_3} dx g(x, \varepsilon) f(x) &= \int_{b_1}^{b_3} dx g'(x, \varepsilon) f(x) \\
&= g(b_1, \varepsilon) \int_{b_1}^{b_2} dx f(x).
\end{aligned} \tag{C.35}$$

The absolute value of this integration is calculated as

$$\begin{aligned}
\left| \int_{b_1}^{b_3} dx g(x, \varepsilon) f(x) \right| &= \left| g(b_1, \varepsilon) \int_{b_1}^{b_2} dx f(x) \right| \\
&\leq |g(b_1, \varepsilon)| \left| \int_{b_1}^{b_2} dx f(x) \right| \\
&= g(b_1, \varepsilon) \left| \int_{b_1}^{b_2} dx f(x) \right| \\
&= g(b_1, \varepsilon) \left| \int_0^{b_2} dx f(x) - \int_0^{b_1} dx f(x) \right| \\
&\leq g(b_1, \varepsilon) \left(\left| \int_0^{b_2} dx f(x) \right| + \left| \int_0^{b_1} dx f(x) \right| \right).
\end{aligned} \tag{C.36}$$

Therefore the limit of this integration is calculated as

$$\begin{aligned}
\lim_{b_1 \rightarrow \infty} \left| \int_{b_1}^{b_3} dx g(x, \varepsilon) f(x) \right| &\leq \lim_{b_1 \rightarrow \infty} g(b_1, \varepsilon) \left(\left| \int_0^{b_2} dx f(x) \right| + \left| \int_0^{b_1} dx f(x) \right| \right) \\
&= 2M \lim_{b_1 \rightarrow \infty} g(b_1, \varepsilon) \\
&= 0.
\end{aligned} \tag{C.37}$$

Because of this relation, we can exchange $\lim_{\varepsilon \rightarrow +0}$ and $\lim_{b \rightarrow +\infty}$. We obtain the relation described as

$$\int_0^\infty dx f(x) = \int_0^\infty dx \sin x = 1. \tag{C.38}$$

By using the equation (Eq. C.25), we obtain the relation described as

$$\begin{aligned}
v_{\mathbf{k}} &= \frac{4\pi\alpha\hbar c}{k^2} \\
&= \frac{4\pi\alpha\hbar c}{|\mathbf{k}|^2}.
\end{aligned} \tag{C.39}$$

By using the equations (Eq. C.16) and (Eq. C.39), the above mathematical proof gives the Hartree-Fock total energy described as

$$\begin{aligned}
E_{\text{HF}} &= \sum_{\mathbf{k} \in \mathbb{Z}_\psi} \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} v_{\mathbf{k}-\mathbf{k}'} \\
&= \sum_{\mathbf{k} \in \mathbb{Z}_\psi} \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} \frac{4\pi\alpha\hbar c}{|\mathbf{k} - \mathbf{k}'|^2} \\
&= E_{\text{HF}}^{\text{Free}} + E_{\text{HF}}^{\text{Exchange}},
\end{aligned} \tag{C.40}$$

where two terms $E_{\text{HF}}^{\text{Free}}$ and $E_{\text{HF}}^{\text{Exchange}}$ are defined as

$$\begin{aligned}
E_{\text{HF}}^{\text{Free}} &= \sum_{\mathbf{k} \in \mathbb{Z}_\psi} \frac{\hbar^2 \mathbf{k}^2}{2m}, \\
E_{\text{HF}}^{\text{Exchange}} &= -\frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} \frac{4\pi\alpha\hbar c}{|\mathbf{k} - \mathbf{k}'|^2}.
\end{aligned} \tag{C.41}$$

We calculate the value of the Hartree-Fock exchange energy $E_{\text{HF}}^{\text{Exchange}}$. We obtain the

relation written as

$$\begin{aligned}
E_{\text{HF}}^{\text{Exchange}} &= -\frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} \frac{4\pi\alpha\hbar c}{|\mathbf{k} - \mathbf{k}'|^2} \\
&= -\left(\frac{L}{2\pi}\right)^6 \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} \left(\frac{2\pi}{L}\right)^6 \frac{4\pi\alpha\hbar c}{|\mathbf{k} - \mathbf{k}'|^2} \\
&= -\frac{V^2}{(2\pi)^6} \frac{1}{2V} \iint_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} d\mathbf{k} d\mathbf{k}' \frac{4\pi\alpha\hbar c}{|\mathbf{k} - \mathbf{k}'|^2} \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar c V}{(2\pi)^6}\right) \iint_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} d\mathbf{k} d\mathbf{k}' \frac{1}{|\mathbf{k} - \mathbf{k}'|^2} \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar c V}{(2\pi)^6}\right) \sum_{s=\pm 1/2} \iint_{0 \leq |\mathbf{k}| \leq k_F, 0 \leq |\mathbf{k}'| \leq k_F} d\mathbf{k} d\mathbf{k}' \frac{1}{|\mathbf{k} - \mathbf{k}'|^2},
\end{aligned} \tag{C.42}$$

where we substitute the integrations of $\mathbf{k}$ and $\mathbf{k}'$ for the summation of them. Here, note the relation described as

$$\sum_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} \left(\frac{2\pi}{L}\right)^3 \left(\frac{2\pi}{L}\right)^3 \rightarrow \iint_{\mathbf{k}, \mathbf{k}' \in \mathbb{Z}_\psi} d\mathbf{k} d\mathbf{k}' \rightarrow \sum_{s=\pm 1/2} \iint_{0 \leq |\mathbf{k}| \leq k_F, 0 \leq |\mathbf{k}'| \leq k_F} d\mathbf{k} d\mathbf{k}', \tag{C.43}$$

where s is a spin of an electron and the spin of the $\mathbf{k}$ th electron and that of the $\mathbf{k}'$ th electron are parallel in the Hartree-Fock exchange energy $E_{\text{HF}}^{\text{Exchange}}$. This relation is called the thermodynamic limit. Here, the Fermi vector k_F is defined as

$$k_F = \sup_{\mathbf{k} \in \mathbb{Z}_\psi} |\mathbf{k}|. \tag{C.44}$$

The absolute values k and k' are defined as

$$\begin{aligned}
k &= |\mathbf{k}|, \\
k' &= |\mathbf{k}'|.
\end{aligned} \tag{C.45}$$

When we use a coordinate transformation as follows:

$$\begin{aligned}
\mathbf{p} &= \frac{1}{2} (\mathbf{k} + \mathbf{k}'), \\
\mathbf{q} &= \mathbf{k} - \mathbf{k}', \\
p &= |\mathbf{p}|, \\
q &= |\mathbf{q}|,
\end{aligned} \tag{C.46}$$

we have only to consider the volume V_{pq} of $\mathbf{p}$ and $\mathbf{q}$ which is an intersection of two spheres with the radii k_F . The Hartree-Fock exchange energy $E_{\text{HF}}^{\text{Exchange}}$ is calculated as

$$\begin{aligned}
E_{\text{HF}}^{\text{Exchange}} &= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar c V}{(2\pi)^6}\right) \sum_{s=\pm 1/2} \iint_{V_{pq}} d\mathbf{p} d\mathbf{q} \frac{1}{q^2} \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar c V}{(2\pi)^6}\right) \sum_{s=\pm 1/2} \int_{0 \leq q \leq 2k_F} dq \frac{1}{q^2} \int_{V_q} d\mathbf{p},
\end{aligned} \tag{C.47}$$

where V_q is the intersection of the two spheres with the radii k_F and the centers of the two spheres are separated at a distance of q .

We consider the volume V_{Ω_0} with a solid angle Ω_0 where q is fixed. The volume V_{Ω_0} is written as

$$\begin{aligned}
V_{\Omega_0} &= \frac{\Omega_0}{4\pi} \left(\frac{4\pi}{3} k_F^3 \right) \\
&= \frac{k_F^3}{3} \Omega_0 \\
&= \frac{k_F^3}{3} \int_0^{\theta_0} d\theta \sin \theta \int_0^{2\pi} d\phi \\
&= \frac{2\pi}{3} k_F^3 [-\cos \theta]_{\theta=0}^{\theta_0} \\
&= \frac{2\pi}{3} k_F^3 (1 - \cos \theta_0) \\
&= \frac{2\pi}{3} k_F^3 \left(1 - \frac{q}{2k_F} \right),
\end{aligned} \tag{C.48}$$

where θ_0 is defined as

$$\begin{aligned}
\cos \theta_0 &= \frac{q/2}{k_F} \\
&= \frac{q}{2k_F}.
\end{aligned} \tag{C.49}$$

When we consider a circular cone with the base radius $k_F \sin \theta_0$, its volume V_c is calculated as

$$\begin{aligned}
V_c &= \frac{1}{3} \pi (k_F \sin \theta_0)^2 \frac{q}{2} \\
&= \frac{1}{3} \pi k_F^2 \left[1 - \left(\frac{q}{2k_F} \right)^2 \right] \frac{q}{2} \\
&= \frac{2\pi}{3} k_F^3 \frac{1}{2k_F} \left[\frac{q}{2} - \frac{q}{2} \left(\frac{q^2}{4k_F^2} \right) \right] \\
&= \frac{2\pi}{3} k_F^3 \left[\frac{q}{4k_F} - \frac{q}{4k_F} \left(\frac{q^2}{4k_F^2} \right) \right] \\
&= \frac{2\pi}{3} k_F^3 \left[\frac{q}{4k_F} - \frac{1}{16} \left(\frac{q}{k_F} \right)^3 \right].
\end{aligned} \tag{C.50}$$

Here, note the relation written as

$$\begin{aligned}
k_F \sin \theta_0 &= k_F \sqrt{1 - \cos^2 \theta_0} \\
&= k_F \sqrt{1 - \left(\frac{q}{2k_F} \right)^2}.
\end{aligned} \tag{C.51}$$

Therefore we obtain the relation described as

$$\begin{aligned}
V_q &= \int_{V_q} d\mathbf{p} \\
&= 2(V_{\Omega_0} - V_c) \\
&= 2 \left[\frac{2\pi}{3} k_F^3 \left(1 - \frac{q}{2k_F} \right) - \left(\frac{2\pi}{3} k_F^3 \left[\frac{q}{4k_F} - \frac{1}{16} \left(\frac{q}{k_F} \right)^3 \right] \right) \right] \\
&= \frac{4\pi}{3} k_F^3 \left[1 - \frac{3}{4} \left(\frac{q}{k_F} \right) + \frac{1}{16} \left(\frac{q}{k_F} \right)^3 \right].
\end{aligned} \tag{C.52}$$

The Hartree-Fock exchange energy is calculated as

$$\begin{aligned}
E_{\text{HF}}^{\text{Exchange}} &= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} \int_{0 \leq q \leq 2k_F} d\mathbf{q} \frac{1}{q^2} \left(\frac{4\pi}{3} k_F^3 \left[1 - \frac{3}{4} \left(\frac{q}{k_F} \right) + \frac{1}{16} \left(\frac{q}{k_F} \right)^3 \right] \right) \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} \int_0^{2k_F} dq \int_0^\pi d\theta \int_0^{2\pi} d\phi q^2 \sin \theta \frac{1}{q^2} \left(\frac{4\pi}{3} k_F^3 \left[1 - \frac{3}{4} \left(\frac{q}{k_F} \right) + \frac{1}{16} \left(\frac{q}{k_F} \right)^3 \right] \right) \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} \frac{(4\pi)^2}{3} k_F^4 \int_0^2 dt \left(1 - \frac{3}{4}t + \frac{1}{16}t^3 \right) \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} \frac{(4\pi)^2}{3} k_F^4 \left[t - \frac{3}{8}t^2 + \frac{1}{64}t^4 \right]_{t=0}^2 \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} \frac{(4\pi)^2}{3} k_F^4 \left(2 - \frac{3}{8} \cdot 4 + \frac{1}{64} \cdot 16 \right) \\
&= -\frac{1}{2} \left(\frac{4\pi\alpha\hbar cV}{(2\pi)^6} \right) \sum_{s=\pm 1/2} 4\pi^2 k_F^4 \\
&= -\left(\frac{(2\pi)\alpha\hbar cV}{(2\pi)^6} \right) (2\pi)^2 k_F^4 \sum_{s=\pm 1/2} 1 \\
&= -\frac{2\alpha\hbar cV k_F^4}{(2\pi)^3},
\end{aligned} \tag{C.53}$$

where the integration of $\sin \theta$ is calculated as

$$\begin{aligned}
\int_0^\pi d\theta \int_0^{2\pi} d\phi \sin \theta &= 2\pi [-\cos \theta]_{\theta=0}^\pi \\
&= 4\pi.
\end{aligned} \tag{C.54}$$

Here, t is defined as

$$\begin{aligned} t &= \frac{q}{k_F}, \\ k_F dt &= dq. \end{aligned} \tag{C.55}$$

By using the thermodynamic limit, the number N of all the electrons is written as

$$\begin{aligned} N &= \sum_{\mathbf{k} \in \mathbb{Z}_\psi} 1 \\ &= \left(\frac{L}{2\pi} \right)^3 \sum_{\mathbf{k} \in \mathbb{Z}_\psi} \left(\frac{2\pi}{L} \right)^3 \\ &= \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} \int_{0 \leq k \leq k_F} d\mathbf{k} \\ &= \frac{V}{(2\pi)^3} \frac{4\pi}{3} k_F^3 \sum_{s=\pm 1/2} 1 \\ &= \frac{V}{8\pi^3} \frac{8\pi}{3} k_F^3 \\ &= \frac{V}{3\pi^2} k_F^3. \end{aligned} \tag{C.56}$$

We can define the radius $r_0 \geq 0$ of the averaged spherical volume occupied by an electron in the Jellium model. The radius r_0 is defined as

$$\begin{aligned} V/N &= \frac{4\pi}{3} r_0^3 = \frac{3\pi^2}{k_F^3} \\ r_0^3 &= \frac{3}{4\pi} \frac{3\pi^2}{k_F^3} \\ r_0 &= \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{k_F}. \end{aligned} \tag{C.57}$$

We define the radius $r_s \geq 0$ described as

$$r_s = \frac{r_0}{a_{\text{Bohr}}}, \tag{C.58}$$

where a_{Bohr} is the Bohr radius. By using the equations (Eq. C.53), (Eq. C.57), and (Eq.

C.58), the averaged Hartree-Fock exchange energy $E_{\text{HF}}^{\text{Exchange}}/N$ is calculated as

$$\begin{aligned}
\frac{E_{\text{HF}}^{\text{Exchange}}}{N} &= -\frac{1}{N} \frac{2\alpha\hbar c V k_{\text{F}}^4}{(2\pi)^3} \\
&= -\frac{2\alpha\hbar c}{(2\pi)^3} \left(\frac{V}{N}\right) \left[\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_0} \right]^4 \\
&= -\frac{2\alpha\hbar c}{8\pi^3} \left(\frac{4\pi}{3} r_0^3\right) \frac{9\pi}{4} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_0^4} \\
&= -\frac{3}{4\pi} (\alpha\hbar c) \left(\frac{9\pi}{4}\right)^{1/3} \left(\frac{a_{\text{Bohr}}}{r_0} \frac{1}{a_{\text{Bohr}}}\right) \\
&= -\frac{3}{4\pi} \left(\frac{\alpha\hbar c}{a_{\text{Bohr}}}\right) \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \\
&\rightarrow -\frac{3}{4\pi} \cdot 2 \cdot \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \\
&= -\frac{3}{2\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \\
&\approx \frac{0.91633}{r_s} [\text{Ry}],
\end{aligned} \tag{C.59}$$

where we use the relations described as

$$\frac{\alpha\hbar c}{a_{\text{Bohr}}} \rightarrow 2 [\text{Ry}], \quad \frac{\hbar^2}{2ma_{\text{Bohr}}^2} \rightarrow 1 [\text{Ry}]. \tag{C.60}$$

This unit system is called the atomic unit system.

We consider the Hartree-Fock free energy $E_{\text{HF}}^{\text{Free}}$. The Hartree-Fock free energy $E_{\text{HF}}^{\text{Free}}$ is

calculated as

$$\begin{aligned}
E_{\text{HF}}^{\text{Free}} &= \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \frac{(\hbar \mathbf{k})^2}{2m} \\
&= \frac{\hbar^2}{2m} \left(\frac{L}{2\pi} \right)^3 \sum_{\mathbf{k} \in \mathbb{Z}_{\psi}} \left(\frac{2\pi}{L} \right)^3 \mathbf{k}^2 \\
&= \frac{\hbar^2}{2m} \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} \int_{0 \leq k \leq k_F} d\mathbf{k} k^2 \\
&= \frac{\hbar^2}{2m} \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} \int_0^{k_F} dk \int_0^{\pi} d\theta \int_0^{2\pi} d\phi (k^2 \sin \theta) k^2 \\
&= \frac{\hbar^2}{2m} \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} 2\pi \int_0^{k_F} dk k^4 \int_0^{\pi} d\theta \sin \theta \\
&= \frac{\hbar^2}{2m} \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} 2\pi \left[\frac{k^5}{5} \right]_{k=0}^{k_F} [-\cos \theta]_{\theta=0}^{\pi} \\
&= \frac{\hbar^2}{2m} \frac{V}{(2\pi)^3} \sum_{s=\pm 1/2} 4\pi \frac{k_F^5}{5} \\
&= \frac{\hbar^2}{2m} \frac{V}{8\pi^3} 2 \cdot 4\pi \frac{k_F^5}{5} \\
&= V \frac{\hbar^2}{2m} \frac{1}{5\pi^2} k_F^5.
\end{aligned} \tag{C.61}$$

The averaged Hartree-Fock free energy $E_{\text{HF}}^{\text{Free}}/N$ is written as

$$\begin{aligned}
\frac{E_{\text{HF}}^{\text{Free}}}{N} &= \frac{V}{N} \frac{\hbar^2}{2m} \frac{1}{5\pi^2} k_{\text{F}}^5 \\
&= \left(\frac{3\pi^2}{k_{\text{F}}^3} \right) \frac{\hbar^2}{2m} \frac{1}{5\pi^2} k_{\text{F}}^5 \\
&= \frac{3}{5} \frac{\hbar^2}{2m} k_{\text{F}}^2 \\
&= \frac{3}{5} \frac{\hbar^2}{2m} \left[\left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_0} \right]^2 \\
&= \frac{3}{5} \frac{\hbar^2}{2m} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_0^2} \\
&= \frac{3}{5} \frac{\hbar^2}{2m} \left[\left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_0} \right]^2 \\
&= \frac{3}{5} \frac{\hbar^2}{2ma_{\text{Bohr}}^2} \left(\frac{9\pi}{4} \right)^{2/3} \frac{a_{\text{Bohr}}^2}{r_0^2} \\
&= \frac{3}{5} \left(\frac{\hbar^2}{2ma_{\text{Bohr}}^2} \right) \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} \\
&\rightarrow \frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} \text{ [Ry]} \\
&\approx \frac{2.20990}{r_s^2}.
\end{aligned} \tag{C.62}$$

We obtain the averaged Hartree-Fock total energy E_{HF} described as

$$\begin{aligned}
E_{\text{HF}} &= N \left[\frac{3}{5} \left(\frac{\hbar^2}{2ma_{\text{Bohr}}^2} \right) \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} - \frac{3}{4\pi} \left(\frac{\alpha\hbar c}{a_{\text{Bohr}}} \right) \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} \right] \\
&\rightarrow N \left[\frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} - \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} \right] \text{ [Ry]} \\
&\approx N \left(\frac{2.210}{r_s^2} - \frac{0.916}{r_s} \right) \text{ [Ry]}.
\end{aligned} \tag{C.63}$$

In addition, Gell-Mann and Brueckner [80] produced a more detailed total energy calculation described as

$$E = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s - 0.096 \text{ [Ry]}. \tag{C.64}$$

The Jellium model has the lowest Hartree-Fock total energy shown in Fig. C.1. The Hartree-Fock Free energy of the Jellium model is dominant at high electron density. The Hartree-Fock exchange energy is, however, dominant at low electron density.

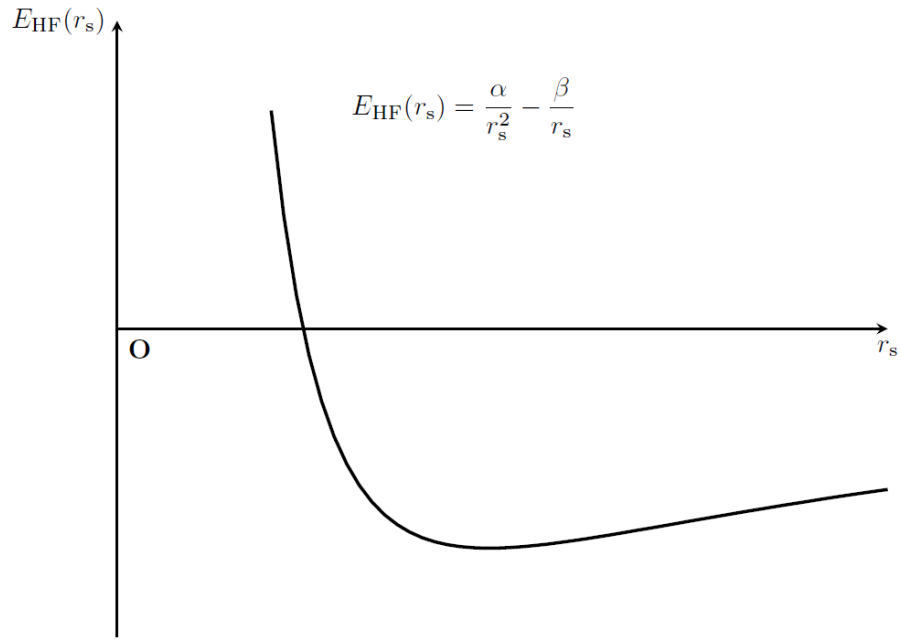


Figure C.1: Conceptual diagram of the Hartree-Fock total energy of the Jellium model. The parameters α and β are constant ($\alpha = 2.210$ and $\beta = 0.916$). The Jellium model has the lowest Hartree-Fock total energy. r_s is the radius of the averaged spherical volume occupied by an electron. E_{HF} is the averaged Hartree-Fock total energy of the Jellium model.

C.1.2 Bulk Modulus

We consider the bulk modulus of the Jellium model. The bulk modulus is derived from the derivative of the pressure of the Jellium model. In advance, by using the equations (Eq. C.57) and (Eq. C.58), we check the relation described as

$$\begin{aligned} r_s &= \left(\frac{3}{4\pi N} \right)^{1/3} V^{1/3} \\ &= AV^{1/3}, \end{aligned} \tag{C.65}$$

where A is defined as

$$A = \left(\frac{3}{4\pi N} \right)^{1/3}. \tag{C.66}$$

Here, note that we regard the Bohr radius as $a_{\text{Bohr}} \rightarrow 1$. The pressure P of the Jellium model is calculated as

$$\begin{aligned} P &= -\frac{d}{dV} E_{\text{HF}}(r_s(V)) \\ &= -\frac{d}{dV} \left[N \left(\frac{\alpha}{r_s^2} - \frac{\beta}{r_s} \right) \right] \\ &= -N \frac{d}{dV} \left[\alpha (AV^{1/3})^{-2} - \beta (AV^{1/3})^{-1} \right] \\ &= -N \frac{d}{dV} \left[\frac{\alpha}{A^2} V^{-2/3} - \frac{\beta}{A} V^{-1/3} \right] \\ &= -N \left[\frac{\alpha}{A^2} \left(-\frac{2}{3} \right) V^{-5/3} - \frac{\beta}{A} \left(-\frac{1}{3} \right) V^{-4/3} \right] \\ &= N \left(\frac{2\alpha}{3A^2} V^{-5/3} - \frac{\beta}{3A} V^{-4/3} \right), \end{aligned} \tag{C.67}$$

where α and β are defined as

$$\begin{aligned} \alpha &= 2.210, \\ \beta &= 0.916. \end{aligned} \tag{C.68}$$

Here, note that the number N of all the electrons is fixed. The bulk modulus B of the Jellium model is calculated as

$$\begin{aligned}
B &= -V \frac{d}{dV} P(V) \\
&= -V \frac{d}{dV} \left[N \left(\frac{2\alpha}{3A^2} V^{-5/3} - \frac{\beta}{3A} V^{-4/3} \right) \right] \\
&= -NV \left[\frac{2\alpha}{3A^2} \left(-\frac{5}{3} \right) V^{-8/3} - \frac{\beta}{3A} \left(-\frac{4}{3} \right) V^{-7/3} \right] \\
&= -NV \left[-\frac{10\alpha}{9A^2} V^{-8/3} + \frac{4\beta}{9A} V^{-7/3} \right] \\
&= N \left[\frac{10\alpha}{9A^2} V^{-5/3} - \frac{4\beta}{9A} V^{-4/3} \right] \\
&= N \left(\frac{10\alpha}{9A^2} \left[\left(\frac{r_s}{A} \right)^3 \right]^{-5/3} - \frac{4\beta}{9A} \left[\left(\frac{r_s}{A} \right)^3 \right]^{-4/3} \right) \\
&= N \left[\frac{10\alpha}{9A^2} \left(\frac{r_s}{A} \right)^{-5} - \frac{4\beta}{9A} \left(\frac{r_s}{A} \right)^{-4} \right] \tag{C.69} \\
&= NA^3 \left(\frac{10\alpha}{9} r_s^{-5} - \frac{4\beta}{9} r_s^{-4} \right) \\
&= N \left(\frac{3}{4\pi N} \right) \left(\frac{10\alpha}{9} r_s^{-5} - \frac{4\beta}{9} r_s^{-4} \right) \\
&= \frac{3}{4\pi} \left(\frac{10\alpha}{9} r_s^{-5} - \frac{4\beta}{9} r_s^{-4} \right) \\
&= \frac{5\alpha}{6\pi} r_s^{-5} - \frac{\beta}{3\pi} r_s^{-4} \\
&= \frac{5\alpha}{6\pi} \frac{1}{r_s^5} - \frac{\beta}{3\pi} \frac{1}{r_s^4} \\
&\approx \frac{0.586}{r_s^5} - \frac{0.0972}{r_s^4}.
\end{aligned}$$

This equation is almost the same as the equation parameterized by Hedin and Lundqvist [78]. The Hedin-Lundqvist expression is described as

$$B_{\text{exchange}} = \left[1 - \left(1 + \frac{0.7734r_s/21.0}{1 + r_s/21.0} \right) \frac{0.52106r_s}{\pi} \right] B_{\text{non-exchange}}, \tag{C.70}$$

where $B_{\text{non-exchange}}$ is the bulk modulus of the homogeneous electron gas model without the exchange effect and B_{exchange} is the bulk modulus of the model with the exchange effect. In the present study, we applied the Hedin-Lundqvist expression to our calculations (see Chapter 8).

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Achievements

Original Papers with Peer Review:

“First-Principles Calculations on the Origin of Mechanical Properties and Electronic Structures of 5*d* Transition Metal Monocarbides *MC* ($M = \text{Hf, Ta, W, Re, Os, Ir, and Pt}$).”

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