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Development of a method of first-principles electronic structure calculation using the optimized effective potentials

（最適化有効ポテンシャル法を用いた
第一原理電子状態計算手法の開発）

Taro Fukazawa

2011年2月

Contents

1 Introduction **5**
1.1 Historical overview 5
1.2 Present work 13

2 Theory **17**
2.1 Density functional theory 17
2.1.1 Hohenberg-Kohn theorem I 17
2.1.2 Hohenberg-Kohn theorem II 26
2.1.3 Kohn-Sham theory 29
2.1.4 Spin-density functional theory 34
2.2 Optimized effective potential 35
2.2.1 Derivation of OEP equations 36
2.2.2 Modified KLI method 38
2.2.3 RPA-level correlation 40

3 Results **51**
3.1 Exact exchange 51
3.2 Test calculation of technique for static RPA-correlation-energy 56
3.3 EXX+RPA 57
3.4 Total energy 60

4 Conclusions **65**

A Notations and formulae **67**
A.1 Definitions 67
A.2 Formulae 68

B Green's function of non-interacting system **69**
B.1 Ring polarization insertion 70

B.2 Dyson equation 72
B.3 Lippmann-Schwinger equation 73

C Korringa-Kohn-Rostoker Green's function method 75
C.1 Cell division 76
C.2 KKR ansatz 77

Chapter 1

Introduction

1.1 Historical overview

Electronic structure calculations by the density functional approach have been popular for a long time. Even before Hohenberg and Kohn established its theoretical basis[1], many calculations based on density functionals, such as the Thomas-Fermi functional, were performed. It is because while the wave function has as many set of space-time variables as the number of electrons, the density is a function of a single coordinate: a theory based only on a density can be more tractable than the one that deals with wave functions.

The discussion by Hohenberg and Kohn[1] consists of two parts. First, they proved the existence of maps from the density of the ground state to any quantities of the system such as the expectation value of an observable $\hat{O}$. In this sense, n_0 can be regarded as a basic variable of physics.

$$n_0 \to \langle \hat{O} \rangle \tag{1.1}$$

Second, they proved the existence of the so-called Hohenberg-Kohn energy functional $E_{\mathrm{HK}}[n, v]$ such that it has a minimum at the ground-state density n_0 and the minimum corresponds to the ground-state energy, provided that v is fixed to the external potential V^{ext} of the system. This establishes a

[1]Their theory can be extended easily to the spin-density functional theory (SDFT), in which basic variables are the spin-densities [2, 3]. This thesis is devoted to the theoretical development on, strictly speaking, the SDFT. However, in this section, I only describe formulations in terms of density alone for simplicity.

mapping:

$$V^{\mathrm{ext}} \to n_0 \tag{1.2}$$

Therefore this functional would enable us to obtain the ground state density by minimizing $E_{\mathrm{HK}}[n, V^{\mathrm{ext}}]$ if the form of this functional was explicitly known. However, the exact expression of the Hohenberg-Kohn functional is known only formally and it is virtually impossible to find out the ground-state density using this exact functional.

Another popular approach to the electronic structure calculation is the single electron approximation. Needless to say, the single electron problem is much easier than most of many-body problems. There are some rationalizations of replacing the many-body electron problem by a single electron problem. Here I would like to introduce two of them related to the present work.

The first one is Slater's approach[4] to the Hartree-Fock problem. Instead of solving the Hartree-Fock equation directly, he proposed an approximate equation in which all the orbitals of single electrons move in the same local potential. The Slater's paper itself is devoted to a further approximation as follows. First, the exchange charge density of the state i

$$\rho_i^{\mathrm{x}}(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv -2 \sum_k \frac{\psi_i^*(\boldsymbol{r}_1)\psi_i(\boldsymbol{r}_2)\psi_k^*(\boldsymbol{r}_2)\psi_k(\boldsymbol{r}_1)}{\psi_i^*(\boldsymbol{r}_1)\psi_i(\boldsymbol{r}_1)} \tag{1.3}$$

in the Hartree-Fock equation is averaged with the weight of density:

$$\rho_i^{\mathrm{x}}(\boldsymbol{r}_1, \boldsymbol{r}_2) \sim \rho^S(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \sum_i \frac{\rho_i(\boldsymbol{r}_1)}{\rho(\boldsymbol{r}_1)} \rho_i^{\mathrm{x}}(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{1.4}$$

Using this approximation, the Hartree-Fock equation becomes

$$\left[-\nabla^2 + V^{\mathrm{ext}}(\boldsymbol{r}) + V^{\mathrm{Hartree}}(\boldsymbol{r}) + V^{\mathrm{S}}(\boldsymbol{r})\right] \psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r}), \tag{1.5}$$

where

$$V^{\mathrm{Hartree}}(\boldsymbol{r}) \equiv \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.6}$$

$$V^{\mathrm{S}}(\boldsymbol{r}) \equiv \int d\boldsymbol{r}' \frac{\rho^S(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{1.7}$$

Now, these potentials are local. Second, in addition to this, he claimed that the leading contribution of the exchange potential should be determined as

a function of the charge density, thus the value evaluated using results of free-electron gas of the local charge density will not be very different from the exact one. Therefore,

$$V^{\mathrm{S}}(\boldsymbol{r}) \sim \frac{1}{V}\int d\boldsymbol{r}\, V^{\mathrm{S,hom}}(n(\boldsymbol{r})) = 2\epsilon_{\mathrm{x}}^{\mathrm{hom}}, \tag{1.8}$$

where $\epsilon_{\mathrm{x}}^{\mathrm{hom}}$ is the exchange-energy density of the homogeneous system.

In a comment for Slater's paper, Sharp and Horton[5] gave a variational approach to Slater's problem. They thought that the uni-potential introduced by Slater should be determined so that the Slater determinant that consists of orbitals in a uni-potential gives a minimum of the Hartree-Fock energy. They also derived an equation that the uni-potential should obey according to this principle. Later, Talman and Shadwick[6] derived the same equation and applied it to calculations of atoms. Today, this variational approach is often mentioned as the optimized effective potential (OEP) method following Talman and Shadwick.

The other single-electron approach I would like to introduce here is the Kohn-Sham scheme [7]. They connected the many-body problem and the single-electron model in terms of the ground-state density. They assumed that there is a non-interacting auxiliary system that reproduces the ground-state density of the many-body system. Under this assumption, they derived a single-electron equation based on the Hohenberg-Kohn theorems.

This scheme itself is exact. However, the lack in the knowledge of the exact form of Hohenberg-Kohn energy functional still prevent practical use of the theory. Thus, Kohn and Sham proposed an approximation to the functional so as to make their scheme into practice. First, they defined the so-called Kohn-Sham energy functional.

$$\begin{aligned} E_{\mathrm{KS}}[n,v] &\equiv T[n] - T_{\mathrm{aux}}[n] + E_{\mathrm{int}}[n] - E_{\mathrm{Hartree}}[n] \\ &\quad + E_{\mathrm{xc}}[n] + \int d\boldsymbol{r}\, v(\boldsymbol{r})n(\boldsymbol{r}) \qquad (1.9) \\ &= E_{\mathrm{HK}}[n,v], \qquad (1.10) \end{aligned}$$

where T_{aux} is the kinetic energy of the auxiliary system, the E_{Hartree} is the Hartree energy given by the density n, and the Kohn-Sham's exchange-correlation functional E_{xc} is defined so that E_{KS} becomes identical to E_{HK}. This exchange-correlation functional is to be approximated, and the efficiency

of an approximation to this exchange-correlation energy $E_{\rm xc}$ determines the precision of the whole calculation.

In their theory, the equations that determine the density of the ground state are

$$\left[-\nabla^2 + V_{\rm ext}(\boldsymbol{r}) + V_{\rm Hartree}(\boldsymbol{r}) + V_{\rm xc}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r}), \tag{1.11}$$

$$V_{\rm xc}(\boldsymbol{r}) \equiv \frac{\delta E_{\rm xc}}{\delta n(\boldsymbol{r})}, \tag{1.12}$$

$$n(\boldsymbol{r}) = \sum_i \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}). \tag{1.13}$$

Then they claimed that if the $n(\boldsymbol{r})$ is sufficiently slowly varying, one can approximate $E_{\rm xc}$ using the exchange-correlation energy density $\epsilon_{\rm xc}^{\rm hom}$ of the homogeneous system, which is a function only of the density:

$$E_{\rm xc}[n] \sim \int d\boldsymbol{r}\ n(\boldsymbol{r})\epsilon_{\rm xc}^{\rm hom}(n(\boldsymbol{r})). \tag{1.14}$$

This approximation is called local density approximation (LDA). In practice, some of parameterizations of $\epsilon_{\rm xc}$ based on Monte Carlo simulations are usually used.

It is worth mentioning that there is a discrepancy between the Kohn-Sham scheme and Slater's method even when the homogeneous system is considered within an exchange-only approximation. In this case, one can see

$$V_{\rm xc}(\boldsymbol{r}) = \frac{4}{3}\epsilon_{\rm x}^{\rm hom}, \tag{1.15}$$

which is inconsistent with the equation (1.8).

Though the "slow varying" assumption of the LDA is not always very convincing, the LDA gives adequate results in predicting properties of wide range of materials. Today, it is known that the LDA happens to be better than expected at birth, and calculations based on the Kohn-Sham scheme with the LDA are now very popular. However, the more systems were investigated using the LDA, the more interesting systems turned out not to be described by the LDA well. Thus, many other approximations are devised to go beyond the LDA and applied. Let us further review the development of the approximation of $E_{\rm xc}$ in order to make our purpose of research clearer.

In order to extend the LDA, it would be most natural to take account of the effects of the gradient of the density ∇n. One might expand $E_{\rm xc}$ as follows:

$$E_{\rm xc}[n] = \int d\boldsymbol{r} \ \left[n(\boldsymbol{r})\epsilon_{\rm xc}(n(\boldsymbol{r})) + |\nabla n(\boldsymbol{r})|^2 B_{\rm xc}(n(\boldsymbol{r})) + \cdots \right]. \tag{1.16}$$

This approach is called the gradient expansion approximation (GEA). However, it was reported by several authors that finite additional terms to the LDA easily introduced a significant error [8, 9]. The GEA seems not to be practical because the summation up to infinite order must be performed to restore the precision of the LDA. Thus, one need to introduce some artifices to devise a new approximate energy functional starting from the LDA.

The generalized gradient approximations (GGAs) (e.g. [10, 11, 12, 13, 14]) are approximations, which still take the effect of the density gradient into account:

$$E_{\rm xc}^{\rm GGA}[n] = \int d\boldsymbol{r} \ f(n, \nabla n) \tag{1.17}$$

$$\equiv \int d\boldsymbol{r} \ n(\boldsymbol{r})\epsilon_{\rm xc}(n(\boldsymbol{r}))F_{\rm xc}(n, \nabla n). \tag{1.18}$$

The GGAs are usually determined to satisfy $F_{\rm xc}(n, 0) = 1$ and some other relations that the exact exchange-correlation functional should obey. (Note that the LDA is exact when the system is homogeneous ($\nabla n = 0$ everywhere).) For example, relations of the exchange-correlation hole, scaling relations, and so on, can be taken into account in the GGA, while the finite order GEA violates them.

Perdew and Zunger [15] focused on the errors come from the self-interaction. The Hartree energy contains the self-interaction terms:

$$E_{\rm Hartree}[n_i] \equiv \int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{n_{i\sigma}(\boldsymbol{r})n_{i\sigma}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{1.19}$$

which is unphysical, and must be canceled by the exchange term. However, approximated exchange term by the LDA may fails to have this feature. Thus, they proposed to subtract the self-interaction terms in both the Hartree energy and the exchange energy. This self-interaction-corrected (SIC) functional is

$$E_{\rm xc}^{\rm SIC}[n] = E_{\rm xc}^{\rm DFA}[n] - \sum_i (E_{\rm Hartree}[n_i] + E_{\rm xc}^{\rm DFA}[n_i]), \tag{1.20}$$

where DFA denotes density functional approximations, such as the LDA or the GGAs. One of the problems in this functional is that it is no longer invariant under the unitary transformation of the orbitals. For this reason, extra treatments are needed during the minimization of the energy functional.

Using hybrid functionals is another way to take the non-local effect into account. Becke[16] was first to justify the use of hybrid functions based on the adiabatic connection approach of the density functional theory developed by several authors [17, 18, 19, 20]. In their adiabatic connection theory, the Kohn-Sham's auxiliary system and the many-body system under consideration are connected using integration of the coupling constant of the coulomb interaction. The exchange-correlation functional can be expressed as

$$E_{\mathrm{xc}} = \int_0^1 d\lambda \ \langle \psi_\lambda | \hat{H}_{\mathrm{int}} | \psi_\lambda \rangle, \tag{1.21}$$

where the $|\psi_\lambda\rangle$ is the eigen-function of the $\hat{H}_\lambda = \hat{H}_0 + \lambda \hat{H}_{\mathrm{int}} + \hat{V}(\lambda)$, and $\hat{V}(\lambda)$ is an external potential chosen so that $\hat{V}(1) = \hat{V}^{\mathrm{ext}}$ and that the density of $|\psi_\lambda\rangle$ becomes always identical to that of $|\psi_1\rangle$. Note that $\langle \psi_0 | \hat{H}_{\mathrm{int}} | \psi_0 \rangle$ is just the exchange energy of the slater determinant composed of the Kohn-Sham orbitals:

$$E_{\mathrm{EXX}} = \sum_{i,j,\sigma} \int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{\psi^*_{i\sigma}(\boldsymbol{r}) \psi_{i\sigma}(\boldsymbol{r}') \psi^*_{j\sigma}(\boldsymbol{r}') \psi_{j\sigma}(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{1.22}$$

Becke discussed the application of the LDA to the integrand of (1.21) and claimed that it seems adequate around $\lambda = 1$ while invalid at $\lambda = 0$. On this ground he proposed to use the LDA value of $\langle \psi_\lambda | \hat{H}_{\mathrm{int}} | \psi_\lambda \rangle$ at $\lambda = 1$, the exact value at $\lambda = 0$, and to approximate the integrand by linear interpolation for $0 < \lambda < 1$. Becke later proposed another hybrid model of function including three semi-empirical parameters a_0, a_x, a_c:

$$E_{\mathrm{xc}}^{\mathrm{B3PW91}} = E_{\mathrm{xc}}^{\mathrm{LDA}} + a_0 (E_{\mathrm{EXX}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + a_x E_{\mathrm{x}}^{\mathrm{B88}} + a_c E_{\mathrm{c}}^{\mathrm{PW91}}. \tag{1.23}$$

In this expression, $E_{\mathrm{x}}^{\mathrm{B88}}$ and $E_{\mathrm{c}}^{\mathrm{PW91}}$ denote a exchange part of the GGA functional called B88([8]) and a GGA correlation functional called PW91([13]), respectively. B3PW91 means "Becke's 3-parameter hybrid functional using the PW91 correlation functional." An alternative version, called B3LYP, using the LYP functional ([12]) instead of the PW91 is also used in literatures.

A rationale for this kind mixing (E_{EXX} plus E^{DFA}) were given by Perdew, Ernzerhof and Burke[21]. They approximated the integrand of (1.21) using a power function:

$$E_{\mathrm{xc},\lambda} \equiv \langle \psi_\lambda | \hat{H}_{\mathrm{int}} | \psi_\lambda \rangle \sim E^{\mathrm{DFA}}_{\mathrm{xc},\lambda} + (E_{\mathrm{EXX}} - E^{\mathrm{DFA}}_{\mathrm{x},\lambda})(1-\lambda)^{n-1}, \tag{1.24}$$

This is an interpolation between E_{EXX} at $\lambda = 0$ (Note that $E^{\mathrm{DFA}}_{\mathrm{c},0}$=0.) and $E^{\mathrm{DFA}}_{\mathrm{xc},1}$ at $\lambda = 1$ as in Becke's justification. The resulting energy functional is

$$E^{\mathrm{PEB}}_{\mathrm{xc}}(n) = E^{\mathrm{DFA}}_{\mathrm{xc}} + \frac{1}{n}(E_{\mathrm{EXX}} - E^{\mathrm{DFA}}_{\mathrm{x}}). \tag{1.25}$$

This includes one parameter, n, and is identical with the E_{DFA} in the limit of $n \to \infty$. Thus, the best choice of n must improve (or give the same results as) the DFA.

These three kinds of energy functionals, (1.20), (1.23) and (1.25), are all dependent on orbitals explicitly. How can one solve the Kohn-Sham problem for them? Minimizing them with respect to the orbitals is one possible way. The resulting equation includes non-local potentials, which depends on the orbitals to be determined, like the Hartree-Fock potential. Therefore, this method is no longer regarded as a Kohn-Sham scheme[2]. One might consider this as an extended Kohn-Sham theory in which Kohn-Sham's effective potential is generalized to non-local one. However, this is not well-established theoretically. Thus, we would not adopt this method in this thesis.

Another possible approach is to constrain the trial orbitals to be single particle solutions for a uni-potential. The uni-potential at the minimum point is nothing but the OEP mentioned above. This constrained search may seem to introduce further reduction of precision to the Kohn-Sham scheme. However, it is not the case. It is because one can treat energy functionals expressed explicitly in terms of orbitals perfectly within the framework of the Kohn-Sham theory, and the resulting equation is almost identical to the OEP method. This will be discussed in detail in Chapter 2.

The importance of the OEP method can be explained also by the adiabatic connection theory of the DFT. The resulting equation (1.21) can be written also as

$$E_{\mathrm{xc}} = \int_0^1 \frac{d\lambda}{\lambda} \langle \psi_\lambda | \lambda \hat{H}_{\mathrm{int}} | \psi_\lambda \rangle. \tag{1.26}$$

[2]Some authors (e.g. [22]) refer to this as "Hartree-Fock-Kohn-Sham" scheme.

Because $\langle\psi_\lambda|\lambda\hat{H}_{\rm int}|\psi_\lambda\rangle$ can be expanded in terms of $|\psi_0\rangle$ using the diagrammatic technique of the many-body perturbation theory and $|\psi_0\rangle$ is a slater determinant of the Kohn-Sham's auxiliary system, this gives another starting point, which is different from the LDA, of constructing an exact exchange-correlation functional. Thus, one can exploit more sophisticated approximations to the exchange-correlation functional if one uses the OEP method. For example, Kotani used the RPA-level correlation functional with the exact exchange energy[23]. Though the calculation was very time-consuming, this functional is self-interaction free, unitary-invariant, and derived by a diagrammatic technique.

The OEP method is thus promising as a way to go beyond the LDA. However, there are two main obstacles to this method so far. One is its theoretical ambiguity in spin-polarized systems, and the other is its heavy time consumption.

Krieger et al. made a perceptive discussion concerning the first problem based on an analysis of an asymptotic behavior of the highest-occupied orbital at $r \to \infty$ [24, 25]. They also showed that if one accepted the use of this prescription, it would resolve the discrepancy between (1.8) and (1.15), and that the exchange-only OEP obeyed (1.15). However, in their argument, the system was assumed to be isolated, and the energy functional could be constructed only from occupied orbitals. Thus the validity of the technique in extended systems such as solids was not clear. This is one of the reason why analyses using the OEP method on spin-polarized solids have not been reported so often.

The other problem is its computational time. Krieger et al. also proposed the so called KLI approximation to the OEP equation. It was important because solving the OEP equation is one of rate-determining processes of calculation. Though there are several ways to justify the KLI approximation [24, 25, 26], the simplest one is replacing the denominator of the Green's

function in the OEP equation by a constant Δ:

$$
\begin{aligned}
G(\boldsymbol{r}, \boldsymbol{r}', E) &= \sum_{\{i|\epsilon_i \neq E\}} \frac{\psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}')}{E - \epsilon_i} && (1.27) \\
&\sim \frac{1}{\Delta} \sum_{\{i|\epsilon_i \neq E\}} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}') && (1.28) \\
&= \frac{1}{\Delta} \left[\delta(\boldsymbol{r} - \boldsymbol{r}') - \sum_{\{i|\epsilon_i = E\}} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}') \right], && (1.29)
\end{aligned}
$$

where ψ_i's are the Kohn-Sham orbitals of the system, and ϵ_i's are their energy eigenvalues. In the resulting KLI equation, the constant Δ vanishes and no extra parameter remains. The original paper of this method itself reported its application to atoms with a SIC functional [24]. The authors also reported the application to the exact-exchange functional[25]. Grabo and Gross have performed the calculation for atoms, taking account of the correlation using the Colle-Salvetti functional[27, 28]. To the solids, there are series of reports by Bylander and Kleinman [29, 30, 31, 32]. All of these reports concluded that the precision was satisfactory.

1.2 Present work

In this research, we set our goal to developing a practical and precise method with a sophisticated approximation going beyond the LDA. The meaning of "practical" should be explained according to the concept of the computational materials design, for which our method is supposed to be used. In Figure 1.1, a model of the computational materials design is depicted. The green, blue, and red gears denote three key activities, and they are linked to the two others by yet other three gears representing analyses (yellow, purple, and light-blue ones). In order to facilitate in this processes, a quantum simulator must have three features, which correspond to the three key activities. First, the quantum simulator itself should be fast enough to be used iteratively in the process. Second, the precision of the simulator must be guaranteed by clear theoretical bases to make the analyses of the results and finding the mechanisms of phenomena possible. Third, the simulator must be versatile enough to verify functionalities of any new systems.

As mentioned in the previous section, the OEP method is very promising

Figure 1.1: The materials design model, used by several authors [33, 34] (This picture itself is painted by the author of this thesis, he referring to the literatures.)

to realize such an ideal quantum simulator. Because this method is applicable to any energy functional expressed in terms of Kohn-Sham orbitals in principle, it is possible to choose any functionals based on clear theoretical reasons. Thus, we adopt the OEP method and have developed several new techniques related to the calculation. There are three main findings in the present work.

1. New equation for OEP The OEP equation known so far has one indefinite constant for a potential in each spin direction (let us call this "SHTS equation" after Sharp and Horton [5], Talman and Shadwick [6]). However, it is clear that the degree of freedom allowed for the potential should be single, corresponding to the choice of the origin of energy. We have derived a new equation that fixes the indefiniteness and completes the description of the OEP.

2. Modification of KLI approximation The KLI method reduces computational tasks greatly and has been reported to be precise enough in many

cases. However, their way to fix the indefiniteness of the SHTS equation depends on the physical situation which is not always applicable. This often causes serious problems in realistic calculations of solids. Therefore, yet adopting their way to approximate the SHTS equation, we introduce an exact way to fix the indefiniteness.

3. Technique for double energy integration We have developed an efficient way to calculate a double integral with respect to energy variables which is related to the calculation of RPA-level correlation. This reduces the computational time greatly. This is very important because the process is one of the rate-determining processes of the whole calculation.

We have developed a code that can calculate the exact-exchange and an RPA-level-correlation functional using the above method. This program is based on the Korringa-Kohn-Rostoker (KKR) Green's function method which has advantages in precision, time consumption, and, more over, in application of our technique to the calculation of the RPA-level correlation energy.

In Section 2, the basic theory of the DFT and the Kohn-Sham theories are given. After that I will show how the equations of the OEP including a new additional equation are derived from the basic theories. The explanation of the modified KLI method and the technique for the calculation of the RPA-level correlation follow them. The results of our program using those theories and techniques are shown in Section 3. Finally, in Section 4, we conclude.

Chapter 2

Theory

2.1 Density functional theory

2.1.1 Hohenberg-Kohn theorem I

The density functional theory developed by Hohenberg and Kohn[1] contains two propositions. In this section we concern ourselves with the first one. The second one will be discussed in the subsequent section. The first one is on the existence of maps from the ground-state density to any kinds of physical quantity of the system including those related to excited states of the system. The existence of these maps follows from the first Hohenberg-Kohn theorem, which concerns the uniqueness of the external potential. Here we assume that the other part of the Hamiltonian is given.

For the sake of the following discussion, we separate the Hamiltonian into two terms:

$$H = H^{\mathrm{com}}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) + \sum_{i=1}^{N} V^{\mathrm{ext}}(\boldsymbol{r}_i) \tag{2.1}$$

Using the Born-Oppenheimer approximation, one may adopt

$$H^{\mathrm{com}}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} V^{2-\mathrm{body}}(\boldsymbol{r}_i, \boldsymbol{r}_j) + C \tag{2.2}$$

with the external potential V^{ext} produced by nuclei, constant C from nucleus-nucleus interactions and $V^{2-\mathrm{body}}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$ of the electron-electron interaction. The Hohenberg-Kohn theorem for non-interacting system will be

also useful later. In this case we will make $V^{2-\mathrm{body}}(\boldsymbol{r}_i, \boldsymbol{r}_j) = 0$ and substitute the so called Kohn-Sham potential for V^{ext}.

Besides this Hamiltonian, it is convenient to define another Hamiltonian which is different from H only in the external potential:

$$H' = H^{\mathrm{com}}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) + \sum_{i=1}^{N} V'^{\mathrm{ext}}(\boldsymbol{r}_i) \tag{2.3}$$

In addition to these, we suppose the followings for the Hamiltonians:

- V^{ext} and V'^{ext} have a common domain of definition $D \subset \mathbb{R}^d$, where d is the dimension of the space.
- Both two Hamiltonians H and H' transform functions whose domain is $\mathfrak{D} \subset \mathbb{R}^{dN}$ to functions that has the same domain $\mathfrak{D}$.
- Both V^{ext} and V'^{ext} are differentiable on D.

This does not exclude the use of the delta function or the theta function as external potentials. The value of these functions at their singular point is regarded as undefined in our treatment.

In the original proof demonstrated by Hohenberg and Kohn, lack of degeneracies in the system is assumed for the simplicity of the argument. They only mentioned that the same theorem is also valid even when there are some degeneracies in the system.

With the non-degeneracy assumption, it is clear that

$$\langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle, \tag{2.4}$$

where Ψ is the ground state of H and Ψ' is a state different from the ground state of H. This relation is a key point of the proof of the theorem. Kohn[9] later give a proof of the same relation (2.4) based on the conjecture that any wave functions can not be an eigenfunction of two different Hamiltonians simultaneously.

This is almost true. However, at the same time, there is a simple counterexample: a one-dimensional non-interacting system with the external potential

$$V^{\mathrm{ext}}(x) = \begin{cases} E & (x < -\epsilon) \\ \infty & (-\epsilon \leq x \leq 0) \\ x^2 & (0 < x) \end{cases} \quad (\epsilon > 0). \tag{2.5}$$

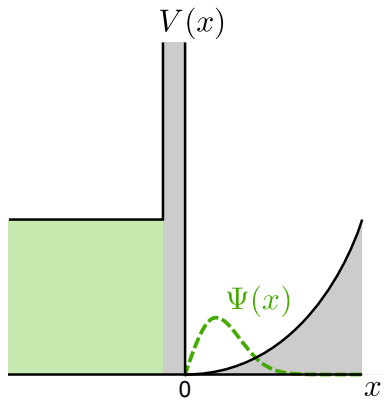


Figure 2.1: An exceptional case that one wave function is allowed by more than two different external potentials. The height of green box can be changed without affecting the shape of the wave function which is non-zero only in $x > 0$.

This system has a solution $\Psi(x) \propto \theta(x) x e^{-x^2}$ whatever value E is (see fig.2.1), and it is clear that this violates the conjecture. Thus, clarifying the condition of the uniqueness of the external potential still remains undone. The next lemma will give us one of such conditions.

Lemma I If a wave function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ is an eigenfunction of both two Hamiltonians H and H' simultaneously, and if $\{\boldsymbol{r}, \boldsymbol{r}, \cdots, \boldsymbol{r}\}$ is a limit point of $\mathcal{D}_\Psi = \{\{\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N\} \in \mathfrak{D} | \Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \neq 0\}$ for all $\boldsymbol{r} \in D$, the external potentials of these two Hamiltonians are different from one another only by a constant.

Proof By the first premise of the lemma,

$$H\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N), \tag{2.6}$$

$$H'\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = E'\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N), \tag{2.7}$$

where E and E' are c-numbers. Thus, for all $\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N$

$$\begin{aligned}
&[H - H' - (E - E')]\,\Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \\
&= \left[\sum_i^N \left\{V^{\mathrm{ext}}(\boldsymbol{r}_i) - V'^{\mathrm{ext}}(\boldsymbol{r}_i)\right\} - (E - E')\right]\Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \\
&= 0.
\end{aligned} \tag{2.8}$$

Substituting $f(\boldsymbol{r}) = V^{\text{ext}}(\boldsymbol{r}_i) - V'^{\text{ext}}(\boldsymbol{r}_i)$ and $\epsilon = E - E'$,

$$\left[\sum_{i=1}^{N} f(\boldsymbol{r}_i) - \epsilon\right] \Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) = 0. \tag{2.9}$$

It follows from the second premise that for any open set $O \subset \mathfrak{D}$ that includes $\{\boldsymbol{r}_0, \cdots, \boldsymbol{r}_0\} \in \mathfrak{D}$, $O \cap \mathcal{D}_\Psi \neq \emptyset$. Thus, there exists a set of $\{\boldsymbol{\Delta}_i\}$ such that $\Delta \equiv |\{\Delta_i\}| = \sqrt{|\boldsymbol{\Delta}_1|^2 + |\boldsymbol{\Delta}_2|^2 + \cdots + |\boldsymbol{\Delta}_N|^2} < \delta$ and $\{\boldsymbol{r}_0 + \boldsymbol{\Delta}_1, \boldsymbol{r}_0 + \boldsymbol{\Delta}_2, \cdots, \boldsymbol{r}_0 + \boldsymbol{\Delta}_N\} \in \mathcal{D}_\Psi$ for any $\delta > 0$ because a ball in $\mathfrak{D}$ whose radius is δ, having its origin at $\{\boldsymbol{r}_0, \boldsymbol{r}_0, \cdots, \boldsymbol{r}_0\}$, is an open set.

It results from (2.9) that

$$\sum_{i=1}^{N} f(\boldsymbol{r}_0 + \boldsymbol{\Delta}_i) - \epsilon = 0 \tag{2.10}$$

for such $\{\Delta_i\}$. Since $f(\boldsymbol{r})$ is differentiable in D, one can utilize the mean value theorem for functions of several variables. Therefore, there exists a certain θ in $0 < \theta < 1$, for which

$$\sum_{i=1}^{N} [f(\boldsymbol{r}_0) + \boldsymbol{\Delta}_i \cdot \nabla f(\boldsymbol{r}_0 + \theta \boldsymbol{\Delta}_i)] - \epsilon \tag{2.11}$$

$$= \sum_{i=1}^{N} [\boldsymbol{\Delta}_i \cdot \nabla f(\boldsymbol{r}_0 + \theta \boldsymbol{\Delta}_i)] + N f(\boldsymbol{r}_0) - \epsilon = 0 \tag{2.12}$$

is satisfied. In the limit of $\delta \to 0$, the first term goes zero. Thus, $N f(\boldsymbol{r}_0) - \epsilon = 0$ must be hold, and this is true for any $\boldsymbol{r}_0 \in D$. Therefore,

$$V^{\text{ext}}(\boldsymbol{r}) - V'^{\text{ext}}(\boldsymbol{r}) = \text{const.} \tag{2.13}$$

for all $\boldsymbol{r} \in D$. Q.E.D.

The second premise of this lemma would be true or convincing for most cases, because there might be a tunneling amplitude in any finite region of the configuration space, no matter how high (but finite) potentials exist in the space. On the other hand, it is easy to make exceptional situation using the infinitely high external potentials with a finite width. In this case, violation of the conclusion of the lemma is rather reasonable, since any values of external potential can be allowed in the region where the particles

are perfectly excluded. However, the same conclusion as that stated in the lemma can hold even if the interaction contains some infinite hight regions and violates the second premise. For example, hardcore interactions clearly prohibit particles from gathering at one point and keep every particles out of a certain finite region around other particles, which is against the premise of the lemma. The next lemma which we are going to show reveals that some kinds of hardcore interactions keep the same conclusion as that of the lemma I undamaged.

Before moving on to the lemma II, it may be useful to introduce a set of slices of $\overline{\mathcal{D}_\Psi}$ (closure of $\mathcal{D}_\Psi$) restricted to D:

$$S_\Psi^{i,\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{N-1}} = \{\boldsymbol{r} \in D \mid \{\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{i-1},\boldsymbol{r},\boldsymbol{r}_i,\cdots,\boldsymbol{r}_{N-1}\} \in \overline{\mathcal{D}_\Psi}\}, \tag{2.14}$$

and related notions. Let $\tilde{S}_\Psi$ denote the set that consists of all $S_\Psi^{i,\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{N-1}}$ above. We may think of the following relation between S^1 and S^n: Suppose that there is a sequence of sets $S^1, S^2, \cdots S^n \in \tilde{S}_\Psi$ and $S^k \cap S^{k+1} \neq \emptyset$ ($^\forall k \in \{1, 2, \cdots, n-1\}$). Then let us denote the binary relation between S^1 and S^n by the symbol $\sim$: $S^1 \sim S^n$. In addition to this, it is convenient to append $\emptyset \sim \emptyset$ to the definition as a special case in order for all the elements $S \in \tilde{S}_\Psi$ to satisfy the reflexivity: $S \sim S$. The symmetry $^\forall S, T \in \tilde{S}, S \sim T \Rightarrow T \sim S$ and the transitivity $^\forall S, T, U \in \tilde{S}, S \sim T, T \sim U \Rightarrow S \sim U$ of the relation are also clear. Thus, one can see that this is a equivalence relation and that $[S] = \{X | X \sim S\}$ is an equivalence class.

Lemma II If a wave function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ is an eigenfunction for both two Hamiltonians H and H' simultaneously, for all $\boldsymbol{r} \in D^{[S]} \equiv \{\boldsymbol{r} \mid X \in [S], \boldsymbol{r} \in X\}$

$$V^{\text{ext}}(\boldsymbol{r}) - V'^{\text{ext}}(\boldsymbol{r}) = C^{[S]}, \tag{2.15}$$

where $C^{[S]}$ is a common c-number to all the point in $D^{[S]}$.

Proof In the same way as the proof of the lemma I up to the (2.9), one can see

$$\left[\sum_{i=1}^{N} f(\boldsymbol{r}_i) - \epsilon\right] \Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) = 0. \tag{2.16}$$

For $\boldsymbol{r} \in D^{[S]}$, there exists $X \in [S]$ and $\boldsymbol{r} \in X = S_{\Psi}^{i,\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{N-1}}$. Since $\{\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{i-1}, \boldsymbol{r}, \boldsymbol{r}_i, \cdots, \boldsymbol{r}_{N-1}\}$ is a limit point of $\mathcal{D}_\Psi$, one reaches

$$f(\boldsymbol{r}) = \epsilon - \sum_{i=1}^{N-1} f(\boldsymbol{r}_i) \tag{2.17}$$

$$\equiv C^X. \tag{2.18}$$

in a similar manner to the remaining part of the proof of the lemma I. The right hand side of this equation is a c-number and common to all the elements of X. This is also common to all the element $Y \in \tilde{S}_\Psi$ such that $X \cap Y \neq \emptyset$ because if there exists $\boldsymbol{r} \in X \cap Y$ then $C^X = f(\boldsymbol{r}) = C^Y$.

It follows from this and the definition of the equivalence relation that this constant is also common to any $Y \in [S]$. It is because if $Y \in [S]$ there is a sequence of set $S^1, \cdots, S^n$ such that

$$X \cap S^1 \neq \emptyset, \tag{2.19}$$

$$S^k \cap S^{k+1} \neq \emptyset \ ({}^\forall k = \{1, \cdots, n-1\}), \tag{2.20}$$

$$S^n \cap Y \neq \emptyset. \tag{2.21}$$

Therefore, $C^X = C^{S^1} = \cdots = C^{S^n} = C^Y \equiv C^{[S]}$. Q.E.D.

Corollary If there exists $S \in \tilde{S}_\Psi$ such that $D \subset D^{[S]}$, two Hamiltonians are different from one another only by a constant.

Thus, we obtain two conditions of the virtual uniqueness of the Hamiltonian for a wave function Ψ:

1. For all $\boldsymbol{r} \in D$, $\{\boldsymbol{r}, \cdots, \boldsymbol{r}\}$ is a limit point of $\mathcal{D}_\Psi$,
2. There exists $S \in \tilde{S}_\Psi$ such that $D \subset D^{[S]}$.

The difference of these two conditions can be seen from an example $\mathcal{D}_\Psi$:

$$\mathcal{D}_\Psi = \{(-\infty, 0) \times (0, \infty), (0, \infty), \times(-\infty, 0)\} \tag{2.22}$$

in a one-dimensional system of two particles (see fig.2.2) with $D = (-\infty, \infty)$. Only the second condition may survive while the first fails. As seen in this example, the first conditions does not cover all the conditions of the second ones.

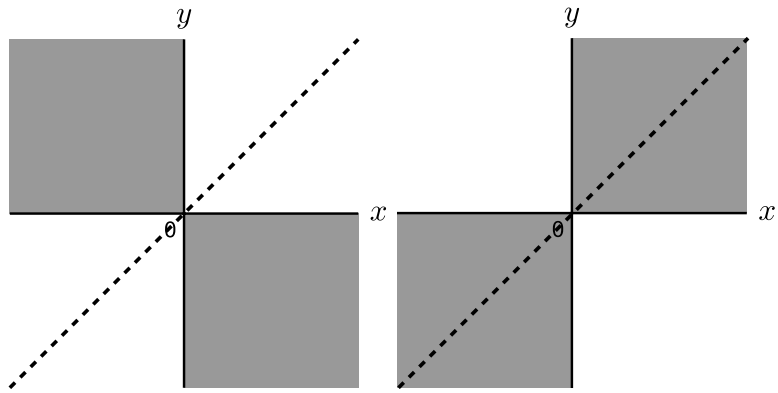


Figure 2.2: Two kinds of D_Ψ in a one-dimensional two-particle system that has the same slice of region $\tilde{S} = \{(-\infty, 0], [0, \infty)\}$. The gray areas denotes a forbidden (undefined) region of D_Ψ. (Left): $\mathcal{D}_\Psi = \{(0, \infty) \times (0, \infty), (-\infty, 0) \times (-\infty, 0)\}$, which satisfies the premise of the lemma I. (Right): $\mathcal{D}_\Psi = \{(0, \infty) \times (-\infty, 0), (-\infty, 0) \times (0, \infty)\}$ which does not satisfy the premise of lemma I. In both cases the premise of the lemma II is fulfilled.

As mentioned above, the first condition seems valid in most realistic Hamiltonians, which contains no finite undefined region but only undefined points. The second condition can play an important role if there is a finite undefined region. One example is a hardcore interaction:

$$V^{2-\text{body}}(x, y) = \begin{cases} \infty & (|x - y| \leq \epsilon) \\ 0 & (|x - y| > \epsilon) \end{cases} \tag{2.23}$$

and another is a selective wall for the particle indicated by x (two different particles in one-dimensional space):

$$V^{2-\text{body}}(x, y) = \begin{cases} \infty & (|x| \leq \epsilon) \\ 0 & (|x| > \epsilon) \end{cases} \tag{2.24}$$

In both cases, the slices of the domain of $V^{2-\text{body}}$ are overlapped one another and all points in the space are covered by the slices (see figure 2.3). In the example of hardcore interaction, if the kind of two particles is different from each other, $\mathcal{D}_\Psi$ is further restricted. It is because the particles can not change the position due to the hardcore interaction and the one dimensionality of the space. As for the selective wall, $\mathcal{D}_\Psi$ is definitely restricted to either

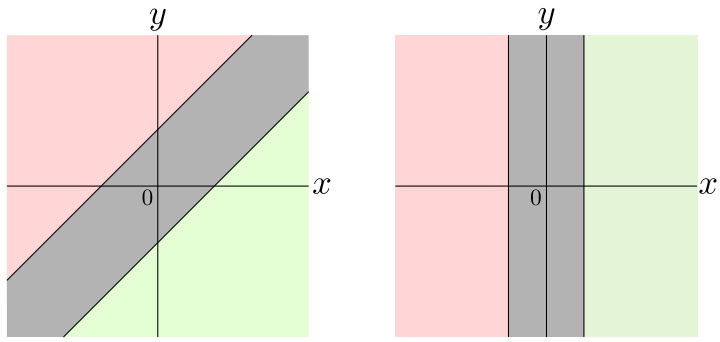


Figure 2.3: $\mathcal{D}_\Psi$'s in (left) the hardcore interaction of (2.23) and (right) the selective wall of (2.24) . Each $V^{2-\text{body}}$ keeps particles out of the Gray region. Due to the one-dimensionality, $\mathcal{D}_\Psi$'s may be further restricted to either red or green region. However, $\mathcal{D}_\Psi$ still satisfies the condition of the lemma II.

$x > 0$ or $x < 0$. However, still $\mathcal{D}_\Psi$ satisfies the second condition. Thus the Hohenberg-Kohn theorem, which we discussed later, can be used in these systems.

Hereafter, we suppose that all the wave functions of the system satisfy either or both these conditions. To the extent of this assumption, the following statement is justified as a corollary of the lemmas.

Corollary If the difference between H and H' is more than a constant, and Ψ and Ψ' are the ground state of these two Hamiltonians respectively then

$$\langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle. \tag{2.25}$$

Because if equality held, Ψ' should be an eigenfunction of H, but this violates the lemmas.

Now we are ready for moving on to the first Hohenberg-Kohn Theorem.

Hohenberg-Kohn theorem I If the ground states Ψ and Ψ' of H and H' respectively has a common density $n_0(\boldsymbol{r})$, the external potentials of these two Hamiltonians are different from one another only by a constant.

Proof Let E and E' denote the eigenvalue of Ψ for H and Ψ' for H', respectively. It follows from the corollary,

$$E = \langle\Psi|H|\Psi\rangle < \langle\Psi'|H|\Psi'\rangle \tag{2.26}$$

$$= \langle\Psi'|H'|\Psi'\rangle - \langle\Psi'|\{H - H'\}|\Psi'\rangle \tag{2.27}$$

$$= E' - \sum_{i=1}^{N} \int d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_N \, |\Psi(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N)|^2 \left\{V^{\text{ext}}(\boldsymbol{r}_i) - V'^{\text{ext}}(\boldsymbol{r}_i)\right\} \tag{2.28}$$

$$= E' - \int d\boldsymbol{r} \; n_0(\boldsymbol{r}) \left\{V^{\text{ext}}(\boldsymbol{r}) - V'^{\text{ext}}(\boldsymbol{r})\right\}, \tag{2.29}$$

where n_0 is the density of Ψ. To prove the theorem by contradiction, suppose n_0 is also the density of Ψ'. In the same way, one has

$$E' < E - \int d\boldsymbol{r} \; n_0(\boldsymbol{r}) \left\{V'^{\text{ext}}(\boldsymbol{r}) - V^{\text{ext}}(\boldsymbol{r})\right\}. \tag{2.30}$$

Adding each side of (2.29) to the same side of (2.30), one reaches

$$E + E' < E + E'. \tag{2.31}$$

This is a contradiction. Q.E.D.

Thus, the theorem has been proved without the assumption of nonexistence of degeneracy in the system. The situation is illustrated in fig.2.4. This theorem is the basis of the density functional theory. Given a common part of the Hamiltonian H_{com} in (2.1), it follows from this theorem that we can restore the remaining part of the Hamiltonian V^{ext} only from the information of the ground-state density n_0 in principle. Since Hamiltonian can be regarded as a functional of the ground-state density, it proves the existence of ways to infer any kinds of physical quantity of the system from the ground-state density. In other words, every observables is a functional of the ground-state density and is universal in the sense that these functionals is exact for any external potentials. Note that observables that are related to excited states of the system can also be regarded as a functional of the ground-state density. It is because excited states of the system can be obtained from the information of the density-functional of Hamiltonian $H[n]$, solving the Schrödinger equation $i\frac{\partial}{\partial t}\Phi = H\Phi$.

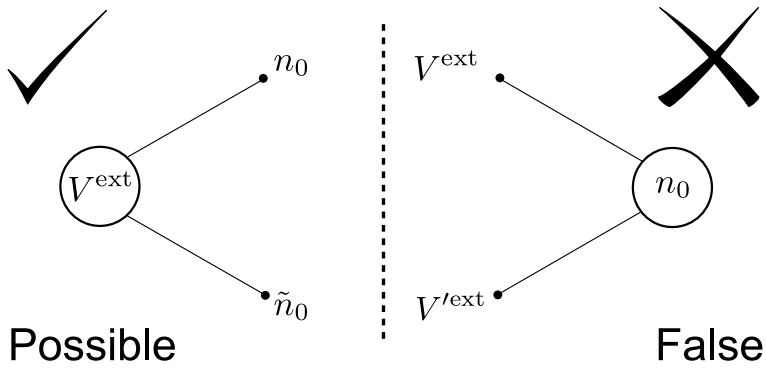


Figure 2.4: Left: The external potential V^{ext} corresponds to two or more ground-state densities when there is degeneracy in the ground states of the system. Right: According to the first Hohenberg-Kohn theorem, no density n_0 can be the ground-state density of two different systems (except difference by a constant) simultaneously.

However, it should be noticed that the domain of these functionals is restricted to the densities that have a corresponding ground state of a systems. Only in this case, n can represent an external potential. Thus, this feature of the density is sometimes called V-representability.

2.1.2 Hohenberg-Kohn theorem II

The second Hohenberg-Kohn theorem is concerned to the determination of the ground-state density for a given external potential. In the ordinary scheme of the quantum mechanics, the Schrödinger equation is solved in order to determine the ground-state density. The second Hohenberg-Kohn theorem offers possibility of an alternative approach. This theorem tells that there exists a (non-universal) functional of density n for each external potentials that is minimized only when n is the ground-state density. This gives us a density-functional approach to the problem.

It is the key point to use the variational principle:

$$\langle \Psi_0 | H | \Psi_0 \rangle \leq \langle \Psi | H | \Psi \rangle, \tag{2.32}$$

where Ψ_0 is one of the ground states of H, and Ψ is a different state from Ψ_0. To the extent of our assumption, the both sides are equal to one another only if Ψ is also a ground state of H.

The left-hand side of this inequality can be expressed by the universal density functional of the ground-state energy $E_0[n_0]$, where n_0 is the density constructed from Ψ_0. However, the right-hand side is not such simple as to be expressed as a density functional. It follows from the first Hohenberg-Kohn theorem that the Hamiltonian $H[n]$ can be regarded as a universal functional of the ground-state density, but there are infinitely many possible ways to define the density functional of a state $|\Psi[n]\rangle$. It might be easiest to define $|\Psi[n]\rangle$ by a representative of the ground-states of $H[n]$ for our purpose because we are going to construct a density functional of n that becomes identical to $\langle\Psi_0|H|\Psi_0\rangle$ only when n is the ground-state density of $H[n_0]$. This definition imposes a restriction on the trial state $|\Psi\rangle$, but it does not change the relation (2.32). In order to remind readers this definition and situation, let $|\Psi_0[n]\rangle$ denote this density functional of state. Thus, the following functional is suitable for our purpose:

$$\tilde{E}_{\mathrm{HK}}[n, n_0] = \langle\Psi_0[n]|H[n_0]|\Psi_0[n]\rangle \tag{2.33}$$

It is clear from the variational principle that $\tilde{E}_{\mathrm{HK}}[n_0, n_0] \leq \tilde{E}_{\mathrm{HK}}[n, n_0]$ and the equality holds only when n is the ground state of $H[n_0]$. However, this $\tilde{E}_{\mathrm{HK}}$ is not useful in order to determine the ground-state density because this minimization itself needs direct information of n_0.

Actually, $\tilde{E}[n, n_0]$ can be transformed into a functional of the trial density n and a fixed external potential V^{ext}. It follows from $H[n_0] = H^{\mathrm{com}} + V^{\mathrm{ext}}[n_0]$ that

$$\tilde{E}_{\mathrm{HK}}[n, n_0] = \langle\Psi_0[n]|H^{\mathrm{com}}|\Psi_0[n]\rangle + \langle\Psi_0[n]|V^{\mathrm{ext}}[n_0]|\Psi_0[n]\rangle \tag{2.34}$$

$$= \langle\Psi_0[n]|H^{\mathrm{com}}|\Psi_0[n]\rangle + \int d\boldsymbol{r}\; V^{\mathrm{ext}}[n_0](\boldsymbol{r})\, n(\boldsymbol{r}). \tag{2.35}$$

The first term is often denoted by $F_{\mathrm{HK}}[n]$. Note that $F_{\mathrm{HK}}[n]$ is a universal functional as well as $\Psi_0[n]$ defined above. Using $E_{\mathrm{HK}}[n, V^{\mathrm{ext}}] \equiv F_{\mathrm{HK}}[n] + \int d\boldsymbol{r}\; V^{\mathrm{ext}}(\boldsymbol{r}) n(\boldsymbol{r})$ instead of $E[n, n_0]$, we see that

$$E_{\mathrm{HK}}[n_0, V^{\mathrm{ext}}] \leq E_{\mathrm{HK}}[n, V^{\mathrm{ext}}], \tag{2.36}$$

and that the equality holds only if n is a ground-state density of $H[n_0]$. Now we need only V^{ext} during the minimization. This is the second Hohenberg-Kohn theorem, which is summarized in the following.

Hohenberg-Kohn theorem II The Hohenberg-Kohn functional E_{HK}:

$$E_{\mathrm{HK}}[n, v] = F_{\mathrm{HK}}[n] + \int d\boldsymbol{r}\ v(\boldsymbol{r})n(\boldsymbol{r}) \tag{2.37}$$

has the following properties:

- Given a fixed V^{ext}, $E_{\mathrm{HK}}[n, V^{\mathrm{ext}}]$ has minimum points only at $n = n_0$, where n_0's are the ground-state densities.
- Given a V^{ext}, the global minimum of $E_{\mathrm{HK}}[n, V^{\mathrm{ext}}]$ with respect to n is identical to the ground-state energy of the system with the external potential V^{ext}.

We have derived the second Hohenberg-Kohn theorem from the variational theorem. In the above discussion, we constrained the trial state $|\Psi\rangle$ to be a ground state of a system. As a result, the domain of the Hohenberg-Kohn functional $E_{\mathrm{HK}}[n, v]$ is restricted to V-representable density n.

Levy [35, 36] and Lieb[37] have pointed out that this restriction can be relaxed, by replacing F_{HK} with the Levy-Lieb functional

$$F_{\mathrm{LL}}[n] = \min_{\Psi \to n} \langle \Psi | H^{\mathrm{com}} | \Psi \rangle, \tag{2.38}$$

where $\Psi \to n$ means that Ψ runs over every state that has a fixed density n. Operating $\min_{\Psi \to n}$ to the right-hand side of (2.32), one obtains

$$\langle \Psi_0 | H[n_0] | \Psi_0 \rangle \leq \min_{\Psi \to n} \langle \Psi | H[n_0] | \Psi \rangle \tag{2.39}$$

$$= F_{\mathrm{LL}}[n] + \int d\boldsymbol{r}\ V^{\mathrm{ext}}[n_0](\boldsymbol{r})n(\boldsymbol{r}), \tag{2.40}$$

and sees that the equality holds only when n is a ground state density of $H[n_0]$.

This $F_{\mathrm{LL}}[n]$ is defined only when there exists a state that produces the density n. In many-electron systems, this is not a trivial problem because wave functions are somehow constrained by the anti-symmetry condition of electrons. The capability of a density to bring itself back to a corresponding N-particle wave function is called N-representability. Fortunately, the N-representability of densities is much more likely than the V-representability [38].

2.1.3 Kohn-Sham theory

The second Hohenberg-Kohn theorem gives us the density-functional approach to the determination of the ground-state density n for a given external potential V^{ext}. However, because the explicit form of the Hohenberg-Kohn functional is not known, this can not be made into practice as it is. Therefore, Kohn and Sham[7] proposed a scheme that is in particular suitable for approximations to the problem. First, they supposed that there is a non-interacting auxiliary system that can reproduce the density of the many-body system, second they derived an equation that the non-interacting system should obey. Finally, they proposed approximations for this non-interacting equation.

Non-interacting system Before moving on to the Kohn-Sham scheme, let us introduce non-interacting system and related notions. The Hamiltonian of the auxiliary system can be expressed as

$$H^{\text{aux}} = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V^{\text{eff}}(\boldsymbol{r}_i), \tag{2.41}$$

where V^{eff} is the effective potential, the external potential of the auxiliary system. Since the Hohenberg-Kohn theorem holds also in the non-interacting Hamiltonian, there exists Hohenberg-Kohn functional of the auxiliary system:

$$E_{\text{HK}}^{\text{aux}}[n, V^{\text{eff}}] = T^{\text{aux}}[n] + \int d\boldsymbol{r}\ V^{\text{eff}}(\boldsymbol{r}) n(\boldsymbol{r}), \tag{2.42}$$

where $T^{\text{aux}}[n]$ is the kinetic-energy functional, which corresponds to $F_{\text{HK}}[n]$ in the general argument above. According to the second Hohenberg-Kohn theorem for non-interacting systems, variation of $E_{\text{HK}}^{\text{aux}}$ with respect to density $n(\boldsymbol{r})$ gives the equation that the ground-state density should satisfy. The resulting equation is

$$\frac{\delta E_{\text{HK}}^{\text{aux}}}{\delta n(\boldsymbol{r})} = \frac{\delta T^{\text{aux}}}{\delta n(\boldsymbol{r})} + V^{\text{eff}}(\boldsymbol{r}) = 0, \tag{2.43}$$

which must be identical with the ordinary scheme to determine the ground-state density, in which we solve the single-particle Schrödinger equation:

$$\left[-\nabla^2 + V^{\text{eff}}(\boldsymbol{r})\right] \psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r}) \tag{2.44}$$

and then construct the ground-state density n_0 using

$$n_0(\boldsymbol{r}) = \sum_i{}' \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}), \tag{2.45}$$

where the prime symbol denote summation for occupied states. Thus, we can use (2.44) and (2.45) in order to solve the equation (2.43).

Kohn-Sham theory Now what we really want to obtain is the ground-state density of

$$H = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} V^{\mathrm{el-el}}(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i=1}^{N} V^{\mathrm{ext}}(\boldsymbol{r}_i). \tag{2.46}$$

$$\tag{2.47}$$

It will be convenient for the following discussion to define T and H_{int} as

$$T = -\sum_{i=1}^{N} \nabla_i^2, \tag{2.48}$$

$$H_{\mathrm{int}} = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} V^{\mathrm{el-el}}(\boldsymbol{r}_i, \boldsymbol{r}_j), \tag{2.49}$$

so that $H = T + H_{\mathrm{int}} + \sum_{i=1}^{N} V^{\mathrm{ext}}(\boldsymbol{r}_i)$.

We are now to derive a non-interacting equation that reproduce the density of the interacting system. The equation (2.43) give us a clue to the derivation. If the Hohenberg-Kohn functional $E_{\mathrm{HK}}[n, v]$ of the interacting system is transformed into the form $E_{\mathrm{HK}}[n, v] = T^{\mathrm{aux}}[n] + E^{\mathrm{rem}}[n, v]$, we can exploit (2.44) and (2.45) with $V^{\mathrm{eff}}(\boldsymbol{r}) = \frac{\delta E^{\mathrm{rem}}}{\delta n(\boldsymbol{r})}$. Based on this idea, Kohn and Sham divided the Hohenberg-Kohn functional as follows:

$$E_{\mathrm{KS}}[n, v] = T^{\mathrm{aux}}[n] + E_{\mathrm{Hartree}}[n] + \int d\boldsymbol{r}\, v(\boldsymbol{r})n(\boldsymbol{r}) + E_{\mathrm{xc}}[n] \tag{2.50}$$

$$\equiv E_{\mathrm{HK}}[n, v], \tag{2.51}$$

where

$$E_{\mathrm{Hartree}}[n] = \int d\boldsymbol{r} \int d\boldsymbol{r}' \, \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{2.52}$$

$$E_{\mathrm{xc}}[n] = T[n] + E_{\mathrm{int}}[n] - T^{\mathrm{aux}}[n] - E_{\mathrm{Hartree}}[n]. \tag{2.53}$$

This E_{xc} is called exchange-correlation functional. The E_{KS} can be defined only when n is V-representable for both non-interacting and interacting Hamiltonian.

Thus, E_{KS} can not be minimized to the ground-state density of the interacting system if the ground-state density of the interacting system is not V-representable for non-interacting Hamiltonian. This is the reason why the assumption of existence of the auxiliary system that reproduces the ground-state density of the interacting system have to be premised.

Using these, the variation of E_{KS} with respect to the density gives

$$\frac{\delta E_{\mathrm{KS}}[n, V^{\mathrm{ext}}]}{\delta n(\boldsymbol{r})} = \frac{\delta T^{\mathrm{aux}}}{\delta n(\boldsymbol{r})} + V_{\mathrm{Hartree}}(\boldsymbol{r}) + V^{\mathrm{ext}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})} = 0, \tag{2.54}$$

where

$$V_{\mathrm{Hartree}}(\boldsymbol{r}) = 2\int d\boldsymbol{r}' \, \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{2.55}$$

Thus, the effective potential of the auxiliary system must be

$$V^{\mathrm{eff}}(\boldsymbol{r}) = V_{\mathrm{Hartree}}(\boldsymbol{r}) + V^{\mathrm{ext}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})}, \tag{2.56}$$

and one can obtain the ground state density using (2.45).

Local density approximation To the extent of our assumptions, the Kohn-Sham theory is an exact theory that can determine the ground-state density of interacting systems. However, it is still not practicable as it seemingly is because the explicit form of $E_{\mathrm{xc}}[n]$ is unknown. The local density approximation (LDA) is an approximation to the $E_{\mathrm{xc}}[n]$ proposed by Kohn and Sham[7]. They claimed that when the density is enough slowly-varying, $E_{\mathrm{xc}}[n(\boldsymbol{r})]$ defined by (2.53) can be approximated efficiently by integration of a function only depends on the density such as $E_{\mathrm{xc}}[n] \sim \int d\boldsymbol{r} f(n(\boldsymbol{r}))$ without any information of the first and higher-order gradients of n. The following notation is preferred in literatures:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int d\boldsymbol{r} \; n(\boldsymbol{r}) \epsilon_{\mathrm{xc}}(n(\boldsymbol{r})) \tag{2.57}$$

This is the local density approximation, and ϵ_{xc} is called exchange-correlation energy density. Because this functional should be universal, ϵ_{xc} must be

common to all the system as long as the LDA is valid. Thus, $\epsilon_{\rm xc}$ is usually determined from the calculated results of homogeneous systems using, for example, Monte Carlo methods. This gives a practical way to calculate the ground-state density of interacting systems.

Alternative approach to obtain $V_{\rm xc}$ In the above discussion to derive the form of $V_{\rm xc}$, we have exploited the ordinary scheme of quantum mechanics to solve (2.43). The derivation can be performed from another viewpoint.

In the alternative approach, the set of (2.44) and (2.45) is the starting point, i.e., these equations are thought to be an ansatz of the ground state. In order to state the scope of the summation clearly, let us replace (2.45) with

$$n_0(\boldsymbol{r}) = \int_{-\infty}^{\mu} dE \sum_i \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})\delta(E-\epsilon_i), \tag{2.58}$$

where μ is to be determined so as to make the integral $\int d\boldsymbol{r}\, n_0(\boldsymbol{r})$ be identical to the number of electron N. We assume that the set of densities that takes the form of (2.45) and (2.58) contains the ground-state density of the interacting system. To the extent of the assumption, it is enough to think only this set of densities during minimization of $E_{\rm KS}[n,v]$ for a fixed v.

According to (2.44) and (2.58), the density is perfectly determined from the information of ψ's, ψ^*'s, and μ. Thus, one can minimize the Kohn-Sham energy $E_{\rm KS}[n,v]$ for fixed v with respect to ψ's, ψ^*'s, and μ with the constraint that the integral of n_0 over the whole space become the number of electrons N instead of minimization with respect to n without constraints.

The Lagrange multiplier method is convenient for this purpose. Letting ξ denote the Lagrange multiplier, we transform the problem into minimization of

$$I = E_{\rm KS}[n,v] + \xi\left[\int d\boldsymbol{r} \int_{-\infty}^{\mu} dE \sum_i \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})\delta(E-\epsilon_i) - N\right] \tag{2.59}$$

with respect to ψ's, ψ^*'s and μ, which should be regarded as independent variables during the minimization.

Let $\tilde{V}_{\rm xc}(\boldsymbol{r})$ denote

$$\tilde{V}_{\rm xc}(\boldsymbol{r}) \equiv V_{\rm eff}(\boldsymbol{r}) - V_{\rm Hartree}(\boldsymbol{r}) - V^{\rm ext}(\boldsymbol{r}) \tag{2.60}$$

Then, one can see that the equation $\frac{\delta I}{\delta \psi_i^*} = 0$ gives

$$\theta(\mu-\epsilon_i)\left[\xi - \tilde{V}_{\rm xc}(\boldsymbol{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})}\right]\psi_i(\boldsymbol{r}) = 0, \tag{2.61}$$

and $\frac{\delta I}{\delta \psi_i} = 0$, the complex conjugate of the equation (2.61). $\frac{\partial I}{\partial \mu} = 0$ gives

$$\int d\boldsymbol{r} \ \left[\xi - \tilde{V}_{\rm xc}(\boldsymbol{r})\right] \left(\sum_i \delta(\mu - \epsilon_i)\psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})\right) + \frac{\partial E_{\rm xc}[n]}{\partial \mu} = 0. \tag{2.62}$$

It follows from (2.61) that

$$\xi - \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})} + \tilde{V}_{\rm xc}(\boldsymbol{r}) = 0, \tag{2.63}$$

which is different from (2.56) only by an additive constant ξ, the freedom of which we just ignored in the previous discussion.

In this case, only the equation (2.61) is significant because substituting $\frac{\partial E_{\rm xc}[n]}{\partial \mu} = \int d\boldsymbol{r} \ \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})} \frac{\partial n(\boldsymbol{r})}{\partial \mu}$ into (2.62) one obtains

$$\int d\boldsymbol{r} \ \left[\xi - \tilde{V}_{\rm xc}(\boldsymbol{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})}\right] \left(\sum_i \delta(\mu - \epsilon_i)\psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})\right) = 0, \tag{2.64}$$

which is automatically satisfied due to (2.63).

Adiabatic connection The adiabatic connection approach to derive the Kohn-Sham functional gives another important perspective [17, 18, 19, 20]. In this scheme, the external potential V_λ is also varied along with the the electric charge parameter, while only the coupling constant is changed in the ordinary scheme of adiabatic connection.

We consider the following Hamiltonian:

$$H_\lambda = T + \lambda H_{\rm int} + V_\lambda^{\rm ext}, \tag{2.65}$$

where $V_\lambda^{\rm ext}$ is a shorthand of $\sum_i V_\lambda^{\rm ext}(\boldsymbol{r}_i)$. In this formalism $V_\lambda^{\rm ext}$ is taken so as to keep the density

$$n_\lambda(\boldsymbol{r}) \equiv \langle \Psi_\lambda | \hat{\psi}^\dagger(\boldsymbol{r})\hat{\psi}(\boldsymbol{r}) | \Psi_\lambda \rangle \tag{2.66}$$

of a parametrized state $|\Psi_\lambda\rangle$ independent on λ, i.e., $n_\lambda(\boldsymbol{r}) = n_1(\boldsymbol{r})$ for all λ in $0 \leq \lambda \leq 1$, where $\hat{\psi}(\boldsymbol{r})$ is the field operator. Thus, $V_1^{\rm ext}$ corresponds to the external potential of the (fully) interacting system, while $V_0^{\rm ext}$ corresponds to the effective potential of the auxiliary system.

The total energy of $|\Psi_1\rangle$ of the interacting system is given as follows:

$$\langle\Psi_1|H_1|\Psi_1\rangle = \langle\Psi_0|H_0|\Psi_0\rangle + \int_0^1 d\lambda\ \frac{\partial}{\partial\lambda}\langle\Psi_\lambda|\{\lambda H_{\rm int} + V_\lambda^{\rm ext}\}|\Psi_\lambda\rangle \tag{2.67}$$

$$= \langle\Psi_0|T|\Psi_0\rangle + \int d\boldsymbol{r}\ V_1^{\rm ext}(\boldsymbol{r})n(\boldsymbol{r}) + \int_0^1 \frac{d\lambda}{\lambda}\langle\Psi_\lambda|\lambda H_{\rm int}|\Psi_\lambda\rangle \tag{2.68}$$

Using the variational principle, the Kohn-Sham energy functional can be constructed from this equation. The resulting exchange-correlation functional is

$$E_{\rm xc} = \int_0^1 \frac{d\lambda}{\lambda}\langle\Psi_\lambda|\lambda H_{\rm int}|\Psi_\lambda\rangle - E_{\rm Hartree}[n], \tag{2.69}$$

which is useful to examine the exact exchange-correlation functional.

2.1.4 Spin-density functional theory

The density functional theory can be extended to the spin-density functional theory (SDFT) [2, 3]. Though the DFT itself is exact within the limit of our assumption, the SDFT is more efficient than the DFT in practical terms.

To extend the theory, the Zeeman term is introduced to the Hamiltonian:

$$H = H^{\rm com} + \sum_i V^{\rm ext}(\boldsymbol{r}_i) + \sum_i H^{\rm ext}(\boldsymbol{r}_i)\sigma_z, \tag{2.70}$$

where the quantization axis is chosen to be z-direction and σ_z is the z-component of the Pauli matrix:

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.71}$$

The wave function can be expressed as

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \begin{pmatrix} \Psi_\uparrow(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) \\ \Psi_\downarrow(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) \end{pmatrix}. \tag{2.72}$$

In this case, the total energy can be written in the following form:

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|H^{\rm com}|\Psi\rangle + \int d\boldsymbol{r}\ V^{\rm ext}(\boldsymbol{r})(n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r}))$$
$$+ \int d\boldsymbol{r}\ H^{\rm ext}(\boldsymbol{r})(n_\uparrow(\boldsymbol{r}) - n_\downarrow(\boldsymbol{r})) \tag{2.73}$$

$$= \langle\Psi|H^{\rm com}|\Psi\rangle + \int d\boldsymbol{r}\, \mathcal{V}_\uparrow^{\rm ext}(\boldsymbol{r})\, n_\uparrow(\boldsymbol{r}) + \int d\boldsymbol{r}\, \mathcal{V}_\downarrow^{\rm ext}(\boldsymbol{r})\, n_\downarrow(\boldsymbol{r}), \tag{2.74}$$

where

$$\mathcal{V}_{\uparrow}^{\mathrm{ext}}(\boldsymbol{r}) \equiv V^{\mathrm{ext}}(\boldsymbol{r}) + H^{\mathrm{ext}}(\boldsymbol{r}), \tag{2.75}$$

$$\mathcal{V}_{\downarrow}^{\mathrm{ext}}(\boldsymbol{r}) \equiv V^{\mathrm{ext}}(\boldsymbol{r}) - H^{\mathrm{ext}}(\boldsymbol{r}), \tag{2.76}$$

The proof of the SDFT analogue of the Hohenberg-Kohn theorem is almost the same as the original theorem. One can see that if $n_{\uparrow}$ and $n_{\downarrow}$ are spin densities for the ground state, no other pair of potentials $\mathcal{V}_{\uparrow}$ and $\mathcal{V}_{\downarrow}$ can produce the same ground-state spin-densities. Thus, $V_{\sigma}^{\mathrm{ext}}$ and $H_{\sigma}^{\mathrm{ext}}$ are also uniquely determined by $n_{\uparrow}$ and $n_{\downarrow}$. Therefore every physical quantity can be regarded as a functional of $n_{\uparrow}$ and $n_{\downarrow}$ in this formalism.

As for the Kohn-Sham scheme, the auxiliary system is chosen as follows:

$$\left[-\nabla^2 + V_{\mathrm{eff},\sigma}(\boldsymbol{r})\right] \psi_{i\sigma}(\boldsymbol{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\boldsymbol{r}), \tag{2.77}$$

and $V_{\sigma}^{\mathrm{eff}}$ are found to be

$$V_{\sigma}^{\mathrm{eff}}(\boldsymbol{r}) = V_{\mathrm{Hartree}}(\boldsymbol{r}) + V^{\mathrm{ext}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\boldsymbol{r})} \tag{2.78}$$

in a similar way to that of the Kohn-Sham equation of the DFT. In the following, we will discuss all theories within the SDFT.

2.2 Optimized effective potential

According to the equation (2.69), the exact exchange-correlation energy can be expressed formally in terms of Kohn-Sham orbitals, orbitals of a non-interacting auxiliary system, because one can expand $\langle\psi_{\lambda}|\lambda H_{\lambda}|\psi_{\lambda}\rangle$ in (2.69) in terms of the Kohn-Sham orbitals using the perturbation theory.

Thus, it is important to know a correct way to minimize such an exchange-correlation functional in terms of the Kohn-Sham orbitals. Sharp and Horton[5], and Talman and Shadwick[6] (SHTS) found that it is convenient to minimize such functionals with respect to the effective potential, and derived an equation that the resulting effective potential should obey. This potential is called optimized effective potential (OEP) following Talman and Shadwick.

However, this alone is not sufficient to obtain the effective potential. The proper treatment provided us with another necessary equation that is missing SHTS, which was first pointed out by the author and Akai[39]. The first subsection is dedicated to this subject.

2.2.1 Derivation of OEP equations

First, we define the auxiliary system of the Kohn–Sham scheme [7] as follows:

$$\left[-\nabla^2 + V_\sigma^{\mathrm{eff}}(\boldsymbol{r})\right]\psi_{i\sigma}(\boldsymbol{r}) = \epsilon_i \psi_{i\sigma}(\boldsymbol{r}), \tag{2.79}$$

$$n_\sigma(\boldsymbol{r}) = \int_{-\infty}^{\mu_\sigma} dE \sum_i \psi_{i\sigma}^*(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r})\delta(E-\epsilon_{i\sigma}). \tag{2.80}$$

In the previous section, we performed minimization of E_{KS} with respect to the Kohn-Sham orbitals, $\{\psi\}$, $\{\psi^*\}$ and the upper boundary of the energy integral μ. Here we are going to minimize E_{KS} with respect to V_σ^{eff} and μ_σ This is possible because n_σ is a functional of V_σ^{eff} and μ_σ, which follows from that the choice of the effective potential determines $\check{n}_\sigma(\boldsymbol{r}, E) \equiv \sum_i \psi_{i\sigma}^*(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r})\delta(E-\epsilon_{i\sigma})$ perfectly. As in the previous section we use a Lagrange multiplier to ensure that the total number of electrons is N:

$$I = E_{\mathrm{KS}} + \xi\left[\sum_\sigma \int_{-\infty}^{\mu_\sigma}\int \check{n}_\sigma(\boldsymbol{r}, E)\, d\boldsymbol{r}\, dE - N\right] \tag{2.81}$$

Although this approaches should yield the same result as the variation with respect to $\{\psi\}$, $\{\psi^*\}$ and μ_σ, which yield (2.78), the variation with respect to V_σ^{eff}, $\frac{\delta I}{\delta V_\sigma^{\mathrm{eff}}(\boldsymbol{r})} = 0$, yields a seemingly different Euler–Lagrange equation known as the OEP equation:

$$\sum_i \int d\boldsymbol{r}'[V_{\mathrm{xc},\sigma}(\boldsymbol{r}') - v_{\mathrm{xc},i\sigma}(\boldsymbol{r}')]G_{i\sigma}(\boldsymbol{r}', \boldsymbol{r})\psi_{i\sigma}^*(\boldsymbol{r}')\psi_{i\sigma}(\boldsymbol{r}) + \mathrm{c.c.} = 0, \tag{2.82}$$

where

$$G_{i\sigma}(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\{j|\epsilon_{j\sigma}\neq\epsilon_{i\sigma}\}} \frac{\psi_{j\sigma}^*(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}')}{\epsilon_{i\sigma}-\epsilon_{j\sigma}}, \tag{2.83}$$

$$V_{\mathrm{xc},\sigma}(\boldsymbol{r}) = V_\sigma^{\mathrm{eff}}(\boldsymbol{r}) - V_{\mathrm{Hartree}}(\boldsymbol{r}) - V_{\mathrm{ext}}(\boldsymbol{r}), \tag{2.84}$$

$$V_{\mathrm{Hartree}}(\boldsymbol{r}) = 2\sum_\sigma \int d\boldsymbol{r}' \frac{n_{\sigma'}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{2.85}$$

$$v_{xc,i\sigma}(\boldsymbol{r}) = \frac{1}{\psi_{i\sigma}^*(\boldsymbol{r})}\frac{\delta E_{\mathrm{xc}}}{\delta\psi_{i\sigma}(\boldsymbol{r})}. \tag{2.86}$$

Equation (2.82) has degrees of freedom that correspond to the choice of the energy origin for each spin. That is, if $V_{\mathrm{xc},\sigma}$ is the solution of the equation,

so is $V_{\mathrm{xc},\sigma} + \alpha_\sigma$, where α_σ is an arbitrary constant. Note that $\alpha_\uparrow$ and $\alpha_\downarrow$ are independent of each other, and hence, as things stand, we would have two degrees of freedom.

On the other hand, $\frac{\partial I}{\partial \mu_\sigma} = 0$ yields

$$\int d\boldsymbol{r}\ \{\xi - V_{\mathrm{xc},\sigma}(\boldsymbol{r})\}\, \check{n}_\sigma(\boldsymbol{r}, \mu_\sigma) + \frac{\partial E_{\mathrm{xc}}}{\partial \mu_\sigma} = 0. \tag{2.87}$$

Once a set of $V_{\mathrm{xc},\uparrow}$ and $V_{\mathrm{xc},\downarrow}$ that satisfies both equation (2.82) and equation (2.87) is fixed for a given ξ, there exists no other degrees of freedom that may give rise to a new solution for (2.87). Therefore it is clear that (2.87) fixes the difference between the additive constants that are permitted in (2.82). A possible procedure determining $V_{\mathrm{xc},\sigma}$ is the following: Let us denote one of sets satisfying (2.82) by $V'_{\mathrm{xc},\sigma}$. The difference between $V_{\mathrm{xc},\sigma}$ and $V'_{\mathrm{xc},\sigma}$ must be a constant α_σ, i.e., $V_{\mathrm{xc},\sigma} = V'_{\mathrm{xc},\sigma} + \alpha_\sigma$. Substituting these into (2.87) yields equation determining α_σ.

In the exact-exchange (EXX) case,

$$E_{\mathrm{xc}}^{\mathrm{EXX}} = -\sum_\sigma \int_{-\infty}^{\mu_\sigma} dE \int_{-\infty}^{\mu_\sigma} dE' \int d\boldsymbol{r}\, d\boldsymbol{r}'\, \frac{\check{n}_\sigma(\boldsymbol{r}, \boldsymbol{r}', E)\check{n}_\sigma(\boldsymbol{r}', \boldsymbol{r}, E')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{2.88}$$

(here, $\check{n}_\sigma(\boldsymbol{r}, \boldsymbol{r}', E) \equiv \sum_i \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}')\delta(E - \epsilon_{i\sigma})$), equation (2.87) becomes

$$\sum_i \delta(\mu_\sigma - \epsilon_{i\sigma}) \int d\boldsymbol{r}\ \{\xi - V_{\mathrm{xc},\sigma}(\boldsymbol{r}) + v_{\mathrm{xc},i\sigma}(\boldsymbol{r})\}\, \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}) = 0. \tag{2.89}$$

This equation is identical to the one proposed by Krieger, Li, and Iafrate[25] if the highest occupied orbital is not degenerate. In this case, ξ is equal to the so-called KLI constant of the highest occupied orbital. In the degenerate case, however, ξ is the average of the KLI constants of the highest occupied orbitals. According to Eq. (2.89), ξ should be common to both the spin directions. Equation (2.89) holds whenever the exchange-correlation functional satisfies the relation

$$\frac{\partial E_{\mathrm{xc}}}{\partial \mu_\sigma} = \sum_i \delta(\mu_\sigma - \epsilon_{i\sigma}) \int d\boldsymbol{r}\ v_{\mathrm{xc},i\sigma}(\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}). \tag{2.90}$$

Another example of the exchange-correlation functional that satisfies the above relation (2.90) is the one used by Kotani [23] wherein the static RPA level approximation was used for the correlation energy, which we will discuss later.

2.2.2 Modified KLI method

In the following calculations, we used the KLI approximation proposed by Krieger, Li, and Iafrate [24, 25] to solve equation (2.82). Among the several ways to reach their results, the most easiest one is to replace the denominator in the definition of the Green's function (2.83) with a constant Δ:

$$G_{i\sigma}(\boldsymbol{r},\boldsymbol{r}',E) = \sum_{\{j|\epsilon_j\neq\epsilon_i\}} \frac{\psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}')}{\epsilon_{i\sigma}-\epsilon_{j\sigma}} \tag{2.91}$$

$$\sim \frac{1}{\Delta}\sum_{\{i|\epsilon_j\neq\epsilon_i\}} \psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}') \tag{2.92}$$

$$= \frac{1}{\Delta}\left[\delta(\boldsymbol{r}-\boldsymbol{r}') - \sum_{\{i|\epsilon_j=\epsilon_i\}} \psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}')\right] \tag{2.93}$$

For the sake of simplicity of the argument, we only deal with a non-degenerate case until we reach the KLI equations. In the presence of degeneracy, the resulting equation can be transformed into the same form as non-degenerate case with a transformation of states to the principle axis (see appendices of [25]). To the extent of this assumption, the Green's function is approximated by

$$G_{i\sigma}(\boldsymbol{r},\boldsymbol{r}',E) \sim \frac{1}{\Delta}\left[\delta(\boldsymbol{r}-\boldsymbol{r}') - \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}')\right]. \tag{2.94}$$

Substituting this into (2.82), one obtains

$$\sum_i \left\{ n_{i\sigma}(\boldsymbol{r}) \left(V^{\mathrm{KLI}}_{\mathrm{xc},\sigma}(\boldsymbol{r}) - v_{\mathrm{xc},i\sigma}(\boldsymbol{r}) - \overline{V^{\mathrm{KLI}}_{\mathrm{xc},\sigma}} + \overline{v_{\mathrm{xc},i\sigma}} \right) \right\} + \mathrm{c.c.} = 0, \tag{2.95}$$

where $V^{\mathrm{KLI}}_{\mathrm{xc}}$ is the exchange-correlation part of the approximated OEP, $n_{i\sigma}(\boldsymbol{r})$ denotes

$$n_{i\sigma}(\boldsymbol{r}) \equiv \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}), \tag{2.96}$$

and the averages indicated by an overbar are defined as

$$\overline{V^{\mathrm{KLI}}_{\mathrm{xc},i\sigma}} \equiv \int d\boldsymbol{r}\, \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}) V^{\mathrm{S}}_{\mathrm{xc},i\sigma}(\boldsymbol{r}), \tag{2.97}$$

$$\overline{v_{\mathrm{xc},i\sigma}} \equiv \int d\boldsymbol{r}\, \psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r}) v_{\mathrm{xc},i\sigma}(\boldsymbol{r}). \tag{2.98}$$

When the approximated Kohn-Sham functional does not depend on unoccupied states, the summation in (2.95) is taken only for occupied states. In

this case the KLI potential can be expressed as a modification to the Slater potential $V_{\rm xc}^{\rm S}$, which is defined [4] as

$$V_{{\rm xc},\sigma}^{\rm S}(\boldsymbol{r}) \equiv \frac{\sum_{i\sigma}' n_{i\sigma}(\boldsymbol{r}) v_{{\rm xc},i\sigma}(\boldsymbol{r})}{\sum_{i\sigma}' n_{i\sigma}(\boldsymbol{r})}. \tag{2.99}$$

(The summation with a prime symbol is for the occupied states.)

Using $V_{\rm xc}^{\rm S}$, it follows from (2.95) that

$$V_{{\rm xc},\sigma}^{\rm KLI}(\boldsymbol{r}) = V_{{\rm xc},\sigma}^{\rm S}(\boldsymbol{r}) + \frac{\sum_{i\sigma}' n_{i\sigma}(\boldsymbol{r}) C_{i\sigma}}{\sum_{i\sigma}' n_{i\sigma}(\boldsymbol{r})}, \tag{2.100}$$

where $C_{i\sigma}$ represents $\overline{V_{{\rm xc},i\sigma}^{\rm KLI}} - \overline{v_{{\rm xc},i\sigma}}$, the so-called KLI constant for the state $i\sigma$. An equation that determines $C_{i\sigma}$ can be obtained by integrating (2.95) over whole the space. One reaches

$$\sum_i{}' (\delta_{ji} - M_{ji,\sigma}) C_{i\sigma} = (\overline{V_{{\rm xc},j\sigma}^{\rm S}} - \overline{v_{{\rm xc},j\sigma}}), \tag{2.101}$$

where M is defined by

$$M_{ji,\sigma} \equiv \int d\boldsymbol{r}\, \frac{n_{j\sigma}(\boldsymbol{r}) n_{i\sigma}(\boldsymbol{r})}{\sum_k' n_{k\sigma}(\boldsymbol{r})}. \tag{2.102}$$

Equation (2.101) still has an additional degree of freedom inherent in equation (2.82). If a set of $C_{i\sigma}$ is a solution for the equation, so is a set of $C_{i\sigma} + \alpha_\sigma$ where α_σ is an arbitrary constant. It is easy to deduce that this corresponds to

$$V_{{\rm eff},\sigma}^{\rm KLI}(\boldsymbol{r}) \to V_{{\rm eff},\sigma}^{\rm KLI}(\boldsymbol{r}) + \alpha_\sigma. \tag{2.103}$$

It can also be seen that there is no other degree of freedom in the KLI equation. In order to prove this, we can make use of the fact that, by adjusting the free constant indicated in (2.103), it is possible to obtain a solution whose last component is zero. Let A denote a matrix whose components are $A_{ij} = \delta_{ij} - M_{ij,\sigma}$. The equation that determines the rest of the components is an $\mathcal{N} \times (\mathcal{N} - 1)$ linear equation, where $\mathcal{N}$ is the size of the square matrix A. That is

$$\left.\begin{bmatrix} A_{11} & \cdots & A_{1,N_\sigma-1} \\ \vdots & \ddots & \vdots \\ \vdots & \ddots & \vdots \\ A_{N_\sigma,1} & \cdots & A_{N_\sigma,N_\sigma-1} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_{N_{\sigma-1}} \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ \vdots \\ 0 \end{bmatrix}\right\} N_\sigma. \tag{2.104}$$

If there is any extra freedom, the corresponding homogeneous equation should have solutions other than the trivial one. A necessary condition for this is that the matrix $I - M'$ is singular, where M' is formed by removing the last row and column from M. In the matrix form,

$$\begin{bmatrix} A_{11} & \cdots & A_{1,N_\sigma-1} \\ \vdots & \ddots & \vdots \\ A_{N_\sigma-1,1} & \cdots & A_{N_\sigma-1,N_\sigma-1} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_{N_{\sigma-1}} \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}. \tag{2.105}$$

Now, consider a matrix $F = \sum_{n=0}^{\infty} M'^n$. Since $\left[\max_j \sum_i M'_{ji}\right]^{-1} > 1$, F is finite. However, F is nothing but the inverse of the matrix $I - M'$ as long as F converges, and hence, $I - M'$ cannot be singular. This proves that there is no extra degree of freedom other than the one implied by (2.103).

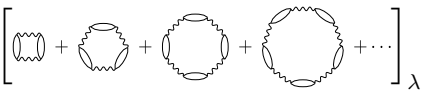
The original KLI scheme contains a method to fix this degree of freedom. Although, from the viewpoint of the equation (2.87), their method is not always correct. However, replacing their method with correct one using (2.87) does not introduce any difficulty in practical calculations. To obtain a solution that satisfies (2.101) and (2.87) simultaneously, we solve (2.101) under the condition that one of the components of the solution is fixed. Then, we choose the additive constants α_σ such that the solution satisfies equation (2.87) with $\xi \to 0$. In this limit, and under the condition that the equation (2.90) holds and the highest occupied orbital is not degenerate, our scheme is identical to the KLI approximation [25].

2.2.3 RPA-level correlation

Using the approach of the adiabatic connection of the DFT, the exact exchange-correlation functional is expressed as (2.69),

$$E_{\mathrm{xc}} = \int_0^1 \frac{d\lambda}{\lambda} \langle \Psi_\lambda | \lambda H_{\mathrm{int}} | \Psi_\lambda \rangle - E_{\mathrm{Hartree}}. \tag{2.106}$$

The first term can be expanded in terms of Kohn-Sham orbitals using the perturbation theory, and the diagrammatic analysis is available to treat this problem. As in the many-body electron analysis, the random phase approximation will be a good starting point to analyze the correlation energy in extended system such as solids. Thus, we use the RPA diagram as follows.

$E_{\mathrm{c}}^{\mathrm{RPA}} = \int_0^1 \frac{d\lambda}{\lambda}$  $\Big]_\lambda$, (2.107)

where the subscript λ means that every wavy line, which indicates the interaction, is accompanied by a single coefficient λ.

It will be helpful to define a product of functions. We use 4-component space-time variable in the following, like $x \equiv (\boldsymbol{r}, t)$. Using this, the product of $f(x, x')$ and $g(x, x')$ is define as

$$fg(x_1, x_2) \equiv \int dx' f(x_1, x') g(x', x_2). \tag{2.108}$$

The identity function $1(x, x')$ is defined as $1(x, x') = \delta(x - x')$ so as to $f1 = 1f$, and a superior -1 is used for indicating the inverse of a function f: $ff^{-1} = f^{-1}f = 1$.

Trace of a function is also useful. Let Tr denote

$$\mathrm{Tr}[f] = \int dx f(x, x). \tag{2.109}$$

It is easy to see that

$$\mathrm{Tr}[fg] = \int dx dx' f(x, x') g(x', x) \tag{2.110}$$

$$= \int dx' dx\, g(x', x) f(x, x') = \mathrm{Tr}[gf], \tag{2.111}$$

thus a product of functions can be cyclically exchanged without changing the value of the trace as in the trace of matrices.

The solid lines in (2.107) all form a ring diagram. Using notations of the Appendix B.1, the ring polarization insertion can be expressed as

$$D(x, x') = \tag{2.112}$$

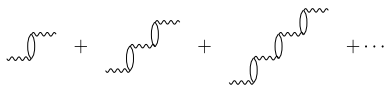
$$= \sum_{\sigma} D^0_{\sigma}(x, x'). \tag{2.113}$$

The formula for the bare coulomb interaction v, which is denoted by wavy line in diagrams, can be written as

$$v(x, x') = \frac{2}{|\boldsymbol{r} - \boldsymbol{r}'|} \delta(t - t'). \tag{2.114}$$

Then, let us define the screened coulomb interaction W as

$$W = \tag{2.115}$$

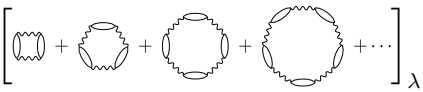


$$= [1 - vD]^{-1} v - v \tag{2.116}$$

$$= [1 - vD]^{-1} vDv. \tag{2.117}$$

Using these, $E_{\mathrm{c}}^{\mathrm{RPA}}$ can be expressed as

$$E_{\mathrm{c}}^{\mathrm{RPA}} = \int_0^1 \frac{d\lambda}{\lambda} \Bigg[\tag{2.118}$$



$$= \int_0^1 \frac{d\lambda}{\lambda} \mathrm{Tr}\left[W_\lambda D\right]. \tag{2.119}$$

This expression will be useful when we discuss the static approximation for the variation of $E_{\mathrm{c}}^{\mathrm{RPA}}$ later. The integration with respect to λ can be performed beforehand, using

$$\int_0^1 \frac{d\lambda}{\lambda} W_\lambda D = \int_0^1 \left\{(1 - \lambda vD)^{-1} - 1\right\} vD \, d\lambda \tag{2.120}$$

$$= -\log(1 - vD) - vD, \tag{2.121}$$

where the logarithm is defined by $\log(1 - A) = -\sum_{n=1}^{\infty} \frac{A^n}{n}$. Thus, $E_{\mathrm{c}}^{\mathrm{RPA}}$ can be also expressed as

$$E_{\mathrm{c}}^{\mathrm{RPA}} = -\mathrm{Tr}[\log(1 - vD) + vD]. \tag{2.122}$$

Before moving on to the approximation, let us consider variation of the $E_{\mathrm{c}}^{\mathrm{RPA}}$ with respect to D and derivative with respect to λ . For this purpose, it is helpful to use $X_\lambda = v_\lambda D$. Using this, $W_\lambda D$ can be expressed as

$$W_\lambda D = (1 - X_\lambda)^{-1} X_\lambda^2. \tag{2.123}$$

First, let us consider the variation of $B = (1 - A)^{-1}$ when A is varied as $A \to A + \delta A$. It is easy to verify

$$\delta B = B(\delta A)B, \tag{2.124}$$

seeing that $(1 - A - \delta A)(B + \delta B) = (B^{-1} + \delta A)(B + \delta B) = 1$ holds up to the first order of variations.

As for the derivative with respect to A, one obtains

$$dB = B(dA)B \tag{2.125}$$

in a similar way to that of the variation.

Using these and (2.111), the variation of the trace of $W_\lambda D$ is expressed as

$$\begin{aligned}\delta \mathrm{Tr}\left[W_\lambda D\right] &= \mathrm{Tr}\left[\delta(1-X_\lambda)^{-1}X_\lambda^2 + (1-X_\lambda)^{-1}\delta X_\lambda^2\right] &(2.126)\\ &= \mathrm{Tr}\left[\left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}\delta X_\lambda\right]. &(2.127)\end{aligned}$$

As for the derivative, we need not to take the trace in order to arrange terms as in (2.127) because $dX_\lambda = Xd\lambda$ commutes with X_λ. Thus,

$$\begin{aligned}d\left[(1-X_\lambda)^{-2}X_\lambda^2\right] &= \left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}dX_\lambda &(2.128)\\ &= \left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}d\lambda\, X. &(2.129)\end{aligned}$$

Noting that $X_{\lambda=0} = 0$, it is seen that the integration over $0 \le \lambda \le 1$ yields

$$(1-X)^{-2}X^2 = \int_0^1 \left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}d\lambda\, X. \tag{2.130}$$

Therefore, using these and $\delta X_\lambda = \lambda\delta X$,

$$\begin{aligned}\delta E_{\mathrm{c}}^{\mathrm{RPA}} &= \int_0^1 \frac{d\lambda}{\lambda}\,\delta\mathrm{Tr}\left[W_\lambda D\right] &(2.131)\\ &= \int_0^1 \frac{d\lambda}{\lambda}\,\mathrm{Tr}\left[\left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}\delta X_\lambda\right] &(2.132)\\ &= \int_0^1 d\lambda\,\mathrm{Tr}\left[\left\{(1-X_\lambda)^{-2}X_\lambda^2 + 2(1-X_\lambda)^{-1}X_\lambda\right\}XX^{-1}\delta X\right] &(2.133)\\ &= \mathrm{Tr}\left[(1-X)^{-1}X\delta X\right] &(2.134)\\ &= \mathrm{Tr}\left[W\delta D\right]. &(2.135)\end{aligned}$$

Thus, all δD's in the variation are arranged and put together to only one δD. In addition, it is seen that the integral of λ in (2.131) have not to be performed when calculating only the correlation part of the OEP, $V_{\mathrm{c}}^{\mathrm{RPA}} = \frac{\delta E_{\mathrm{c}}^{\mathrm{RPA}}}{\delta n}$.

Static approximation However, calculation based directly on the equation (2.135) still takes too much computational time for our purpose because

we need to construct the OEPs many times until the potential converges and satisfies both (2.82) and (2.87).

Therefore, we adopt the static approximation, which greatly reduces the computational time. Let the tilde symbol denote a Fourier transform of time domain (A.3) of a function like $\tilde{f}(\omega)$. If $\tilde{W}$ varies slowly enough with respect to ω, W can be approximated accurately as

$$W(\boldsymbol{r}, \boldsymbol{r}', \tau) = \frac{1}{2\pi} \int d\omega e^{-i\omega\tau} \tilde{W}(\boldsymbol{r}, \boldsymbol{r}', \omega) \tag{2.136}$$

$$\sim \tilde{W}(\boldsymbol{r}, \boldsymbol{r}', 0) \int d\omega\, e^{-i\omega\tau} \tag{2.137}$$

$$= \tilde{W}(\boldsymbol{r}, \boldsymbol{r}', 0)\, \delta(t - t'). \tag{2.138}$$

Using this, the variation of the correlation energy becomes

$$\delta E_{\mathrm{c}}^{\mathrm{sRPA}} = \mathrm{Tr}\left[\tilde{W}(\boldsymbol{r}, \boldsymbol{r}', 0)\delta(t - t')\delta D(\boldsymbol{r}', \boldsymbol{r}, t' - t)\right] \tag{2.139}$$

$$= \int d\boldsymbol{r}\, d\boldsymbol{r}' \tilde{W}(\boldsymbol{r}, \boldsymbol{r}', 0)\delta D(\boldsymbol{r}', \boldsymbol{r}, 0). \tag{2.140}$$

Within this approximation, all the integrations with respect to time and frequency vanish. Thus, hereafter, let the integrations indicated by the product of the functions and Tr be performed only for the space, and omit the time and frequency variables whenever they are zero, so that

$$\delta E_{\mathrm{c}}^{\mathrm{sRPA}} = \int d\boldsymbol{r} \int d\boldsymbol{r}' \tilde{W}(\boldsymbol{r}, \boldsymbol{r}', 0)\delta D(\boldsymbol{r}', \boldsymbol{r}, 0) = \mathrm{Tr}\left[\tilde{W}\delta D\right]. \tag{2.141}$$

It can be seen that only $\omega = 0$ component of the polarization insertion $\tilde{D}(\boldsymbol{r}, \boldsymbol{r}, \omega)$ is included in $\tilde{W}$ above. It follows from the relation of a Fourier transform of a convolution that

$$\tilde{W}(\boldsymbol{r}, \boldsymbol{r}') = \left([\tilde{1} - \tilde{v}\tilde{D}]^{-1}\tilde{v}\tilde{D}\tilde{v}\right)(\boldsymbol{r}, \boldsymbol{r}'), \tag{2.142}$$

where $\tilde{D}$ denotes the function $\tilde{D}(\boldsymbol{r}, \boldsymbol{r}', 0)$ along to the notation we have just made. Therefore, the equation (2.141) contains two kinds of the polarization insertion, D and $\tilde{D}$. Calculations of both two are summarized in the appendix B.1. It can be seen from (B.12) that D depends only on density of the system. Therefore, the numerical calculation related to D is not very difficult because it consists of the occupied orbitals. Note that the variation of the correlation energy is attributed only to δD in (2.141). Therefore, the use of the KLI approximation for this functional is justified and one can see that the relation (2.90) holds for the correlation as well as EXX.

Static polarization insertion However, as for $\tilde{D}$ we need to devise a efficient way to calculate. It follows from (B.21) that

$$\begin{aligned}
\tilde{D}_\sigma(\boldsymbol{r},\boldsymbol{r}') &= 2\sum_{i,j}\frac{\theta(\epsilon_{i\sigma}-\epsilon_F)\theta(\epsilon_F-\epsilon_{j\sigma})}{\epsilon_{j\sigma}-\epsilon_{i\sigma}+i\eta} \\
&\quad\times\psi_{i\sigma}(\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r}')\psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}') && (2.143)\\
&= \int_{\epsilon_F}^{\infty}dE\int_{-\infty}^{\epsilon_F}dE'\frac{2}{E'-E+i\eta}\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)\,\check{n}_\sigma(\boldsymbol{r}',\boldsymbol{r},E') && (2.144)\\
&= 2\int_{-\infty}^{\epsilon_F}dE'\,\check{n}_\sigma(\boldsymbol{r}',\boldsymbol{r},E')\int_{\epsilon_F}^{\infty}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E'-E+i\eta} && (2.145)\\
&= 2\int_{-\infty}^{\epsilon_F}dE'\,\check{n}_\sigma(\boldsymbol{r}',\boldsymbol{r},E')\,f(\boldsymbol{r},\boldsymbol{r}',E'), && (2.146)
\end{aligned}$$

where f is defined as $f(\boldsymbol{r},\boldsymbol{r}',E') = \int_{\epsilon_F}^{\infty}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E'-E+i\eta}$. Due to the existence of f, it seems that the calculation of $\tilde{D}$ must involve unoccupied Kohn-Sham orbitals, which can cause problems if there is no clear criterion of choosing finite set of the unoccupied orbitals that are taken into account. This can be avoided as follows. First, f is transformed as

$$\begin{aligned}
f(\boldsymbol{r},\boldsymbol{r}',E') &= \int_{\epsilon_F}^{\infty}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E'-E+i\eta} && (2.147)\\
&= \int_{-\infty}^{\infty}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E'-E+i\eta} - \int_{-\infty}^{\epsilon_F}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E'-E+i\eta} && (2.148)\\
&= G^{\mathrm{R}}_\sigma(\boldsymbol{r},\boldsymbol{r}',E') + \int_{-\infty}^{\epsilon_F}dE\,\frac{\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'-i\eta}. && (2.149)
\end{aligned}$$

Second, in order to deform the path of the integration of the second term onto upper half of the complex plane, one can use $\check{n}_\sigma(\boldsymbol{r},\boldsymbol{r}',E) = -\frac{1}{\pi}\mathrm{Im}\,G^R(\boldsymbol{r},\boldsymbol{r}',E)$ and the following relation:

$$\begin{aligned}
\mathrm{Im}\left[\frac{z}{\epsilon+i\eta}\right] &= \frac{\mathrm{Im}z}{\epsilon-i\eta} - z\frac{\eta}{\epsilon^2+\eta^2} && (2.150)\\
&\to \frac{\mathrm{Im}z}{\epsilon-i\eta} + i\pi z\delta(\epsilon)\ (\eta\to 0). && (2.151)
\end{aligned}$$

Finally, using these, f becomes

$$
\begin{aligned}
f(\boldsymbol{r},\boldsymbol{r}',E') &= G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E') - \frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\epsilon_F} dE\,\frac{G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta} \\
&\quad - \int_{-\infty}^{\epsilon_F} dE\,\delta(E-E')G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E) \qquad (2.152)\\
&= G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E') - \frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\epsilon_F} dE\,\frac{G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta} \\
&\quad - \theta(\epsilon_F-E')G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E) \qquad (2.153)\\
&= \theta(E'-\epsilon_F)G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E') - \frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\epsilon_F} dE\,\frac{G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta}. \qquad (2.154)
\end{aligned}
$$

Now, the first term does not contribute to (2.146), and it seems possible to deform the path of the second term onto the upper half-plane.

However, there are two points of which we should be careful concerning the second term. First, if η in the second term is the same variable as the infinitesimal energy shift of G^{R}_{σ} in the denominator, the integrand of this term has poles of 2nd order, and thus the integral can not be defined. This ill-behavior is due to the addition of $\int_{-\infty}^{\epsilon_F}\frac{\check{n}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta}dE$ in (2.148) and replacing $\check{n}$ with $-\frac{1}{\pi}\mathrm{Im}\,G^{\mathrm{R}}_{\sigma}$. However, this η does not have to be identical with that of the Green's function because (2.147) itself is independent from the infinitesimal variable in the Green's function which corresponds to the $\check{n}$ as long as the additional term converges to $\sum_i \theta(\epsilon_F-\epsilon_{i\sigma})\frac{n_{i\sigma}(\boldsymbol{r},\boldsymbol{r}')}{\epsilon_{i\sigma}-E'+i\eta}$. Thus, use of a path in upper analytic half-plane that detour the poles is justified because all the poles can be regarded as of first order.

Second, the numerical treatment of the second term is difficult when dealt as a function of E'. This is because the singular function $\frac{1}{\epsilon_{i\sigma}-E'+i\eta}$ will be left after integration with respect to E due to $\check{n}_{\sigma}$ which is contained in G^{R}_{σ}. This problem will be solved if the path of E' in the equation (2.146) is deformed so as to detour the poles on the real axis of E'. However, deformation of a path is allowed only when the integrand is analytic in a region that covers the trace of deformed path. Therefore, we have to replace the integrand with an analytic continuation of itself in order to deform the path.

We have found such an analytic continuation as follows. First, an imaginary part of a function $g(x)$ can be expressed as $\mathrm{Im}[g(x)] = g(x) - \overline{g(x)}$ when x is real. Think of $g(z)$ that is a continuation of $g(x)$ and analytic in the upper half-plane. Using $\overline{g(\overline{z})}$ which is defined and analytic in lower half-plane, this is expressed as $\mathrm{Im}[g(x)] = \lim_{z\to x+i0} g(z) - \overline{g(\overline{z})}$. Thus, the

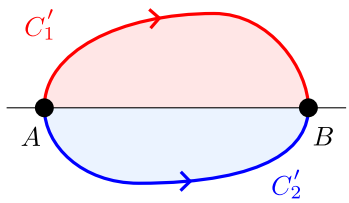


Figure 2.5: The paths of the integral in (2.156). When $g(z)$ is analytic in a region in the upper half-plan, $\overline{g(\overline{z})}$ is defined in the conjugate region in the lower half-plane and one can show that this function is also analytic in the domain. Thus, the value of the integrals does not depend on the paths as long as both the region cut by C_1' and real axis (pink region) and the region cut by C_2' and real axis (light blue region) do not contain any singularities of the functions.

integration of $g(x)$ for $A < x < B$ can be transformed into the sum of the two integrals along C_1' and C_2' that are on the upper and lower half-plane respectively, and that start from point A and end at point B (See fig.2.5):

$$\mathrm{Im}\int_A^B g(x)dx = \lim_{z\to x+i0}\left\{g(z) - \overline{g(\overline{z})}\right\} \tag{2.155}$$

$$= \int_{C_1'} g(z)dz - \int_{C_2'} \overline{g(\overline{z})}dz. \tag{2.156}$$

The direct application of this to the second term of (2.154) gives

$$-\frac{1}{2i}\left[\int_{C_1} dE\frac{G_\sigma^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta} - \int_{C_2} dE\frac{\overline{G_\sigma^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\overline{E})}}{E-\overline{E'}-i\eta}\right], \tag{2.157}$$

which itself is not an analytic function of E'. However, it is clear that the following function

$$F(\boldsymbol{r},\boldsymbol{r}',E') \equiv -\frac{1}{2i}\left[\int_{C_1} dE\frac{G_\sigma^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',E)}{E-E'+i\eta} - \int_{C_2} dE\frac{\overline{G_\sigma^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\overline{E})}}{E-E'-i\eta}\right] \tag{2.158}$$

is analytic as a function of E' and identical with the (2.154) on the real axis of E', where C_1 is a path from $-\infty$ (which can be replaced with any energy below the energy of the lowest occupied orbital) to ϵ_F on the upper-half plane and C_2 on the lower-half plane.

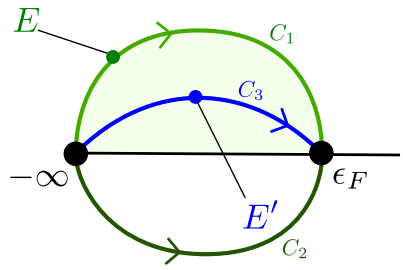


Figure 2.6: The paths in (2.162) projected to one complex plane.

Using $F(\boldsymbol{r}, \boldsymbol{r}', E')$ and noting that this function is real when E' is real, the equation(2.146) can be transformed to the following expression:

$$\tilde{D}_\sigma(\boldsymbol{r}, \boldsymbol{r}') = 2 \int_{-\infty}^{\epsilon_F} dE' \, \check{n}_\sigma(\boldsymbol{r}', \boldsymbol{r}, E') \, F(\boldsymbol{r}, \boldsymbol{r}', E') \tag{2.159}$$

$$= -\frac{2}{\pi} \int_{-\infty}^{\epsilon_F} dE' \, \mathrm{Im} \left[G_\sigma^{\mathrm{R}}(\boldsymbol{r}', \boldsymbol{r}, E') \right] F(\boldsymbol{r}, \boldsymbol{r}', E') \tag{2.160}$$

$$= -\frac{2}{\pi} \mathrm{Im} \left[\int_{-\infty}^{\epsilon_F} dE' \, G_\sigma^{\mathrm{R}}(\boldsymbol{r}', \boldsymbol{r}, E') \, F(\boldsymbol{r}, \boldsymbol{r}', E') \right]. \tag{2.161}$$

Now, we are prepared for deforming the path of this integral. The path should not cross C_1 projected to the complex plane of E' because $F(\boldsymbol{r}, \boldsymbol{r}', E')$ is singular at the crossing point, and simultaneously the path should be on the upper-half plane because the integral contains the retarded Green's function (See fig.2.6). Let C_3 denote one of such a path, then finally we obtain

$$\tilde{D}_\sigma(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{\pi} \mathrm{Re} \left[\int_{C_3} dE' \, G_\sigma^{\mathrm{R}}(\boldsymbol{r}', \boldsymbol{r}, E') \right.$$
$$\left. \times \left\{ \int_{C_1} dE \frac{G_\sigma^{\mathrm{R}}(\boldsymbol{r}, \boldsymbol{r}', E)}{E - E' + i\eta} - \int_{C_2} dE \frac{\overline{G_\sigma^{\mathrm{R}}(\boldsymbol{r}, \boldsymbol{r}', \overline{E})}}{E - E' - i\eta} \right\} \right]. \tag{2.162}$$

The path C_2 can be chosen to be identical with the conjugate path of C_1. In this case, the integral in the curly brackets need only the information of the values of G^{R} on C_1. The integral with respect to E', however, involves G^{R} on the different path C_3. Therefore, we need the values of G^R on two paths on the upper-half plane. The Korringa-Kohn-Rostoker(KKR) Green's function method is convenient for this purpose because it can directly calculate the retarded Green's function of complex energies on the upper-half plane.

Energy calculation Besides the ground-state density, the ground-state energy is another quantity that the Kohn-Sham scheme enables us to calculate. Thus, it is also important to calculate the $E_{\mathrm{c}}^{\mathrm{RPA}}$ itself in order to obtain the total energy. In the following calculation, we applied (2.138) also to the $E_{\mathrm{c}}^{\mathrm{RPA}}$, i.e.,

$$E_{\mathrm{c}}^{\mathrm{sRPA}} = \int_0^1 \frac{d\lambda}{\lambda} \mathrm{Tr}\left[\tilde{W}_\lambda D\right]. \tag{2.163}$$

It should be remarked that one can not obtain (2.141) from this equation because variation of this involves both the variation of D and $\tilde{D}$. However, as far as the static approximation to the screened Coulomb interaction is valid, this approximation is also efficient and this does not harm to the results of the calculation very much.

An approximation to the expression (2.122) of $E_{\mathrm{c}}^{\mathrm{RPA}}$ may be also possible. However, we adopted the direct calculation of (2.163) in the following. There are three main reasons for this. First, it seems difficult to devise a simple and physically transparent approximation to (2.122), which must be consistent with the approximation for the variation of the correlation energy. Second, the λ-dependence of the integrand of (2.69) is an interesting information of the system. For example, the hybrid functional methods can be theoretically justified as approximations to the integrand as mentioned in the first chapter. Third, it is easy to implement the method because one can reuse the module that generates $\tilde{W}$ with a little modification in order to calculate $\tilde{W}_\lambda$. Admittedly, it takes long time to calculate many W_λ's for various λ in $0 \leq \lambda \leq 1$. However, this calculation is performed once for all after the convergence of the potential, and it will take much less time than the whole calculation process. Thus, one may put higher priority on the reliability over the efficiency of the calculation.

Chapter 3

Results

3.1 Exact exchange

First, we apply the method described in the previous chapter to crystalline alkali metals with the exchange-only E_{xc} using the atomic sphere approximation (ASA) for the shape of the effective potentials. The results of the calculation without correlation terms may not be very different from those which includes the correlation energy for such systems. This provides a stringent test for the method because the incorrect treatment of the additive constants can easily yield an artificial magnetic field. This occasionally allows an unphysical magnetization to remain after the convergence of a self-consistent procedure.

The total density of states (DOS) of Li, Na, and K are shown in figure3.1. As expected, all of them are nonmagnetic. We confirmed that neither the local nor the global energy minima existed for any magnetic solutions.

We also calculated the electronic structures of ferromagnetic Fe and antiferromagnetic MnO within the same framework. The results can be compared with those obtained by Kotani and Akai [40], who performed calculations using the KKR–EXX method.

Figure 3.2 shows the exchange potential obtained by the present scheme. The V_{x} graphs have shallow dips around $r = 0.5$ (a.u.), which corresponds to exchange holes. The dip turns out to be shallower than that obtained in [40].

The total DOS of these systems are shown in figure 3.3. Although the exchange splitting of our results seems slightly smaller than those in [40], the overall agreement between the two is satisfactory. This implies that, at least

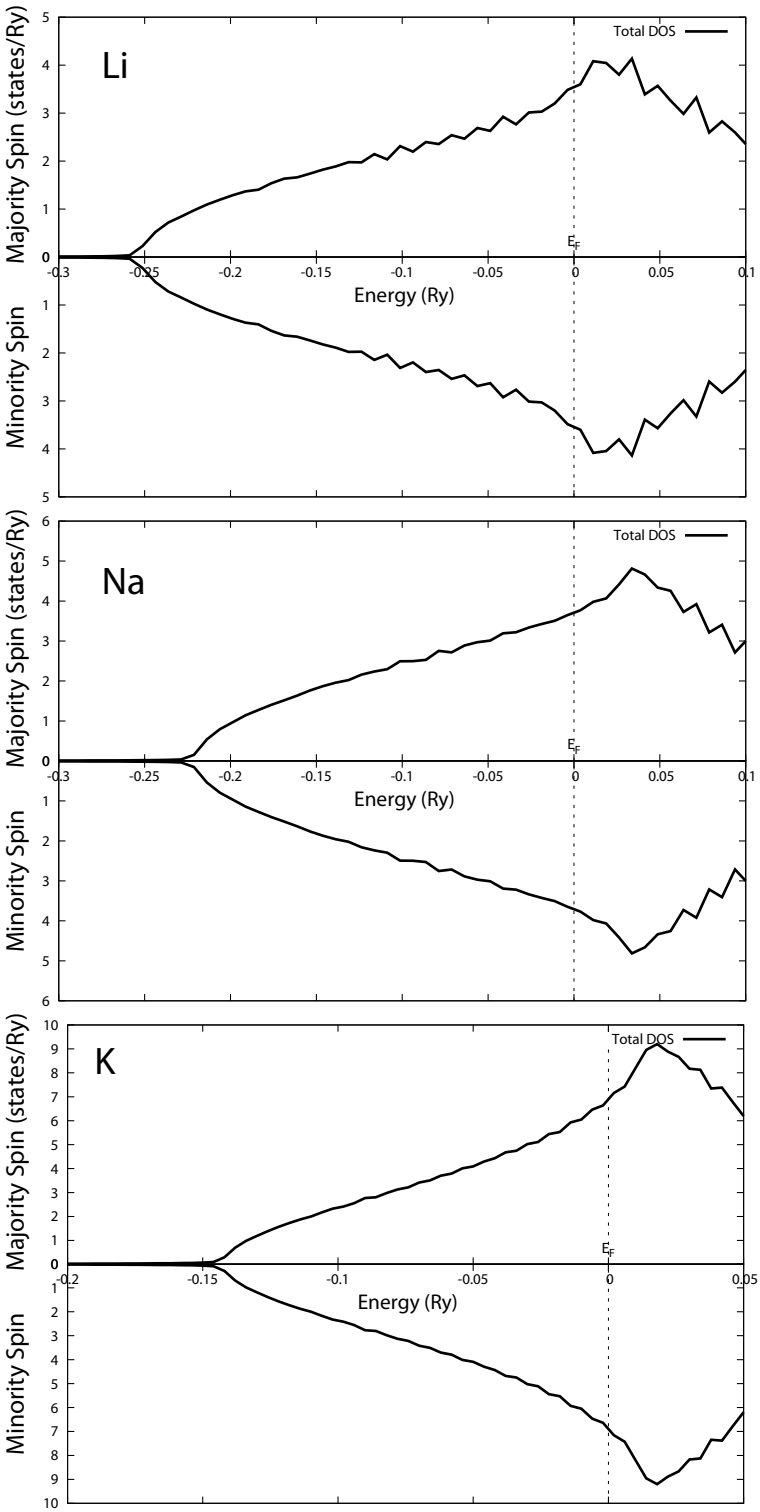


Figure 3.1: Total DOS of Li, Na, and K calculated by using modified KLI method (see 2.2.2) in combination with the KKR method within the framework of the EXX.

for these systems, using the KLI method does not affect the features of the OEP significantly.

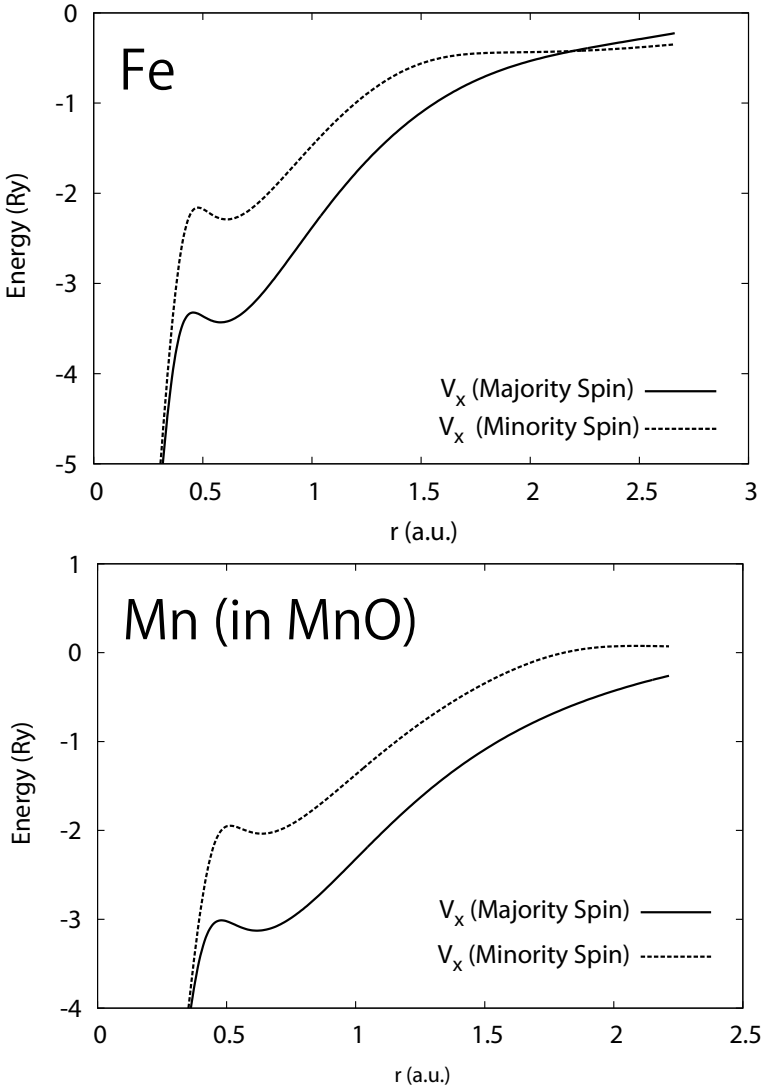


Figure 3.2: Exchange potentials of Fe and MnO calculated by the modified KLI method (see 2.2.2) within EXX.

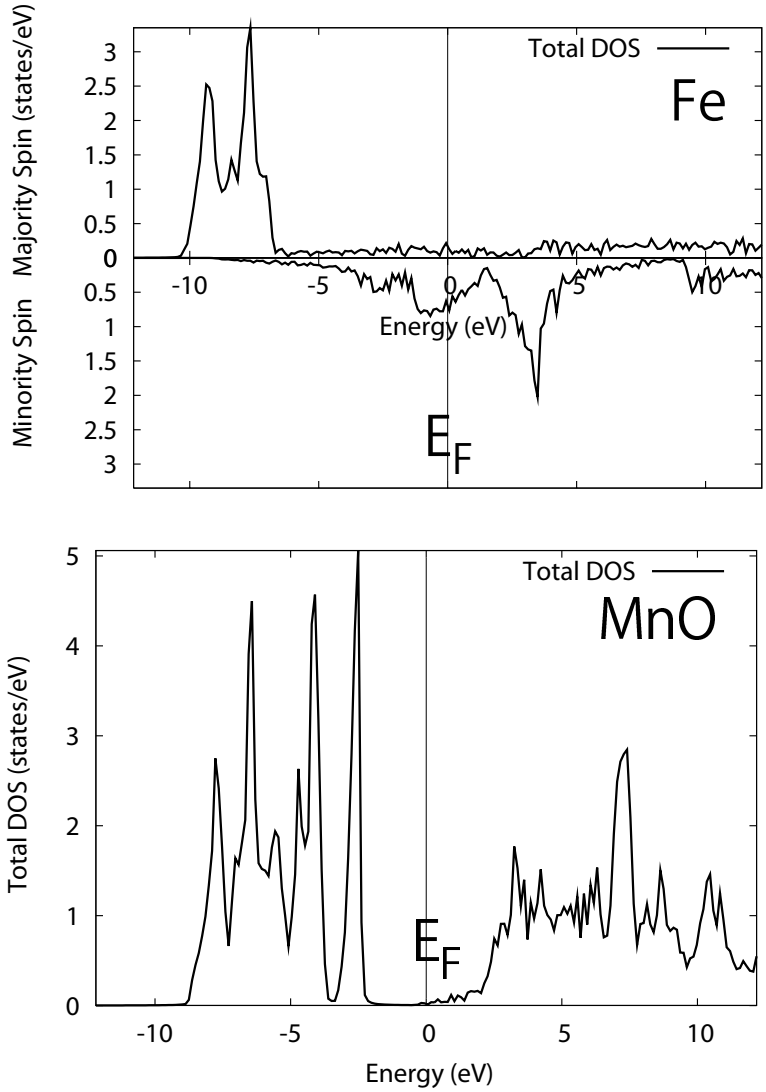


Figure 3.3: Total DOS of Fe and MnO calculated by the modified KLI method (see 2.2.2) within EXX.

3.2 Test calculation of technique for static RPA-correlation-energy

We performed test calculations in order to see the efficiency of our new method to calculate the static polarization insertion. As representative examples, we chose two model Green's functions.

The first model Green's function is

$$G_1(E) = \frac{1}{E + A + i\eta} + \frac{1}{E - A + i\eta}, \tag{3.1}$$

whose imaginary part consists of two delta-functions (See figure 3.2):

$$\check{n}_1(E) = \mathrm{Im}\, G_1(E) = -\frac{1}{\pi}\{\delta(E - A) + \delta(E + A)\}. \tag{3.2}$$

The second one is

$$G_2(E) = \log\left(\frac{E + B + C}{E - B + C}\right) + \log\left(\frac{E + B - C}{E - B - C}\right), \tag{3.3}$$

whose imaginary part consists of two box-shaped functions (See figure 3.2):

$$\begin{aligned} \check{n}_2(E) &= \mathrm{Im}\, G_2(E) \\ &= -\frac{1}{\pi}[\{\theta(E + B + C) - \theta(E - B + C)\} \\ &\quad + \{\theta(E + B - C) - \theta(E - B - C)\}]. \end{aligned} \tag{3.4}$$

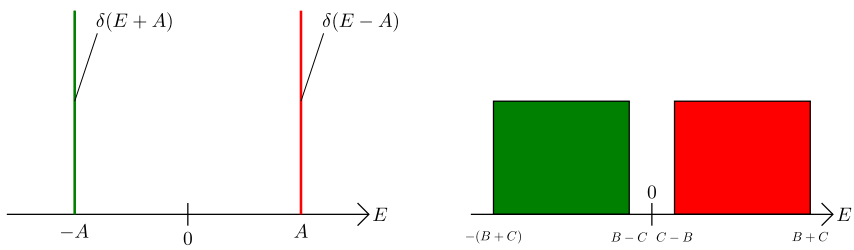


Figure 3.4: The imaginary part of the model Green's function of (3.1) (Left) and of (3.3) (Right). In the calculations, the green region was treated as occupied states, and red as unoccupied.

Using these, the calculations based on (2.162) (hereafter, "new method") are compared with those based on (2.145) (hereafter, "direct method"). The values $A = 0.5$, $B = 0.5$ and $C = 0.55$ are used and the Fermi energy is set $\epsilon_F = 0$ in the calculation. For the direct method, the path of the integral is shifted upward by 10^{-3} in order to detour poles of the integrand. Correspondingly, the end point of the path of the integral for new method is also shifted by 10^{-3}.

The model Green's functions are simple enough to calculate the exact value of the polarization insertion $\tilde{D}$ using (2.145). Thus relative errors of each calculations are also available. The log-log graphs in figure 3.5 shows that the relative error decreases as the number of energy mesh used in the numerical integration increases.

The top graph in figure 3.5 is of the model Green's function G_1. Both methods reduce the relative error, as the number of mesh increases. However, it can be seen that the new method is much more efficient than the direct method. This is not surprising because the integration of δ-function along near the real axis is extremely hard.

On the contrary, the imaginary part of the second model Green's function is smooth along the real axis. However, as shown in the bottom graph in figure 3.5, the new method is still more efficient than the direct method. This is because new method can use mesh, which is fine near the real axis and coarse far from the real axis. This feature greatly improves the precision of the integration because all poles are located on the real axis in the calculation.

3.3 EXX+RPA

We have also implemented the RPA-level calculation in the KKR code using the new method to calculate the polarization insertion. During the construction of the correlation functional, the Kohn-Sham orbitals are coarse-grained in order to accelerate the calculation. We found that the loss of precision was insignificant for final results when the number of the radial mesh was reduced from 400 to 200. Thus, we applied this to all the calculations in the following.

The figure 3.6 shows comparison of the total DOS of ferromagnetic Fe with that of the LDA, which is considered to be accurate enough for this system. The result can be also compared with that of the EXX calculation, which is given in the top graph of figure 3.3. The results of EXX calculation

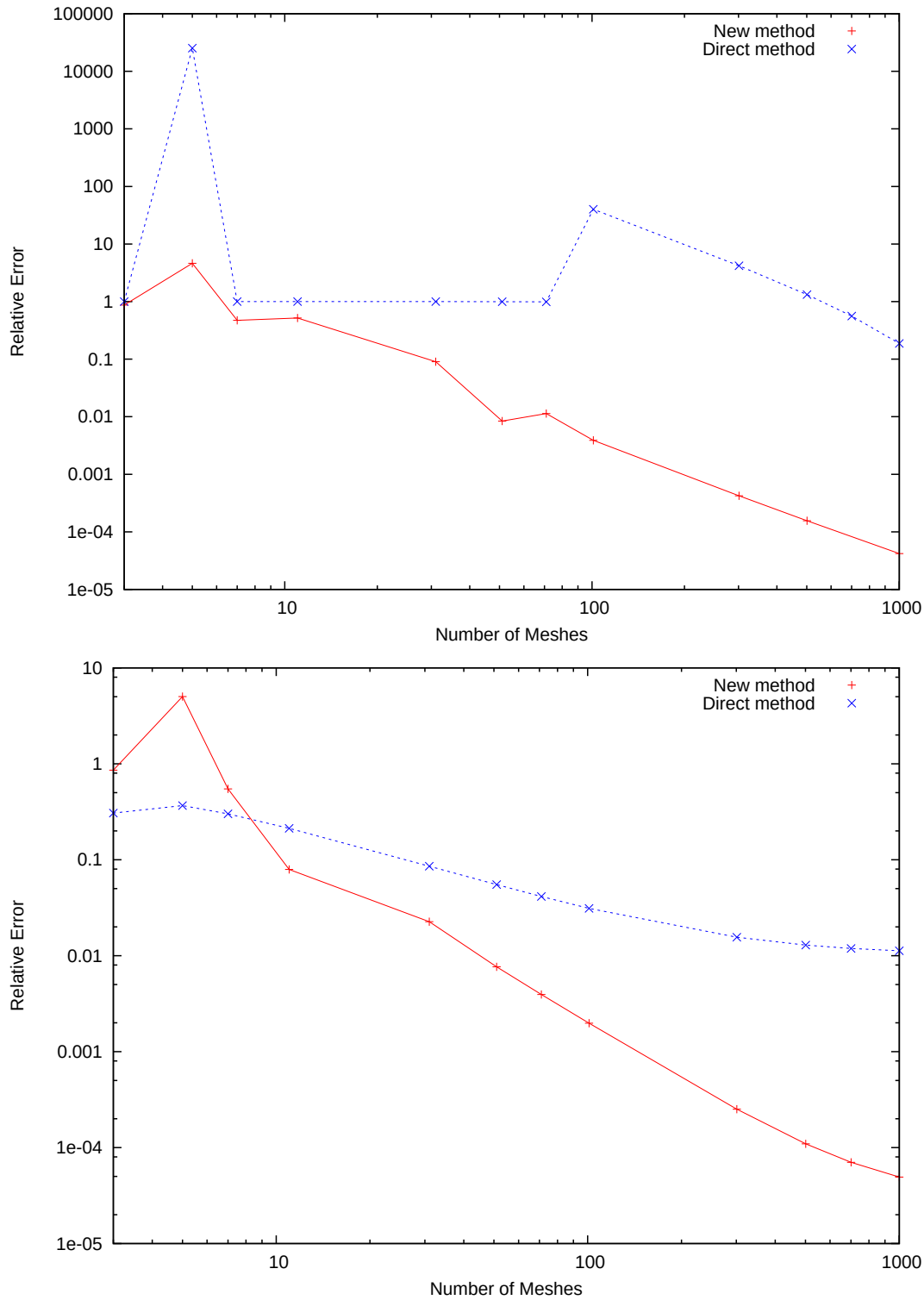


Figure 3.5: The log-log plots of the relative errors of the calculated polarization insertion versus the number of mesh for numerical integration. In the calculation, (top) the model Green's function G_1 and (bottom) G_2 are used.

shows that the splitting of up- and down-spin states are too large compared with that of the LDA. Our new method (EXX+RPA), which takes account of the RPA-level correlation, produces a similar result as that of the LDA.

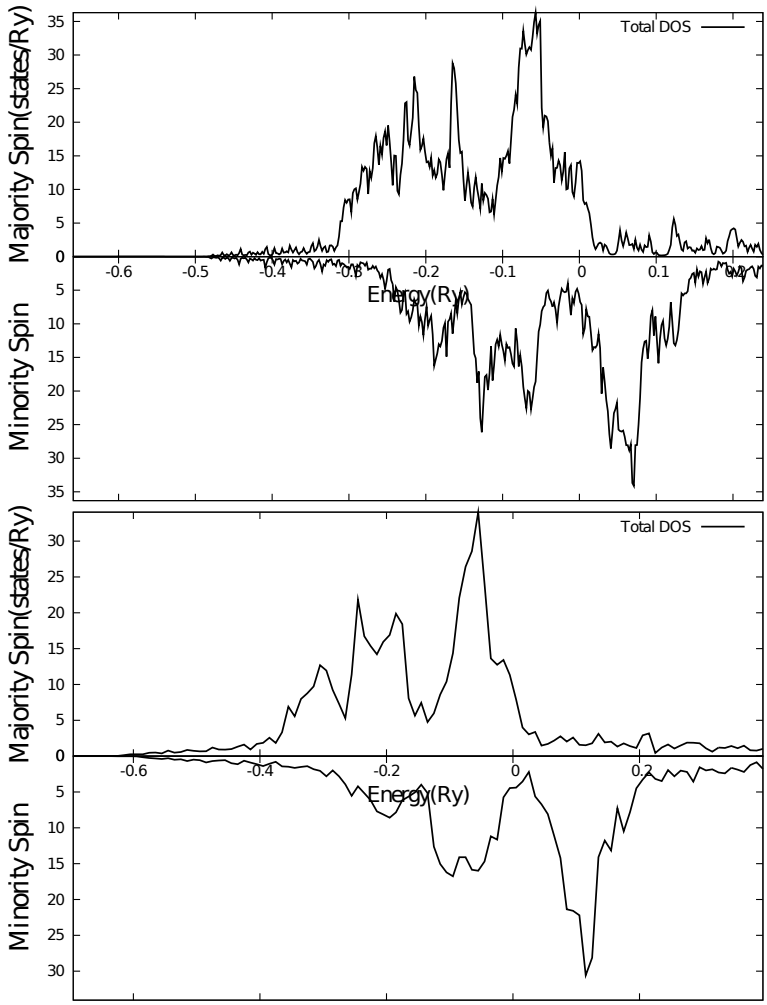


Figure 3.6: Total DOS of Fe calculated within (Top) EXX+RPA and (Bottom) LDA.

The table 3.1 shows the calculated magnetic moments for Fe, Co, Ni within the EXX+RPA, EXX, and LDA. In addition, we compare them with the magnetic moments calculated by Kotani [23] and those obtained by experiments [41, 42, 43]. It is a common tendency seen in all our results in the table that the exchange-splittings, which are overestimated in the EXX, are

(μ_B)	EXX+RPA	EXX	LDA	Kotani[23]	Exp. [41, 42, 43]
Fe	2.60	3.38	2.28	2.05	2.12
Co	1.50	2.26	1.60	1.57	1.59
Ni	0.61	0.82	0.59	0.57	0.56

Table 3.1: The predicted magnetic moments of ferromagnetic Fe, Co and Ni obtained by our KKR-OEP-KLI code, those of Kotani's direct OEP calculation [23], and those from experiments [41, 42, 43].

reduced considerably within the EXX+RPA. However, the predicted magnetic moments are still larger than that of the EXX+RPA results by Kotani, the experimental values, and that of the LDA. These discrepancies can attributed to the use of the KLI approximation because our methods are considered theoretically more accurate than that of Kotani's except the point that we use the KLI approximation.

3.4 Total energy

The total energy calculations were also performed for non-magnetic Na and ferromagnetic Fe. Based on the equation (2.163), we used 240 mesh for the lambda integration in the following results.

We found that the numerical integration along the real axis is virtually impossible due to singular behavior of the integrand along the real axis. The figure 3.7 shows the behaviors of the integrands of Fe and Na. These singularities are due to $(\tilde{1}-\lambda\tilde{v}\tilde{D})^{-1}$ in the expression (2.142) of the screened coulomb interaction (v must be accompanied by λ in the calculation of (2.163)).

Thus, we deformed the path of λ to detour the poles, which could be justified as follows. In the formalism of the adiabatic connection, what we really want to know is the difference of the values of anti-derivative at the ends of path,$\lambda = 0$ and $\lambda = 1$. If there is no pole the integral gives the correct difference. However, the presence of poles may introduce ambiguities of the integral. Fortunately, $\tilde{v}\tilde{D}$ is a real function. Thus, if there is a pole of $(\tilde{1} - \lambda\tilde{v}\tilde{D})^{-1}$ on the real axis of λ, and the pole is of first order, the residue of the pole must be real. In this case, it contributes only imaginary part of the integral. On the other hand, we know that the difference must be real.

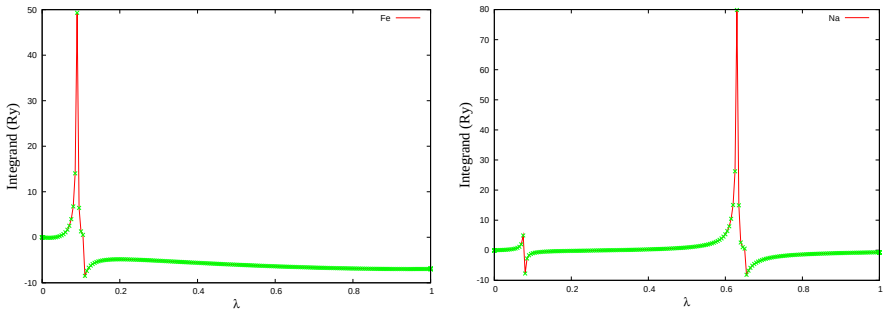


Figure 3.7: The green crosses indicate the value of the integrand of (2.163) along with the real axis of λ. The red line connects neighboring points just in order to serve a guide to the eye.

Thus, just dropping the imaginary part after integration will give the correct difference.

The path of the λ integral is illustrated in the figure 3.8 with the value of the integrand for both Fe and Na case. The lambda runs along the three sides of the rectangle which height is 0.1 and width is 1. It can be seen that the integrands are smooth enough to be numerically integrated along the path.

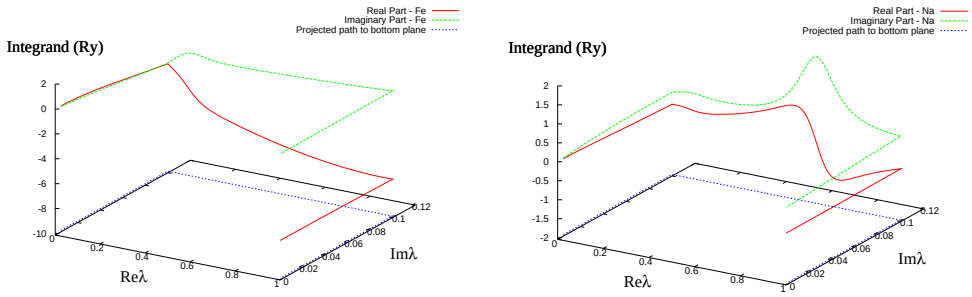


Figure 3.8: The real part (red) and the imaginary part (green) of the integrand of (2.163) on the deformed path of λ, which is shown as the blue lines on the bottom plane of the graphs.

Two graphs in the figure 3.9 shows the variation of the total energy with respect to the lattice constant of the ferromagnetic Fe and non-magnetic Na respectively. The table 3.2 compares the estimated lattice constants with

that from the experiments and that from the LDA calculations. Though the EXX+RPA scheme predicts smaller values than those obtained by experiments, it falls closer than those of the LDA.

(a.u.)	Exp.	EXX+RPA	LDA
Fe	5.42	5.30	5.24
Na	7.99	7.82	7.68

Table 3.2: The calculated lattice constants calculated by the KKR-OEP-KLI code compared with the experimental values.

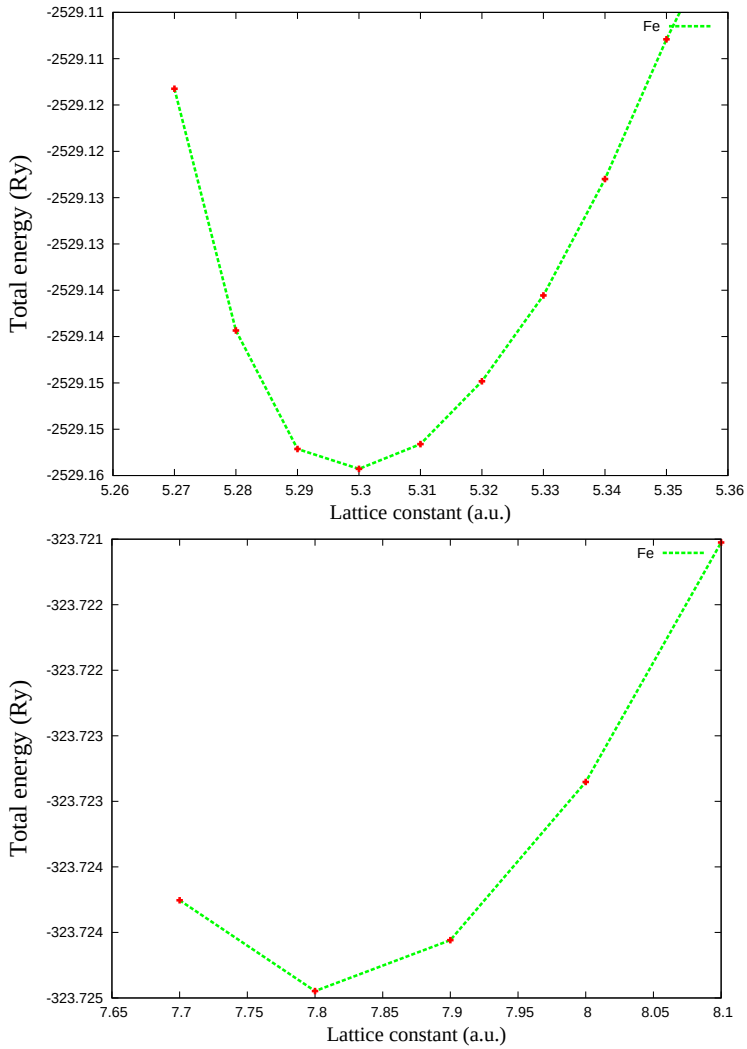


Figure 3.9: Variations of the total energy of (top) Fe and (bottom) Na with respect to the lattice constant calculated within the framework of the EXX+RPA.

Chapter 4

Conclusions

We have proposed a new scheme of calculating the optimized effective potential. This includes several fundamental findings on the OEP theory. The OEP must be determined according to the set of two equations:

$$\begin{cases} \sum_i \int d\boldsymbol{r}'[V_{\mathrm{xc},\sigma}(\boldsymbol{r}') - v_{\mathrm{xc},i\sigma}(\boldsymbol{r}')]G_{i\sigma}(\boldsymbol{r}',\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r}')\psi_{i\sigma}(\boldsymbol{r}) + \mathrm{c.c.} = 0 \\ \\ \int d\boldsymbol{r}\ \{\xi - V_{\mathrm{xc},\sigma}(\boldsymbol{r})\}\,\check{n}_\sigma(\boldsymbol{r},\mu_\sigma) + \dfrac{\partial E_{\mathrm{xc}}}{\partial \mu_\sigma} = 0 \end{cases} \tag{4.1}$$

The first equation is derived by Sharp and Horton [5], and Talman and Shadwick [6] (appeared as (2.82) in chapter 2), and the second (2.87) is given by the author and Akai [39]. The new technique to calculate the RPA-level correlation is also demonstrated. The static polarization-insertion is analytically transformed into the other expression (2.162), which is more convenient in numerical calculations.

These techniques are implemented in the KKR code with the modified KLI approximation, which is constructed in accordance with (2.87) by the modification. For the calculation within the framework of the EXX, the use of the KLI seems adequate. However, there are yet discernible discrepancies between results obtained by our code and results of the direct method reported by Kotani [23]. We also proposed the approximate way to calculate the correlation energy, which is needed for the total energy calculation. It is remarked that our scheme with the modified KLI method still seems to have an advantage in predicting lattice constants over the LDA.

The disagreement of our method with the direct OEP calculation should be attributed to the use of the KLI approximation. Thus, another approx-

imation going beyond the KLI approximation or efficient way to calculate the OEP directly should be investigated as our further steps. Fortunately, most of our findings are independent from the KLI approximation. Therefore, we believe that they are also useful in future developments based on the optimized effective potential theory.

Appendix A

Notations and formulae

In this appendix, several definitions and formulae used in this thesis are listed.

A.1 Definitions

Rydberg Units (Slater Units) The Rydberg units are used through this thesis. These units are defined by the following relation of the physical constants:

$$\hbar = 2m_e = \frac{e^2}{2} = 4\pi\epsilon_0 = 1, \tag{A.1}$$

where, $\hbar$ is the Dirac constant, m_e is the mass of the electron, e is the electric charge of the electron, and ϵ_0 is the dielectric constant of vacuum.

Fourier transforms The Fourier transforms are defined as follows. Note that there is a slight difference between those of time and space.

$$f(\boldsymbol{x}) = \frac{1}{2\pi}\int dk\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\tilde{f}(k) \tag{A.2}$$

$$f(t) = \frac{1}{2\pi}\int d\omega\, e^{-i\omega t}\tilde{f}(\omega) \tag{A.3}$$

Heisenberg representation The Heisenberg representation is denoted by subscript of H, and the Schroödinger representation S. The states and operators of these two are related to one another as:

$$|\Psi^{\mathrm{H}}\rangle = e^{i\hat{H}t}|\Psi^{\mathrm{S}}\rangle \tag{A.4}$$

$$\hat{O}^{\mathrm{S}} \equiv e^{i\hat{H}t}\hat{O}^{\mathrm{S}}e^{-i\hat{H}t}, \tag{A.5}$$

where $\hat{H}$ is the Hamiltonian, $|\Psi^{\mathrm{S}}\rangle$ is a state and $\hat{O}^{\mathrm{S}}$ is an operator in the Schrödinger representation. The states and operators without both superiors denotes that of Schrödinger representation.

T-product T-product is defined as

$$\mathrm{T}\{A(\boldsymbol{r},t)B(\boldsymbol{r}',t')\} = \begin{cases} A(\boldsymbol{r},t)B(\boldsymbol{r}',t') & (t > t') \\ -B(\boldsymbol{r}',t')A(\boldsymbol{r},t) & (t < t') \end{cases}. \tag{A.6}$$

It is enough because we only apply T-product on the anti-commuting operators.

A.2 Formulae

Fourier transforms of θ-function The Fourier transforms of θ-function appears several times in the text. Letting η denote a infinitesimal real value, the following relation can be seen:

$$\theta(t-t') = \frac{1}{2\pi}\int d\omega\, e^{-i\omega(t-t')}\left[\frac{i}{\omega+i\eta}\right], \tag{A.7}$$

$$\theta(t'-t) = \frac{1}{2\pi}\int d\omega\, e^{-i\omega(t-t')}\left[\frac{-i}{\omega-i\eta}\right]. \tag{A.8}$$

Therefore, one obtains

$$\theta(t-t')e^{-i\alpha(t-t')} = \frac{1}{2\pi}\int d\omega\, e^{-i\omega(t-t')}\left[\frac{i}{\omega-\alpha+i\eta}\right], \tag{A.9}$$

$$\theta(t'-t)e^{-i\alpha(t-t')} = \frac{1}{2\pi}\int d\omega\, e^{-i\omega(t-t')}\left[\frac{-i}{\omega-\alpha-i\eta}\right]. \tag{A.10}$$

Appendix B

Green's function of non-interacting system

In this thesis, two kinds of the Green's function, the causal and retarded Green's function, are utilized. In general, they are defined as follows.

Causal Green's function

$$iG_{\sigma\sigma'}(x,x') \equiv \langle g^{\mathrm{H}}|\mathrm{T}\{\hat{\psi}^{\mathrm{H}}_{\sigma}(x)\hat{\psi}^{\dagger\mathrm{H}}_{\sigma'}(x')\}|g^{\mathrm{H}}\rangle, \tag{B.1}$$

Retarded Green's function

$$iG^{R}_{\sigma\sigma'}(x,x') \equiv \theta(t-t')\langle g^{\mathrm{H}}|\hat{\psi}^{\mathrm{H}}_{\sigma}(x)\hat{\psi}^{\dagger\mathrm{H}}_{\sigma'}(x')|g^{\mathrm{H}}\rangle, \tag{B.2}$$

where $|g^{\mathrm{H}}\rangle$ is the ground state of the system, $\hat{\psi}^{\mathrm{H}}_{\sigma}$ is the field operator, both in the Heisenberg representation, and four-dimensional space-time-coordinate variables such as $x \equiv (\boldsymbol{r}, t)$ are used.

This appendix summarizes useful formulae related to the Green's function of non-interacting systems. In this thesis, we deal with the Green's function many times, but all of them are those for non-interacting systems. In this case, it can be seen that the spin off-diagonal part of these Green's functions vanish. Thus, it is convenient to let G_{σ} denote the diagonal component of $G_{\sigma\sigma'}$:

$$G_{\sigma\sigma'}(x,x') = \delta_{\sigma\sigma'}G_{\sigma}(x,x'), \tag{B.3}$$

and G^{R}_{σ} the counterpart of $G^{\mathrm{R}}_{\sigma\sigma'}$. We use these notation throughout in this thesis.

The first section of Appendix B is devoted to a summary of calculations related to the ring diagram, which appears in section 2.2.3. The second and third sections describe the relations used in the construction of the Korringa–Kohn–Rostoker (KKR) Green's function method (see Appendix C).

B.1 Ring polarization insertion

In this section, quantities related to the following ring polarization-insertion D are calculated. In non-interacting systems,

$$D(x, x') = \tag{B.4}$$

$$= -i \sum_{\sigma\sigma'} G_{\sigma\sigma'}(x, x') G_{\sigma\sigma'}(x', x) \tag{B.5}$$

$$= -i \sum_{\sigma} G_{\sigma}(x, x') G_{\sigma}(x', x) \tag{B.6}$$

$$= \sum_{\sigma} D_{\sigma}(x, x'), \tag{B.7}$$

where D_σ is defined as

$$D_\sigma(x, x') \equiv -iG_\sigma(x, x')G_\sigma(x', x). \tag{B.8}$$

In section 2.2.3, the value of $D_\sigma(x, x') = D_\sigma(\boldsymbol{r}, \boldsymbol{r}', t - t')$ at $t = t'$ and the frequency component of the Fourier transform of D_σ at $\omega = 0$ play important roles. Thus, we calculate both two in this section.

In order to calculate $D_\sigma(\boldsymbol{r}, \boldsymbol{r}', 0)$ we calculate the value of Green's functions $G_\sigma(\boldsymbol{r}, t, \boldsymbol{r}', t')$ when the difference between t and t' is infinitesimally small. Let t^+ denote $t^+ = t + 0$. Then,

$$\begin{aligned} iG_\sigma(\boldsymbol{r}, t, \boldsymbol{r}', t^+) &= -\langle g_{\mathrm{H}} | \hat{\psi}^\dagger_{\sigma\mathrm{H}}(x') \hat{\psi}_{\sigma\mathrm{H}}(x) | g_{\mathrm{H}} \rangle \\ &= -\sum_{i:\text{occupied}} \psi^*_{i\sigma}(\boldsymbol{r}') \psi_{i\sigma}(\boldsymbol{r}) \qquad \text{(B.9)} \\ &\equiv -n_\sigma(\boldsymbol{r}', \boldsymbol{r}), \qquad \text{(B.10)} \end{aligned}$$

where $\psi_{i\sigma}(\boldsymbol{r})$ is the ith eigen-function of the non-interacting system, which has the spin σ. In a similar way, one obtains

$$\begin{aligned} iG_\sigma(\boldsymbol{r}, t^+, \boldsymbol{r}', t) &= \langle g_{\mathrm{H}} | \hat{\psi}_{\sigma\mathrm{H}}(x) \hat{\psi}^\dagger_{\sigma\mathrm{H}}(x') | g_{\mathrm{H}} \rangle \\ &= -n_\sigma(\boldsymbol{r}', \boldsymbol{r}) + \delta(\boldsymbol{r} - \boldsymbol{r}'). \qquad \text{(B.11)} \end{aligned}$$

Therefore, one reaches

$$\begin{aligned} iD_\sigma(\boldsymbol{r}, t, \boldsymbol{r}', t^+) &= iD_\sigma(\boldsymbol{r}, t^+, \boldsymbol{r}', t) \\ &= n_\sigma(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}') - |n_\sigma(\boldsymbol{r}, \boldsymbol{r}')|^2. \end{aligned} \tag{B.12}$$

Next, we move on to the Fourier component of D_σ. Let $\tilde{D}_\sigma(\boldsymbol{r}, \boldsymbol{r}', \omega)$ denote the frequency component of the Fourier transform of $D_\sigma(\boldsymbol{r}, \boldsymbol{r}', t - t')$ and $\tilde{G}_\sigma$ the frequency component of G_σ.

Let us begin with $\langle g^{\mathrm{H}}|\hat{\psi}_\sigma^{\mathrm{H}}(x)\hat{\psi}_\sigma^{\mathrm{H}\dagger}(x')|g^{\mathrm{H}}\rangle$ in the expression of the causal Green's function. Letting $|n^{\mathrm{S}}\rangle$ denote an energy eigenstate in Schrödinger's representation, one obtains

$$\langle g^{\mathrm{H}}|\hat{\psi}_\sigma^{\mathrm{H}}(x)\hat{\psi}_\sigma^{\mathrm{H}\dagger}(x')|g^{\mathrm{H}}\rangle = \sum_{|n\rangle} \langle g^{\mathrm{H}}|\hat{\psi}_\sigma^{\mathrm{H}}(x)|n^{\mathrm{S}}\rangle\langle n^{\mathrm{S}}|\hat{\psi}_\sigma^{\mathrm{H}\dagger}(x')|g^{\mathrm{H}}\rangle \tag{B.13}$$

$$= \sum_{|n\rangle} e^{-i(E_n - E_0)(t-t')} \langle g^{\mathrm{S}}|\hat{\psi}_\sigma^{\mathrm{S}}(x)|n^{\mathrm{S}}\rangle\langle n^{\mathrm{S}}|\hat{\psi}_\sigma^{\dagger\mathrm{S}}(x')|g^{\mathrm{S}}\rangle, \tag{B.14}$$

where E_n is the energy of $|n\rangle$ and E_0 is the that of $|g\rangle$. The contributions comes only from $|n\rangle$ that is different from $|g\rangle$ by one extra orbital $|n\rangle$, and the other terms vanish due to orthogonality between the states. Consequently, this can be expressed in terms of $\psi_{i\sigma}$, its energy eigenvalue $\epsilon_{i\sigma}$, and the Fermi energy, ϵ_F, of $|g\rangle$:

$$\langle g^{\mathrm{H}}|\hat{\psi}_\sigma^{\mathrm{H}}(x)\hat{\psi}_\sigma^{\dagger\mathrm{H}}(x')|g^{\mathrm{H}}\rangle = \sum_i e^{-i(\epsilon_{i\sigma} - \epsilon_F)(t-t')}\theta(\epsilon_{i\sigma} - \epsilon_F)\psi_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}^*(\boldsymbol{r}'). \tag{B.15}$$

By a similar analysis, one finds

$$\langle g^{\mathrm{H}}|\hat{\psi}_\sigma^{\dagger\mathrm{H}}(x')\hat{\psi}_\sigma^{\mathrm{H}}(x)|g^{\mathrm{H}}\rangle = \sum_i e^{i(\epsilon_{i\sigma} - \epsilon_F)(t-t')}\theta(\epsilon_F - \epsilon_{i\sigma})\psi_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}^*(\boldsymbol{r}'). \tag{B.16}$$

The causal Green's function is constructed from these two expression:

$$\begin{aligned} iG_\sigma(x, x') &= \theta(t - t')\langle g_{\mathrm{H}}|\hat{\psi}_{\sigma\mathrm{H}}(x)\hat{\psi}_{\sigma\mathrm{H}}^\dagger(x')|g_{\mathrm{H}}\rangle \\ &\quad - \theta(t' - t)\langle g_{\mathrm{H}}|\hat{\psi}_{\sigma\mathrm{H}}^\dagger(x')\hat{\psi}_{\sigma\mathrm{H}}(x)|g_{\mathrm{H}}\rangle \\ &= \theta(t - t')\sum_i e^{-i(\epsilon_{i\sigma} - \epsilon_F)(t-t')}\theta(\epsilon_{i\sigma} - \epsilon_F)\psi_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}^*(\boldsymbol{r}') \\ &\quad - \theta(t' - t)\sum_i e^{i(\epsilon_{i\sigma} - \epsilon_F)(t-t')}\theta(\epsilon_F - \epsilon_{i\sigma})\psi_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}^*(\boldsymbol{r}'). \end{aligned} \tag{B.17}$$

Therefore, the polarization insertion can be expressed as

$$D_\sigma(x,x') = i \times iG_\sigma(x,x') \times iG_\sigma(x',x) \tag{B.18}$$

$$\begin{aligned} &= \sum_{i,j}\{\theta(t-t')\theta(\epsilon_{i\sigma}-\epsilon_F)\theta(\epsilon_F-\epsilon_{j\sigma}) \\ &\quad - \theta(t'-t)\theta(\epsilon_F-\epsilon_{i\sigma})\theta(\epsilon_{j\sigma}-\epsilon_F)\} \\ &\quad \times e^{-i(\epsilon_{i\sigma}-\epsilon_{j\sigma})(t-t')}\psi_{i\sigma}(\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r}')\psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}'), \end{aligned} \tag{B.19}$$

which follows from the definition. Using (A.9) and (A.10) in Appendix A, we finally obtain the Fourier transform of $D_\sigma(x,x')$ as for $t-t'$:

$$\begin{aligned} \tilde{D}_\sigma(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{i,j}&\left\{\frac{\theta(\epsilon_{i\sigma}-\epsilon_F)\theta(\epsilon_F-\epsilon_{j\sigma})}{\omega-(\epsilon_{i\sigma}-\epsilon_{j\sigma})+i\eta} - \frac{\theta(\epsilon_F-\epsilon_{i\sigma})\theta(\epsilon_{j\sigma}-\epsilon_F)}{\omega-(\epsilon_{j\sigma}-\epsilon_{i\sigma})-i\eta}\right\} \\ &\times \psi_{i\sigma}(\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r}')\psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}'). \end{aligned} \tag{B.20}$$

Substituting $\omega = 0$ as a special case, we obtain

$$\begin{aligned} \tilde{D}_\sigma(\boldsymbol{r},\boldsymbol{r}',\omega=0) = 2\sum_{i,j}&\frac{\theta(\epsilon_{i\sigma}-\epsilon_F)\theta(\epsilon_F-\epsilon_{j\sigma})}{\epsilon_{j\sigma}-\epsilon_{i\sigma}+i\eta} \\ &\times \psi_{i\sigma}(\boldsymbol{r})\psi^*_{i\sigma}(\boldsymbol{r}')\psi^*_{j\sigma}(\boldsymbol{r})\psi_{j\sigma}(\boldsymbol{r}'). \end{aligned} \tag{B.21}$$

B.2 Dyson equation

In this section, a relation between two different Green's functions is discussed. One is a Green's function of $\hat{H}_0$ and the other $\hat{H}$, where these two Hamiltonians are connected by a relation:

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{B.22}$$

Here, only the relations between the retarded Green's functions of two systems are discussed because they are enough to cover the scope of this thesis.

It is convenient to begin with the following expressions of the Green's functions:

$$\hat{g}(E) = \left(E - \hat{H}_0 + i\eta\right)^{-1}, \tag{B.23}$$

$$\hat{G}(E) = \left(E - \hat{H} + i\eta\right)^{-1}, \tag{B.24}$$

which are true for the retarded Green's functions of non-interacting systems in the frequency domain. Here, η is a real positive number, which should be taken $\eta \to 0$ at the end of the calculations.

These two Green's functions are connected by the Dyson equation:

$$\hat{G}(E) = \hat{g}(E) + \hat{g}(E)\hat{V}\hat{G}(E). \tag{B.25}$$

A proof is given by a simple transformation of the right hand side.

$$\begin{aligned}
(\text{r.h.s.}) &= \hat{g}(E) + \hat{g}(E)\left[\hat{H} - \hat{H}_0\right]\hat{G}(E) && \text{(B.26)}\\
&= \hat{g}(E) + \hat{g}(E)\left[(E - \hat{H}_0 + i\eta) - (E - \hat{H} + i\eta)\right]\hat{G}(E) && \text{(B.27)}\\
&= \hat{g}(E) + \hat{g}(E)\left[\hat{g}^{-1}(E) - \hat{G}^{-1}(E)\right]\hat{G}(E) && \text{(B.28)}\\
&= \hat{G}(E). && \text{(B.29)}
\end{aligned}$$

The following relation also be given by a similar transformation.

$$\hat{G}(E) = \hat{g}(E) + \hat{G}(E)\hat{V}\hat{g}(E) \tag{B.30}$$

These relations hold for any η common to the both Green's functions. If one use different infinitesimal value from one another, say η and η', the Dyson equation can be justified at the limit of $\eta, \eta' \to 0$.

B.3 Lippmann-Schwinger equation

Wave-functions of two systems can be related by the Green's function via following Lippmann-Schwinger equation. Let $|\phi_i\rangle$ denote an eigenfunction of $\hat{H}_0$, whose eigenvalue is E_i, then

$$\lim_{\eta\to 0} \hat{H}\left[1 + \hat{G}(E_i)\hat{V}\right]|\phi_i\rangle = E_i\left[1 + \hat{G}(E_i)\hat{V}\right]|\phi_i\rangle. \tag{B.31}$$

Thus in the limit of $\eta \to 0$, $\left[1 + \hat{G}(E_i)\hat{V}\right]|\phi_i\rangle$ can be regarded as an eigenfunction of $\hat{H}$, whose eigenvalue is E_i. Though this relation can be derived more algebraic manner, existence (or non-existence) of $\left[1 + \hat{G}(E_i)\hat{V}\right]|\phi_i\rangle$ can be seen clearly if one use the eigenfunction expansion of Green's function:

$$\hat{g}(E) = \sum_i |\phi_i\rangle \frac{1}{E - E_i + i\eta}\langle\phi_i|, \tag{B.32}$$

$$\hat{G}(E) = \sum_i |\varphi_i\rangle \frac{1}{E - E_i + i\eta}\langle\varphi_i|, \tag{B.33}$$

where eigenfunctions of $\hat{H}$ are denoted by $|\varphi_i\rangle$. It follows from (B.30) that $1+\hat{G}(E)\hat{V}=\hat{G}(E)\hat{g}^{-1}(E)$. Using these, one can see

$$\begin{aligned}
\left[1+\hat{G}(E_i)\hat{V}\right]|\phi_i\rangle &= \hat{G}(E_i)\hat{g}^{-1}(E_i)|\phi_i\rangle && \text{(B.34)}\\
&= \sum_{j,k}\frac{E_i-E_k+i\eta}{E_i-E_j+i\eta}|\varphi_j\rangle\langle\varphi_j|\phi_k\rangle\langle\phi_k|\phi_i\rangle && \text{(B.35)}\\
&= \sum_{j}\frac{i\eta}{E_i-E_j+i\eta}|\varphi_j\rangle\langle\varphi_j|\phi_i\rangle && \text{(B.36)}\\
&\xrightarrow[\eta\to 0]{} \sum_{j}\delta_{E_i,E_j}|\varphi_j\rangle\langle\varphi_j|\phi_i\rangle. && \text{(B.37)}
\end{aligned}$$

Thus (B.31) always holds. Note that we used the common infinitesimal value η for both $\hat{g}$ and $\hat{G}$, and the resulting relation holds only when the way taking the limit is correctly chosen. This arbitrariness was not found in the derivation of the Dyson equation.

Appendix C

Korringa-Kohn-Rostoker Green's function method

The Korringa-Kohn-Rostoker(KKR) Green's function method is a way to construct a Green's function of a non-interacting system from the Green's function of the free space. This method is established by Korringa [44] and Kohn and Rostoker [45]. In this scheme, the space is divided into cells. Then the single scattering problem of the each divided potential is solved. It is one of advantages of the method that one can construct the Green's function of the whole system from such separated information of each solution that is obtained without considering the connection of the orbitals to that of the neighboring cells.

In terms of the Kohn-Sham scheme, the KKR method offers a way to obtain the ground-state density $n_0(\boldsymbol{r})$ of the Kohn-Sham system by the relation,

$$n_0(\boldsymbol{r}) = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\epsilon_F} dE\, G(\boldsymbol{r}, \boldsymbol{r}, E), \tag{C.1}$$

where $G(\boldsymbol{r}, \boldsymbol{r}', E)$ denotes the retarded Green's function in the position representation and ϵ_F is the Fermi energy. This relation itself holds in general. However, it will be enough to confirm this from (B.33), which is valid only

in non-interacting systems:

$$-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\epsilon_F} G(\boldsymbol{r},\boldsymbol{r},E) = -\frac{1}{\pi}\int_{-\infty}^{\epsilon_F}\mathrm{Im}\sum_i \frac{\langle \boldsymbol{r}|\varphi_i\rangle\langle\varphi_i|\boldsymbol{r}\rangle}{E-E_i+i\eta} \tag{C.2}$$

$$= \sum_i \int_{-\infty}^{\epsilon_F} \delta(E-E_i)\,|p\langle\varphi_i|\boldsymbol{r}\rangle|^2 \tag{C.3}$$

$$\equiv n_0(\boldsymbol{r}). \tag{C.4}$$

Appendix C is devoted to deriving the KKR equation, which gives the way to construct the Green's function in such a way as mentioned above.

C.1 Cell division

In this section we are going to discuss the KKR's construction of Green's function in somewhat a generalized way. First, we introduce "cell" restriction operators $\hat{P}_m$, which satisfy the following relations.

$$\hat{P}_m^\dagger = \hat{P}_m \tag{C.5}$$

$$\hat{P}_m\hat{P}_n = \delta_{m,n}\hat{P}_m \tag{C.6}$$

$$\sum_m \hat{P}_m = 1 \tag{C.7}$$

For example, let us think of dividing the space into cells. One can verify operators defined by

$$\mathcal{P}_m = \int d\boldsymbol{r}\ \Theta_m(\boldsymbol{r})|\boldsymbol{r}\rangle\langle\boldsymbol{r}| \tag{C.8}$$

satisfy (C.5)-(C.7), where $\Theta_m(\boldsymbol{r})$, the shape function, is a unity when $\boldsymbol{r}$ is in the mth cell, zero otherwise.

Then, we define the single-scattering Hamiltonian of mth "cell" using cell restriction operators.

$$\hat{H}_m^{\mathrm{s}} = \hat{H}_0 + \hat{V}_m, \tag{C.9}$$

where $\hat{V}_m \equiv \hat{P}_m\hat{V}\hat{P}_m$, and we also let $\hat{G}_m^{\mathrm{s}}$ denote Green's function of this Hamiltonian. Now we assume that $\hat{V}$ in the Hamiltonian $H = \hat{H}_0 + \hat{V}$ satisfies

$$\hat{P}_m\hat{V}\hat{P}_n = \delta_{mn}\hat{P}_m\hat{V}\hat{P}_m. \tag{C.10}$$

This relation holds, for example, when one uses (C.8) as the cell-restriction operators and the $\hat{V}$ is local (when the potential is expressed as $V(\boldsymbol{r})$ in the position representation). Note that it follows from (C.7) that

$$\hat{V} = \sum_{mn} \hat{P}_m \hat{V} \hat{P}_n = \sum_m \hat{V}_m. \tag{C.11}$$

In the following section, we also use cell-restricted solutions. For example, let $|J_i\rangle$ denote a solution of the $\hat{H}_0$, then the restricted solutions to the mth "cell" is defined as

$$|\tilde{J}_{m,i}\rangle \equiv \hat{P}_m |J_i\rangle. \tag{C.12}$$

Note that $|\tilde{J}_{m,i}\rangle$ is not necessarily a solution of the each corresponding Hamiltonian because $\hat{P}_m$ do not always commute with the Hamiltonian.

As for solutions of $\hat{H}^{\mathrm{s}}_m$, it follows from the Lippmann-Schwinger equation (B.31) that $\left[1 + \hat{G}^{\mathrm{s}}_m \hat{V}_m\right] |J_i\rangle$ can be regarded as a solution of $\hat{H}^{\mathrm{s}}_m$, where $\hat{V}_m \equiv \hat{P}_m \hat{V} \hat{P}_m$. Thus, letting $|\mathcal{J}_{m,i}\rangle \equiv \left[1 + \hat{G}^{\mathrm{s}}_m \hat{V}_m\right] |J_i\rangle$, we define a restricted solutions of Hamiltonian $\hat{H}^{\mathrm{s}}_m$ to the mth "cell" as

$$\begin{aligned} |\tilde{\mathcal{J}}_{m,i}\rangle &\equiv \hat{P}_m |\mathcal{J}_{m,i}\rangle & \text{(C.13)} \\ &= \hat{P}_m \left[1 + \hat{G}^{\mathrm{s}}_m \hat{V}_m\right] |J_i\rangle. & \text{(C.14)} \end{aligned}$$

C.2 KKR ansatz

In this section the Green's function $\hat{G}$ is constructed on the assumption that $\hat{G}$ can be expressed as follows:

$$\hat{G} = \sum_m \hat{P}_m \hat{G}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{\mathcal{J}}_i, m\rangle G^{ij}_{mn} \langle \tilde{\mathcal{J}}_j, n|. \tag{C.15}$$

The first term consists of cell-restricted Green's functions of the single-scattering Hamiltonians. Thus, this term has singular behaviors asymptotically as same as those of the Green's function of $\hat{H}$. The remaining part of the Green's function may well be expanded in terms of the regular solutions of $\hat{H}$. In this expression, thus, the coefficient G^{ij}_{mn} are to be determined. A similar assumption is applied to Green's function $\hat{g}$:

$$\hat{g} = \sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \tag{C.16}$$

$\hat{g}^{\mathrm{s}}_m$ in this expression has not been defined yet. We consider one that satisfies

$$\hat{g}^{\mathrm{s}}_m = \hat{g}^{\mathrm{s}}_m + \hat{g}^{\mathrm{s}}_m \hat{V}_m \hat{G}^{\mathrm{s}}_m. \tag{C.17}$$

For example, if one use $\hat{g}^{\mathrm{s}}_m = \hat{g}$, the last equation becomes nothing but the Dyson equation for the Hamiltonian (C.9). This choice is preferred when the free-space Hamiltonian is used as H_0. Besides this, one can relate Green's functions of two different Hamiltonians that have H'_0 in common, say, $\hat{H}_0 = \hat{H}'_0 + \hat{V}_1$ and $\hat{H} = H'_0 + \hat{V}_2$. In this case, the Green's function of a single-scattering Hamiltonian $\hat{H}^{\mathrm{s}}_{0,m} = \hat{H}'_0 + \hat{V}_{1,m}$ can be used as $\hat{g}^{\mathrm{s}}_m$, which is different from $\hat{g}$. It can be seen that (C.17) holds with $\hat{V} = \hat{V}_2 - \hat{V}_1$.

The KKR equation relates G^{ij}_{mn} of the expansion of $\hat{G}$ to the coefficient g^{ij}_{mn}. In order to derive the equation, the Dyson equation (B.25) is exploited. Let us begin with the right-hand side of (B.25). Substituting (C.15) and (C.16) to $\hat{g} + \hat{g}\hat{V}\hat{G}$, one obtains

$$\begin{aligned}
&\hat{g} + \hat{g}\hat{V}\hat{G} \\
&= \sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \\
&\quad + \left[\sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \right] \\
&\quad \times \left[\sum_k \hat{V}_k \right] \left[\sum_p \hat{P}_p \hat{G}^{\mathrm{s}}_m \hat{P}_p + \sum_{pqrs} |\tilde{\mathcal{J}}_p, r\rangle G^{pq}_{rs} \langle \tilde{\mathcal{J}}_q, s| \right].
\end{aligned} \tag{C.18}$$

It follows from the relation (C.6) that this equals

$$\begin{aligned}
&= \sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \\
&\quad + \left[\sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{V}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n \right] \\
&\quad \times \left[\sum_p \hat{P}_p \hat{G}^{\mathrm{s}}_m \hat{P}_p + \sum_{pqrs} |\tilde{\mathcal{J}}_p, r\rangle G^{pq}_{rs} \langle \tilde{\mathcal{J}}_q, s| \right]
\end{aligned} \tag{C.19}$$

$$
\begin{aligned}
&= \sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \\
&\quad + \sum_m \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{V}_m \hat{G}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n \hat{G}^{\mathrm{s}}_n \hat{P}_n \\
&\quad + \sum_{ijmn} \hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{V}_m |\mathcal{J}_i, m\rangle G^{ij}_{mn} \langle \mathcal{J}_j, n| \\
&\quad + \sum_{ijmn} \sum_{pqs} |\tilde{J}_i, m\rangle G^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n |\mathcal{J}_p, n\rangle G^{pq}_{ns} \langle \mathcal{J}_q, s|
\end{aligned} \tag{C.20}
$$

It follows from the Lippmann-Schwinger relation for restricted solutions (C.14) and (C.6) that $\hat{P}_m \hat{G}^{\mathrm{s}}_m \hat{V}_m |\tilde{J}_i\rangle = |\tilde{\mathcal{J}}_i\rangle - |\tilde{J}_i\rangle$. Exchanging the role of the referred and referring Hamiltonian for one another, it is also seen that $\hat{P}_m \hat{g}^{\mathrm{s}}_m \hat{V}_m |\tilde{\mathcal{J}}_i\rangle = |\tilde{\mathcal{J}}_i\rangle - |\tilde{J}_i\rangle$. Using these,

$$
\begin{aligned}
&= \sum_m \hat{P}_m \left\{ \hat{g}^{\mathrm{s}}_m + \hat{g}^{\mathrm{s}}_m \hat{V}_m \hat{G}^{\mathrm{s}}_m \right\} \hat{P}_m + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{J}_j, n| \\
&\quad + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \left\{ \langle \tilde{\mathcal{J}}_j, n| - \langle \tilde{J}_j, n| \right\} \\
&\quad + \sum_{ijmn} \left\{ |\tilde{\mathcal{J}}_i, m\rangle - |\tilde{J}_i, m\rangle \right\} G^{ij}_{mn} \langle \mathcal{J}_j, n| \\
&\quad + \sum_{ijmn} \sum_{pqs} |\tilde{J}_i, m\rangle G^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n |\mathcal{J}_p, n\rangle G^{pq}_{ns} \langle \mathcal{J}_q, s|.
\end{aligned} \tag{C.21}
$$

Here we utilize the equation (C.17) and reach

$$
\begin{aligned}
&= \sum_m \hat{P}_m \hat{G}^{\mathrm{s}}_m \hat{P}_m \\
&\quad + \sum_{ijmn} |\tilde{J}_i, m\rangle g^{ij}_{mn} \langle \tilde{\mathcal{J}}_j, n| \\
&\quad + \sum_{ijmn} \left\{ |\tilde{\mathcal{J}}_i, m\rangle - |\tilde{J}_i, m\rangle \right\} G^{ij}_{mn} \langle \mathcal{J}_j, n| \\
&\quad + \sum_{ijmn} \sum_{pqs} |\tilde{J}_i, m\rangle G^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n |\tilde{\mathcal{J}}_i, n\rangle G^{pq}_{ns} \langle \tilde{\mathcal{J}}_q, s|
\end{aligned} \tag{C.22}
$$

$$
\begin{aligned}
&= \sum_m \hat{P}_m \hat{G}^{\mathrm{s}}_m \hat{P}_m + \sum_{ijmn} |\mathcal{J}_i, m\rangle G^{ij}_{mn} \langle \tilde{\mathcal{J}}_i, m| \\
&+ \sum_{iqms} |\tilde{\mathcal{J}}_i, m\rangle \left[g^{iq}_{ms} + \sum_{jnp} g^{ij}_{mn} \langle \tilde{J}_j, n| \hat{V}_n |\tilde{\mathcal{J}}_p, n\rangle G^{pq}_{ns} - G^{iq}_{ms} \right] \langle \mathcal{J}_q, s|.
\end{aligned} \tag{C.23}
$$

In order to get this expression identical with (C.15), the expression in the square brackets in the last line must be zero. This gives the recursive equation to determine the coefficient in (C.15):

$$G^{ij}_{mn} = g^{ij}_{mn} + \sum_{kpq} g^{ik}_{mp} \langle \tilde{J}_k, p | \hat{V}_p | \tilde{\mathcal{J}}_q, p \rangle G^{qj}_{pn}, \tag{C.24}$$

which is called KKR equation. According to this, Green's function G can be constructed from the cell-restricted solutions of both two systems and the information of g^{ij}_{mn}. In practice, the free-space Hamiltonian is often used as H_0 and cell-division is defined as (C.8) with conveniently chosen $\Theta_m(\boldsymbol{r})$ and the value of $\langle \tilde{J}_k, p | \hat{V}_p | \tilde{\mathcal{J}}_q, p \rangle$ is calculated from the phase shift of the single-scattering Hamiltonians.

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