

## 学位論文（要約）

Development and application of  
the GW+Bethe-Salpeter method for the study of  
excitonic states in molecules

(分子のエキシトン状態研究のための  
GW+Bethe-Salpeter 法の開発と応用)

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# Abstract

In this thesis, we show our development of the first-principles  $GW$ +Bethe-Salpeter equation (BSE) method, which is based on many-body perturbation theory (MBPT), to extend its applicability and improve its accuracy. The  $GW$ +BSE method is recognized as a powerful and predictive tool for investigating optical spectra of condensed matter. However, there are still much room for development to maximize the potential. Our direction to go is in the development of the post-calculation analysis, or the exciton analysis. The conventional analysis method has been based on state-by-state visualization of the one-electron wave function, which is not only cumbersome and ambiguous but also illegitimate. In chapter 6, we propose a method to analyze the exciton wave function and to classify excitons using two dimensionless parameters automatically and quantitatively. We expect that this method is an important step toward realization of an automatic classification required for a data-driven material design of organic solar cells. The second direction to go is to develop numerical procedures to solve  $GW$ +BSE to adapt to the recent massively parallel computers, which make it possible to increasing larger scale calculation year by year. In Chapter 7, we demonstrate that our  $GW$ +BSE code can accurately calculate carbon nanocages involving 198 atoms. By this, we can greatly extend the target of the study. The third direction to go is to improve the accuracy of the  $GW$ +BSE calculation. The inaccuracy is often associated with applying the  $GW$ +BSE method originally developed for extended systems to an isolated system. Indeed, the excitation energy of small molecules is seriously underestimated. This is considered due to neglect of the functional derivative of the electron-hole interaction kernel of BSE. In Chapter 4, we newly formulate this term as the second-order correction, and in Chapter 8, we investigate the effect of the second-order correction on small molecules. We find that the second-order correction close to the experimental results, but the amount of the correction is insufficient to overcome the underestimated excitation energies by about 1 eV. The result suggests that the second-order correction should be taken into account under the self-consistent  $GW$  scheme instead of the  $G_0W_0$  scheme taken in the present study.

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# Table of Acronyms

<b>AO</b>	Atomic orbital
<b>BO</b>	Born-Oppenheimer
<b>BSE</b>	Bethe-Salpeter equation
<b>BZ</b>	Brillouin zone
<b>CIS</b>	Configuration interaction singlets
<b>DFT</b>	Density functional theory
<b>EA</b>	Electron affinity
<i>e-h</i>	electron-hole
<b>FFT</b>	Fast Fourier transform
<i>GWA</i>	<i>GW</i> approximation
<b>GPP</b>	Generalized plasmon-pole
<b>HFA</b>	Hartree-Fock approximation
<b>HOMO</b>	Highest occupied Molecular Orbital
<b>IP</b>	Ionization potential
<b>KS</b>	Kohn-Sham
<b>LDA</b>	Local density approximation
<b>LUMO</b>	Lowest unoccupied molecular orbital
<b>MBPT</b>	Many-body perturbation theory
<b>PW</b>	Plane wave
<b>RPA</b>	Random phase approximation
<b>SCF</b>	Self-consistent field
<b>TDA</b>	Tamm-Dancoff approximation
<b>TDDFT</b>	Time-dependent density functional theory
<b>xc</b>	Exchange-correlation

# Chapter 1

## Introduction

In condensed matter sciences, optical properties are extremely important in various fields such as optoelectronics, photovoltaics and photochemistry. The materials science will be greatly advanced if the optical properties can be accurately simulated from first-principles, and in addition, if the optical properties can be done systematically, the advance will be accelerated via a data-driven approach.

The first-principles calculation based on the many-body perturbation theory (MBPT) is particularly important in understanding the spectroscopic measurement, such as photoemission spectroscopy (PES) and absorption spectroscopy, because the calculation directly corresponds to the spectroscopic process. In PES, light is incident on a sample to measure the kinetic energy of the photoelectron, and the electronic property such as the ionization potential is investigated. In absorption spectroscopy, light is incident on a sample to measure the amount of the transmitted light, and the absorbance is expressed as a function of the photon energy: the peak position of the spectrum gives the excitation energy of the sample, and the peak intensity gives the transition probability. That is, in those spectroscopic measurement, light is incident as an external perturbation or a probe, and the excited state is investigated by measuring the response of the system. Therefore, a spectroscopy is considered as one of the perturbative methods to study linear or nonlinear response to an electron and a photon, to which MBPT is directly relevant.

One may consider the density functional theory (DFT)<sup>1-3)</sup> is also relevant to the spectroscopy, but the standard DFT cannot be legitimately used because the theory is justified to the ground state calculation. Of course, DFT was extended to time-dependent (TD) systems, or to excited states,

but the exchange-correlation functional of the TD-DFT has so far been developed only for a nearly adiabatic electron dynamics and, in addition, the charge-transfer excitation and the Rydberg excitation are often inaccurately predicted.

In order to treat the excited state, the first-principles Green's function method has been developed on the basis of MBPT and provided us with a post-DFT approach to the excitation of a real material. The excitation or quasi-particle (QP) spectra are directly probed in a wide range of spectroscopic experiments, which is highly advantageous to intuitively understand the calculation results. The development was independently pioneered by Hybertsen *et al.*<sup>4)</sup> and Strinati *et al.*<sup>5,6)</sup>. They showed, for several semiconductors and insulators, that the band gap comparable to the experimental one can be obtained by using the *GW* approximation (*GWA*)<sup>7-9)</sup> to describe the self-energy operator simply as a product of the one-particle Green's function (*G*) and the dynamically screened Coulomb interaction (*W*) within the random phase approximation (RPA). Thereafter, *GWA* has been successfully applied to wide variety of materials. Later, the *GWA* was applied to the self-energy operator appearing in the equation of motion of the two-particle Green's function, known as the Bethe-Salpeter equation (BSE)<sup>10-17)</sup>. Application of the *GW*+BSE method was pioneered by Onida *et al.*<sup>13)</sup> who demonstrated, for an isolated sodium tetramer, that the optical spectra comparable to the experimental one are successfully obtained by incorporating the excitonic effect beyond the one-particle picture. The *GW*+BSE method has now been recognized as one of the most reliable first-principles methods for the calculation of optical spectra.<sup>18-20)</sup>

In spite of the methodological developments done so far, the *GW*+BSE method is not as popular as DFT yet. This is not solely due to the fact that the *GW*+BSE calculation is much more time-consuming. We consider it is also due to the fact that the potential ability of this method has not been made clear yet. For example, it is not clear what is the maximum size of the system practically accessible with the modern supercomputers and what is the typical accuracy feasibly achievable within *GWA*. In addition, methods to get relevant information from the calculation have not been well prepared yet. The aim of this thesis is to answer some of these questions via demonstration calculations. We use a massively parallelized code to perform an unprecedentedly large scale calculation, to remove approximations so far made in addition to *GWA*, and to develop an analysis method of the exciton wave function.

To answer the first question, we will demonstrate in Chapter 7 that the *GW*+BSE method with our program can accurately calculate carbon



nanocages involving 198 atoms.

To answer the second question, we will demonstrate in chapter 6, a practical classification method of excitons. Although excitons are conceptually classified into local-, Rydberg-, or charge-transfer type, their classification has been ambiguous so far. The conventional analysis method has been based on state-by-state visualization of the one-electron wave function. In chapter 6, we will propose a quantitative characterization method of exciton as a step toward enabling a data-driven material design of organic solar cells.<sup>21)</sup>

To answer the third question, we will analyze the excitation energy of small molecules. In  $GW+BSE$  formalism, the electron-hole ( $e-h$ ) interaction kernel  $K$  have been approximated in addition to  $GWA$ . The  $e-h$  interaction kernel  $K$  is defined by the functional derivative of the self-energy operator  $\Sigma$  with respect to the one-particle Green's function  $G$ , that is,  $K := i\delta(\Sigma^H + \Sigma^{xc})/\delta G$ , where  $\Sigma^H$  and  $\Sigma^{xc}$  are the Hartree and exchange-correlation (xc) term, respectively. As  $\Sigma^{xc} = iGW$ , the kernel can be written as  $K = K^x - W - G\delta W/\delta G$ , where the first term  $K^x(= i\delta\Sigma^H/\delta G)$  is called the bare Coulomb exchange interaction, the second term corresponds to the screened Coulomb direct interaction  $K^d := -W$  and the third term  $G\delta W/\delta G =: K'$  corresponds to the second-order correction of  $W$  which has been neglected so far. This approximation was justified for semiconductor systems in which excitons are weakly bound and the binding energy is typically dozen of meV.<sup>22)</sup> However, this approximation has been controversial for molecular systems. It was recently reported that the calculated optical gaps of small molecules are underestimated by about 1 eV and their binding energies are extremely large (about 10 eV)<sup>23,24)</sup>, which implies the screening is significantly small and the second-order correction is not negligible. In Chapter 8, we will demonstrate the effect of the second-order correction on small molecules.

This thesis is organized as follows: In Chapters 2-5, we will describe basic theories and methods in our  $GW+BSE$  method. In Chapter 2, we will briefly describe DFT. In Chapter 3, we will describe the Hedin's equations and  $GWA$ . In Chapter 4, we will describe not only  $GW+BSE$  formalism, but our formulation of the second-order correction. In chapter 5, we will describe our all-electron mixed basis approach.

In Chapter 6-8, we will describe demonstrations and applications by our  $GW+BSE$  method. In Chapter 6, we will develop an exciton analysis method to extend practicability of the  $GW+BSE$  method. In Chapter 7, we will calculate carbon nanocages involving 198 atoms to demonstrate applicability of the  $GW+BSE$  method. In Chapter 8, we will investigate the

effect of the second-order correction to develop further improvement of the  $GW+BSE$  method.

In Chapter 9, we will give summary and conclusion.

We use the Hartree atomic unit in this thesis.

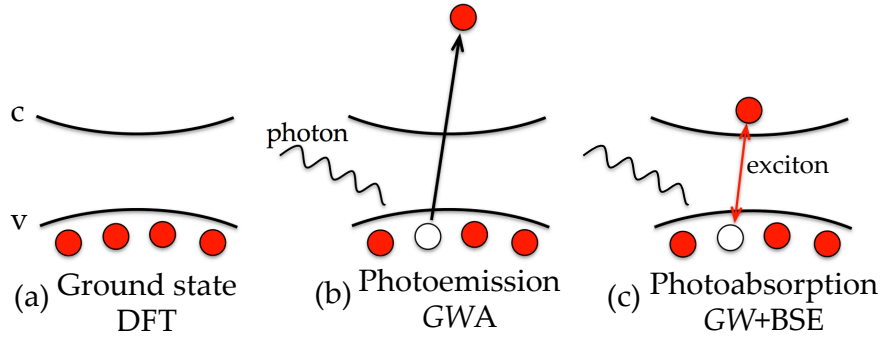


Figure 1.1: Physics and corresponding calculation method.

## Chapter 2

# Density Functional Theory

The density functional theory (DFT)<sup>1-3</sup> is one of the most successful methods for calculating the many-electron system. DFT is important in our theory because the solution of the Kohn-Sham (KS) equation is taken as a unperturbed term in the Green's function method. Here, we briefly describe DFT.

Hamiltonian of an interacting  $N$ -electron system is given as

$$H = T + V_{ee} + V_{ext}, \quad (2.1)$$

where the first, second and third term corresponds to the kinetic energy, the electron-electron Coulomb repulsive interaction and the electron-nuclear attractive interaction or external potential, respectively. These are written explicitly as

$$T = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 \right) \quad (2.2)$$

$$V_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.3)$$

$$V_{ext} = \sum_{i=1}^N v_{ext}(\mathbf{r}_i), \text{ where } v_{ext}(\mathbf{r}) = - \sum_J^{\text{Allnuclei}} \frac{Z_J}{|\mathbf{r} - \mathbf{R}_J|}. \quad (2.4)$$

The Schrödinger equation is given as follows:

$$H\Psi(\mathbf{r}^N) = E\Psi(\mathbf{r}^N), \quad (2.5)$$

where  $\mathbf{r}^N$  is an abbreviation of  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ . We introduce the density operator  $\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ . By using this operator, the density  $n(\mathbf{r})$  is expressed as follows:

$$\begin{aligned} n(\mathbf{r}) &= (\Psi, \hat{n}(\mathbf{r}) \Psi) \\ &= \int \Psi^*(\mathbf{r}^N) \hat{n}(\mathbf{r}) \Psi(\mathbf{r}^N) d\mathbf{r}^N. \end{aligned} \quad (2.6)$$

In addition, the expectation value of an external potential  $V_{\text{ext}}$  is expressed as follows:

$$\begin{aligned} (\Psi, V_{\text{ext}} \Psi) &= \int \Psi^*(\mathbf{r}^N) \left[ \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) \right] \Psi(\mathbf{r}^N) d\mathbf{r}^N \\ &= \int \Psi^*(\mathbf{r}^N) \left[ \int \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i) d\mathbf{r} \right] \Psi(\mathbf{r}^N) d\mathbf{r}^N \\ &= \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.7)$$

In 1964, Hohenberg-Kohn (HK) proved the basic theorem of DFT<sup>1)</sup>. The theorem is divided into two parts.

**Hohenberg-Kohn theorem 1**

If a ground state is not degenerated, the external potential  $V_{\text{ext}}(\mathbf{r})$  is uniquely determined by the density  $n(\mathbf{r})$ , besides a trivial additive constant.

**(proof)**

We assume that there exists two external potentials  $V_{\text{ext}}$  and  $V'_{\text{ext}}$  which are different more than an additive constant and give a common electronic density  $n$ . Let the Hamiltonians  $H$  and  $H'$  include  $V_{\text{ext}}$  and  $V'_{\text{ext}}$ , respectively. As a preparation, we prove that  $H$  and  $H'$  do not have a common eigenstate  $\Psi$ . Here we assume that

$$\begin{aligned} H\Psi &= E\Psi, \\ H'\Psi &= E'\Psi. \end{aligned}$$

Taking difference between the above two equations, we obtain

$$(V_{\text{ext}} - V'_{\text{ext}})\Psi = (E - E')\Psi.$$

$\Psi$  identically is not equal to zero, and  $V_{\text{ext}} - V'_{\text{ext}} = E - E'$ , which is a contradiction to the assumption that two potentials are different more than an additive constant.

From here on, let  $\Psi$  and  $\Psi'$  are eigenstates for  $H$  and  $H'$ , respectively. Let us consider the following two Schrödinger equations

$$\begin{aligned} H\Psi &= E\Psi, \\ H'\Psi' &= E'\Psi'. \end{aligned}$$

By considering  $\Psi \neq \Psi'$  and the Schrödinger-Ritz variational principle, we obtain the following inequality

$$\begin{aligned} E = (\Psi, \hat{H}\Psi) &< (\Psi', \hat{H}\Psi') \\ &= (\Psi', (\hat{H}' - \hat{V}'_{\text{ext}} + \hat{V}_{\text{ext}})\Psi') \\ &= E' + \int [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \end{aligned}$$

Similarly for  $E'$ , we obtain

$$E' < E + \int [v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})]n(\mathbf{r})d\mathbf{r}.$$

Adding two above inequalities, we obtain

$$E + E' < E + E',$$

which is a contradiction.

Since  $n(\mathbf{r})$  uniquely determines  $V_{\text{ext}}$ , it also determines the ground state wave function  $\Psi$ , which should be obtained by solving the full many-body Schrödinger equation. Therefore, there exists a unique and universal functional of the electronic density  $n(\mathbf{r})$  which determines the ground state. Defining the functional  $F$  as

$$F[n(\mathbf{r})] := (\Psi, (T + V_{\text{ee}})\Psi), \quad (2.8)$$

we can express the ground state energy as follows:

$$E_v[n(\mathbf{r})] = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]. \quad (2.9)$$

Next we prove the HK second theorem which corresponds to the variational principle to the ground state energy.

**Hohenberg-Kohn theorem 2**

$E_v[n(\mathbf{r})]$  takes the minimum value for the exact  $n(\mathbf{r})$ .

(proof)

$$\begin{aligned}
E_v[\Psi'] &= (\Psi', V_{\text{ext}}\Psi') + (\Psi', (T + V_{\text{ee}})\Psi') \\
&= \int v_{\text{ext}}(\mathbf{r})n'(\mathbf{r})d\mathbf{r} + F[n'(\mathbf{r})] \\
&> E_v[\Psi] = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})].
\end{aligned}$$

The HK second theorem states that if  $E_v[n]$  takes the minimum value,  $n[\mathbf{r}]$  is the correct density of the ground state. As a preparation, we transform  $E_v[n]$  as follows:

$$E_v[n] = T_s[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + J[n] + E_{\text{xc}}[n], \quad (2.10)$$

$$J[n] := \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.11)$$

Here,  $T_s[n]$  is the kinetic energy of the non-interacting reference system, and the subscript "s" indicates *single-particle*;  $J[n]$  corresponds to the classical electrostatic energy (so-called Hartree term),  $E_{\text{xc}}$  is the exchange-correlation (xc) energy which is the sum of the exchange and the correlation energy.  $E_{\text{xc}}$  is defined as follows:

$$E_{\text{xc}}[n] := F[n] - T_s[n] - J[n]. \quad (2.12)$$

Defining  $T[n] := (\Psi, T\Psi)$  and  $E_{\text{ee}}[n] := (\Psi, V_{\text{ee}}\Psi)$ , we have

$$E_{\text{xc}}[n] = (T[n] - T_s[n]) + (E_{\text{ee}}[n] - J[n]). \quad (2.13)$$

The first term of r.h.s is the difference between the kinetic energies of the real and reference system, the second term is the electron-electron interacting energy except for the classical electrostatic energy. In this reference system, each electron is in motion under an effective potential  $v_{\text{eff}}$

$$\left[ -\frac{1}{2}\nabla^2 + v_{\text{eff}}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (2.14)$$

Since there is no interaction in this reference system, the many-body wave function is expressed by the Slater determinant consisting of the one-electron orbital (KS orbital)  $\{\phi_i\}$ . Therefore the density  $n(\mathbf{r})$  is given as follows:

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (2.15)$$

Since the kinetic energy operator is the one-body operator, kinetic energy  $T_s$  in the reference system is given as follows:

$$T_s[n] = \sum_{i=1}^N \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle. \quad (2.16)$$

By using Eq. (2.14),  $T_s$  is also expressed as follows:

$$T_s = \sum_{i=1}^N \varepsilon_i - \int v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}. \quad (2.17)$$

We determine  $v_{\text{eff}}(\mathbf{r})$  by using the variational method. In Eq. (2.17), taking variance as  $\phi_i \rightarrow \phi_i + \delta\phi_i$ , we obtain

$$\begin{aligned} \sum_{i=1}^N \left( \langle \delta\phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle + \text{c.c.} \right) &= \sum_{i=1}^N \delta\varepsilon_i - \int \delta v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \int v_{\text{eff}}(\mathbf{r}) \sum_{i=1}^N (\delta\phi_i^* \phi_i + \text{c.c.}) d\mathbf{r} \\ \sum_{i=1}^N \left( \langle \delta\phi_i | -\frac{1}{2} \nabla^2 + v_{\text{eff}} | \phi_i \rangle + \text{c.c.} \right) &= \sum_{i=1}^N \delta\varepsilon_i - \int \delta v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ \sum_{i=1}^N \varepsilon_i \delta \langle \phi_i | \phi_i \rangle &= \sum_{i=1}^N \delta\varepsilon_i - \int \delta v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ \therefore \sum_{i=1}^N \delta\varepsilon_i &= \int \delta v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.18)$$

By using Eqs. (2.17), (2.18), a variation of  $E_v[n]$  is given as follows:

$$\delta E_v[n] = - \int \delta n(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) d\mathbf{r} + \int \delta n(\mathbf{r}) \left[ v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right] d\mathbf{r}. \quad (2.19)$$

Under the constraint of a fixed number of electrons

$$\int d\mathbf{r} \delta n(\mathbf{r}) = 0, \quad (2.20)$$

if  $\delta E_v = 0$  for  $\delta n(\mathbf{r})$ , then we obtain

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}), \quad (2.21)$$

besides a trivial additive constant. Here, we defined the xc potential  $v_{\text{xc}}(\mathbf{r})$

$$v_{\text{xc}}(\mathbf{r}) := \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (2.22)$$

Substituting Eq. (2.17) into Eq. (2.10), we obtain

$$E_v[n] = \sum_i \varepsilon_i - J[n] + E_{\text{xc}}[n] - \int v_{\text{xc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}. \quad (2.23)$$

Consequently, if we obtain the eigenvalues  $\{\varepsilon_i\}$  and the eigenfunctions  $\{\phi_i\}$  for the KS equation, we can immediately calculate the total energy from the above equation.

Summarizing the above, if we solve the one-body problem or KS equation, we can calculate the exact total energy of the ground state. However, we have never mentioned specific expression of the xc energy  $E_{\text{xc}}$  and its functional derivative  $v_{\text{xc}}$ . That is, in order to perform specific calculations, we need the expression for  $E_{\text{xc}}$  even though it is approximate.

If we find the exact xc energy  $E_{\text{xc}}$  and its functional derivative  $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n]/\delta n(\mathbf{r})$ , we can generally resolve the many-electron problem. However, it is highly difficult. We introduce the local density approximation (LDA) for the xc energy

$$E_{\text{xc}}[n] \simeq \int n(\mathbf{r})\varepsilon_{\text{xc}}(n)d\mathbf{r}, \quad (2.24)$$

where  $\varepsilon_{\text{xc}}(n)$  denotes the xc energy per particle of a homogeneous electron gas of density  $n$ . The corresponding xc potential  $v_{\text{xc}}(\mathbf{r})$  becomes

$$v_{\text{xc}}(\mathbf{r}) = \varepsilon_{\text{xc}}(n(\mathbf{r})) + \left. \frac{d\varepsilon_{\text{xc}}(n)}{dn} \right|_{n=n(\mathbf{r})}. \quad (2.25)$$

The xc energy density  $\varepsilon_{\text{xc}}$  is a sum of the exchange part  $\varepsilon_{\text{x}}$  and the correlation part  $\varepsilon_{\text{c}}$ . The exchange energy density is exactly given by

$$\varepsilon_{\text{x}}(r_s) = -\frac{0.4582}{r_s} \text{ Ha}, \quad (2.26)$$

where  $r_s$  is the dimensionless parameter defined by

$$r_s = \left( \frac{3}{4\pi n} \right)^{\frac{1}{3}}.$$



The most accurate correlation energy was calculated using quantum Monte Carlo simulations by Ceperley and Alder<sup>25)</sup>, and has been parametrized by Perdew and Zunger<sup>26)</sup>

$$\varepsilon_c(r_s) = \begin{cases} -0.1413/(1 + 1.0529\sqrt{r_s} + 0.3334r_s) \text{ Ha} & \text{for } r_s \geq 1 \\ -0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.0020r_s \ln r_s \text{ Ha} & \text{for } r_s \leq 1. \end{cases}$$

Although the KS equation is the eigenvalue equation, the potential  $v_{\text{eff}}[n](\mathbf{r})$  is dependent on the eigenfunction  $\{\phi_i\}$  which we seek. Thus, we need to self-consistently solve the KS equation. Firstly, we specify an initial density which, in general, is expressed by a sum of the density of each atom. Next we calculate  $v_{\text{eff}}$  or the KS Hamiltonian and subsequently calculate the eigenvalue  $\varepsilon_i$  and the eigenfunction  $\phi_i$  via diagonalization. Finally, we check the difference of the input and output density. If the difference is sufficiently small, we terminate the calculation, otherwise we make a new density for the next step. We iterate this procedure until it is converged.

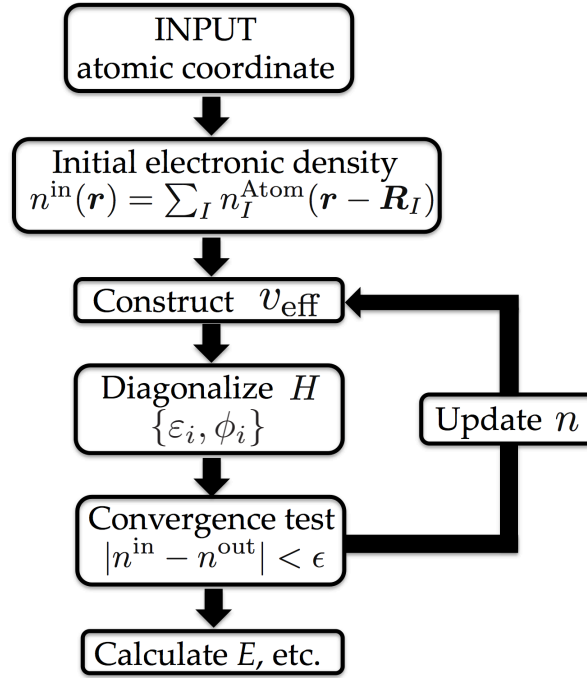


Figure 2.1: Flowchart of the SCF calculation.

## Chapter 3

# Hedin's equations and $GW$ approximation

### 3.1 Schwinger's trick

From this section, we introduce the second quantization and abbreviated notations  $i = \{\mathbf{r}_i, \sigma_i\}$  and  $\mathbf{i} = \{\mathbf{r}_i, \sigma_i, t_i\}$ . The Hamiltonian of interacting electrons is given as follows:

$$H = \int d1 \psi^\dagger(1) h(\mathbf{r}_1) \psi(1) + \frac{1}{2} \int d1 d1' \psi^\dagger(1) \psi^\dagger(1') v(\mathbf{r}_1, \mathbf{r}_1') \psi(1') \psi(1), \quad (3.1)$$

where

$$h(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}), \quad (3.2)$$

$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.3)$$

We also consider the following external perturbation  $H'$

$$H'(t_2) = \int d2 u(\mathbf{2}) n(2), \quad (3.4)$$

where  $u(\mathbf{2})$  is an arbitrary external potential which is put to zero at the end, and  $n(2) = \psi^\dagger(2) \psi(2)$  is the number density operator. Note that we consider the Hamiltonian  $H$  including two-body operator is the unperturbed term, and  $H'$  is the perturbation. We define the interaction picture as follows:

$$\psi(\mathbf{1}) := e^{iHt_1} \psi(1) e^{-iHt_1}. \quad (3.5)$$

In the interaction picture, Eq. (3.4) becomes

$$H'_I(t_2) = e^{iHt_2} H'(t_2) e^{-iHt_2} \quad (3.6)$$

$$= \int d\mathbf{2} u(\mathbf{2}) n(\mathbf{2}). \quad (3.7)$$

We introduce the (formal) operator  $S(t_a, t_b)$

$$S(t_a, t_b) = \exp \left[ -i \int_{t_b}^{t_a} dt_2 H'_I(t_2) \right], \quad (3.8)$$

and its simplified operator  $S$

$$S := S(-\infty, \infty) = \exp \left[ -i \int d\mathbf{2} u(\mathbf{2}) n(\mathbf{2}) \right]. \quad (3.9)$$

Note that  $T[S(t_a, t_b)]$  and  $T[S]$  are the time evolution operator and  $S$ -matrix, respectively, where  $T$  is the Dyson's time-ordering operator. By using the above preparation, the generalized one-particle Green's function  $G$  is defined as follows:

$$G(\mathbf{1}, \mathbf{1}') := -i \frac{\langle N, 0 | T[S \psi(\mathbf{1}) \psi^\dagger(\mathbf{1}')] | N, 0 \rangle}{\langle N, 0 | T[S] | N, 0 \rangle}, \quad (3.10)$$

where  $|N, 0\rangle$  is the ground state of the unperturbed  $N$ -electrons system. Similarly, the generalized two-particle Green's function  $G_2$  is defined as follows:

$$G_2(\mathbf{1}, \mathbf{1}', \mathbf{2}, \mathbf{2}') := (-i)^2 \frac{\langle N, 0 | T[S \psi(\mathbf{1}) \psi(\mathbf{2}) \psi^\dagger(\mathbf{2}') \psi^\dagger(\mathbf{1}')] | N, 0 \rangle}{\langle N, 0 | T[S] | N, 0 \rangle}. \quad (3.11)$$

Eqs. (3.10) and (3.11) reduce to the definition of the ordinary Green's functions as  $u \rightarrow 0$ . Notice also that all the  $u$ -dependence in the generalized Green's functions is contained in the operator  $S$ . Applying the chain rule shown in Appendix B, first order variation of  $G$  caused by  $u$  is given as

$$\delta G(\mathbf{1}, \mathbf{1}') = -i \frac{\langle N, 0 | T[\delta S \psi(\mathbf{1}) \psi^\dagger(\mathbf{1}')] | N, 0 \rangle}{\langle N, 0 | T[S] | N, 0 \rangle} - G(\mathbf{1}, \mathbf{1}') \frac{\langle N, 0 | T[\delta S] | N, 0 \rangle}{\langle N, 0 | T[S] | N, 0 \rangle}, \quad (3.12)$$

where

$$\delta S = -iS \int d\mathbf{2} \delta u(\mathbf{2}) n(\mathbf{2}). \quad (3.13)$$

We obtain the Schwinger's trick<sup>7, 17, 27)</sup> from the above equation

$$\frac{\delta G(\mathbf{1}, \mathbf{1}')}{\delta u(\mathbf{2})} = -G_2(\mathbf{1}, \mathbf{1}', \mathbf{2}, \mathbf{2}^+) + iG(\mathbf{1}, \mathbf{1}') \langle n(\mathbf{2}) \rangle. \quad (3.14)$$

This identity allows us to truncate the hierarchy of Green's functions. In the hierarchy, the equation of motion for the one-particle Green's function includes the two-particle Green's function, and similarly the equation of motion for the two-particle Green's function include the three-particle Green's function and so on. It is conceivable that this hierarchical structure makes impossible to exactly solve the Green's function of many-electron systems. However, the Schwinger's trick shows that the two-particle Green's function can be expressed by the one-particle Green's function although the functional derivative term with respect to  $u$  is unknown. Since linear-response functions such as the polarizability are naturally defined as the functional derivative with respect to an external perturbation, this form is advantageous for relating to physical quantities. From the next section, we will derive the Hedin's equations from the Schwinger's trick (3.14).

To discuss coupling of external perturbations to momentum, energy, or angular momentum densities, as well as to number density, it is convenient to consider a nonlocal external potential  $u(\mathbf{2}, \mathbf{2}')$  in space and time. That is, the operator  $S$  is generalized as follows:

$$S = \exp \left[ -i \int d\mathbf{2}\mathbf{2}' \psi^\dagger(\mathbf{2}) u(\mathbf{2}, \mathbf{2}') \psi(\mathbf{2}') \right]. \quad (3.15)$$

We find that  $u(\mathbf{2}, \mathbf{2}')$  represents a disturbance in which a particle is removed from the system at  $\mathbf{2}$  and added at  $\mathbf{2}'$ . In addition, the Schwinger's trick (3.14) is easily generalized as follows:

$$\frac{\delta G(\mathbf{1}, \mathbf{1}')}{\delta u(\mathbf{2}, \mathbf{2}')} = -G_2(\mathbf{1}, \mathbf{1}', \mathbf{2}', \mathbf{2}) + G(\mathbf{1}, \mathbf{1}') G(\mathbf{2}', \mathbf{2}). \quad (3.16)$$

In Chapter 4, the above generalization plays an essential role.

## 3.2 The Dyson equation

Before considering the equation of motion for the one-particle Green's function  $G$ , we summarize the following properties of the operator  $S$

- group property

$$T[S(t_a, t_b)] = T[S(t_a, t_b)] T[S(t_b, t_c)]; \quad (3.17)$$

- assuming  $t_a > t_1 > t_2 > t_b$ , decomposition property

$$T[S(t_a, t_b) \psi(\mathbf{1}) \psi(\mathbf{2})] = T[S(t_a, t_1)] \psi(\mathbf{1}) T[S(t_1, t_2)] \psi(\mathbf{2}) T[S(t_2, t_b)]; \quad (3.18)$$

- time derivatives

$$\frac{\partial}{\partial t_a} T[S(t_a, t_b)] = -iH'_I(t_a)T[S(t_a, t_b)], \quad (3.19a)$$

$$\frac{\partial}{\partial t_b} T[S(t_a, t_b)] = iT[S(t_a, t_b)]H'_I(t_b). \quad (3.19b)$$

Moreover, the time derivative of the field operator is given as

$$\frac{\partial}{\partial t_1} \psi(\mathbf{1}) = -i \left[ h(1) + \int d\mathbf{3} v(\mathbf{1}, \mathbf{3}) \psi^\dagger(\mathbf{3}) \psi(\mathbf{3}) \right] \psi(\mathbf{1}), \quad (3.20)$$

where  $v(\mathbf{1}, \mathbf{3}) = v(\mathbf{r}_1, \mathbf{r}_3) \delta(t_1 - t_3)$ . From here on, we consider the time-derivative of the one-particle Green's function and omit the denominator  $\langle N, 0 | T[S] | N, 0 \rangle$  for simplicity. Then, we have

$$i \frac{\partial}{\partial t_1} G(\mathbf{1}, \mathbf{1}') = \frac{\partial}{\partial t_1} \left[ \theta(t_1 - t'_1) \langle N, 0 | T[S(\infty, t_1)] \psi(\mathbf{1}) T[S(t_1, t'_1)] \psi^\dagger(\mathbf{1}') T[S(t'_1, -\infty)] | N, 0 \rangle \right. \\ \left. - \theta(t'_1 - t_1) \langle N, 0 | T[S(\infty, t'_1)] \psi^\dagger(\mathbf{1}') T[S(t'_1, t_1)] \psi(\mathbf{1}) T[S(t_1, -\infty)] | N, 0 \rangle \right]. \quad (3.21)$$

Now we evaluate the time-derivative appearing on the r.h.s of Eq. (3.21). Firstly, noting that  $\partial/\partial t \theta(t) = \delta(t)$  and  $S(t, t) = 1$ , the derivative of  $\theta$  yields

$$R_1 = \delta(t_1 - t'_1) \langle N, 0 | T[S e^{iHt_1} \{ \psi(1), \psi^\dagger(1') \} e^{-iHt_1}] | N, 0 \rangle \\ = \delta(\mathbf{1}, \mathbf{1}').$$

Secondly, taking the derivative of four  $S$ s, we get

$$R_2 = \left[ i\theta(t_1 - t'_1) \langle N, 0 | T[S(\infty, t_1)] [H'_I(t_1), \psi(\mathbf{1})] T[S(t_1, t'_1)] \psi^\dagger(\mathbf{1}') T[S(t'_1, -\infty)] | N, 0 \rangle \right. \\ \left. - i\theta(t'_1 - t_1) \langle N, 0 | T[S(\infty, t'_1)] \psi^\dagger(\mathbf{1}') T[S(t'_1, t_1)] [H'_I(t_1), \psi(\mathbf{1})] T[S(t_1, -\infty)] | N, 0 \rangle \right],$$

by using  $[AB, C] = A\{B, C\} - \{A, C\}B$ , we obtain

$$[H'(t_1), \psi(1)] = -u(\mathbf{1})\psi(1),$$

that is, the above equation becomes

$$R_2 = -u(\mathbf{1})G(\mathbf{1}, \mathbf{1}').$$

Thirdly, taking the derivative of the field operator  $\psi$ , we get

$$R_3 = h(1)G(\mathbf{1}, \mathbf{1}') - i \int d\mathbf{2} v(\mathbf{1}, \mathbf{2}) G_2(\mathbf{1}, \mathbf{1}', \mathbf{2}^+, \mathbf{2}^{++}),$$

where we wrote  $\psi^\dagger(\mathbf{2})\psi(\mathbf{2})\psi(\mathbf{1}) = -\psi(\mathbf{1})\psi(\mathbf{2}^+)\psi^\dagger(\mathbf{2}^{++})$  in order to remain the time order. Summing  $R_1$ - $R_3$ , we obtain

$$\left[ i \frac{\partial}{\partial t_1} - h(\mathbf{1}) - u(\mathbf{1}) \right] G(\mathbf{1}, \mathbf{1}') + i \int d\mathbf{2} v(\mathbf{1}, \mathbf{2}) G_2(\mathbf{1}, \mathbf{1}', \mathbf{2}^+, \mathbf{2}^{++}) = \delta(\mathbf{1}, \mathbf{1}'). \quad (3.22)$$

Substituting the Schwinger's trick (3.14) to the above equation, we can rewrite Eq. (3.22) as

$$\left[ i \frac{\partial}{\partial t_1} - h(\mathbf{1}) - u(\mathbf{1}) - v^H(\mathbf{1}) \right] G(\mathbf{1}, \mathbf{1}') - i \int d\mathbf{2} v(\mathbf{1}^+, \mathbf{2}) \frac{\delta G(\mathbf{1}, \mathbf{1}')}{\delta u(\mathbf{2})} = \delta(\mathbf{1}, \mathbf{1}'), \quad (3.23)$$

where we defined the Hartree potential  $v^H$  as follows:

$$v^H(\mathbf{1}) := \int d\mathbf{2} v(\mathbf{1}, \mathbf{2}) \langle n(\mathbf{2}) \rangle. \quad (3.24)$$

Here we define the self-energy operator  $\Sigma$  as follows:

$$\Sigma(\mathbf{1}, \mathbf{1}') := v^H(\mathbf{1})\delta(\mathbf{1}, \mathbf{1}') + i \int d\mathbf{2} \mathbf{3} v(\mathbf{1}^+, \mathbf{2}) \frac{\delta G(\mathbf{1}, \mathbf{3})}{\delta u(\mathbf{2})} G^{-1}(\mathbf{3}, \mathbf{1}') \quad (3.25)$$

$$=: \Sigma^H(\mathbf{1}, \mathbf{1}') + \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{1}') \quad (3.26)$$

Finally, we obtain the differential form of the Dyson equation

$$\left[ i \frac{\partial}{\partial t_1} - h(\mathbf{1}) \right] G(\mathbf{1}, \mathbf{1}') - \int d\mathbf{2} \Sigma(\mathbf{1}, \mathbf{2}) G(\mathbf{2}, \mathbf{1}') = \delta(\mathbf{1}, \mathbf{1}'), \quad (3.27)$$

where we omitted the infinitesimal potential  $u$ . We introduce the unperturbed one-particle Green's function  $G^{(0)}$  as follows:

$$\left[ i \frac{\partial}{\partial t_1} - h(\mathbf{1}) \right] G^{(0)}(\mathbf{1}, \mathbf{1}') = \delta(\mathbf{1}, \mathbf{1}'), \quad (3.28)$$

using the above, Eq. (3.27) becomes

$$\begin{aligned} & \int d\mathbf{2} G^{(0)-1}(\mathbf{1}, \mathbf{2}) G(\mathbf{2}, \mathbf{1}') - \int d\mathbf{2} \Sigma(\mathbf{1}, \mathbf{2}) G(\mathbf{2}, \mathbf{1}') = \delta(\mathbf{1}, \mathbf{1}') \\ \therefore G(\mathbf{1}, \mathbf{1}') &= G^{(0)}(\mathbf{1}, \mathbf{1}') + \int d\mathbf{2} \mathbf{3} G^{(0)}(\mathbf{1}, \mathbf{2}) \Sigma(\mathbf{2}, \mathbf{3}) G(\mathbf{3}, \mathbf{1}'). \end{aligned} \quad (3.29)$$

This is the integral form of the Dyson equation.

### 3.3 Polarizability, vertex function and dynamically screened Coulomb interaction

The self-energy operator  $\Sigma$  still depends on the infinitesimal potential  $u$ . In this section, by introducing linear response functions, we remove this dependency. As a preparation, we introduce the *total* potential  $V$  which is the sum of the infinitesimal potential  $u$  and the Hartree potential  $v^H$

$$V(\mathbf{1}) := u(\mathbf{1}) + v^H(\mathbf{1}). \quad (3.30)$$

We define the irreducible vertex function  $\Gamma$  as follows:

$$\Gamma(\mathbf{1}, \mathbf{2}; \mathbf{3}) := -\frac{\delta G^{-1}(\mathbf{1}, \mathbf{2})}{\delta V(\mathbf{3})} \quad (3.31)$$

$$\begin{aligned} &= -\frac{\delta}{\delta V(\mathbf{3})} \left[ G^{(0)-1}(\mathbf{1}, \mathbf{2}) - V(\mathbf{1})\delta(\mathbf{1}, \mathbf{2}) - \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2}) \right] \\ &= \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}) + \frac{\delta \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2})}{\delta V(\mathbf{3})}. \end{aligned} \quad (3.32)$$

We can rewrite the vertex function  $\Gamma$  as an integral form by using the chain rule and Eq. (B.5) in Appendix B

$$\begin{aligned} \Gamma(\mathbf{1}, \mathbf{2}; \mathbf{3}) &= \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}) + \int d\mathbf{4}\mathbf{5} \frac{\delta \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2})}{\delta G(\mathbf{4}, \mathbf{5})} \frac{\delta G(\mathbf{4}, \mathbf{5})}{\delta V(\mathbf{3})} \\ &= \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}) - \int d\mathbf{4}\mathbf{5}\mathbf{6}\mathbf{7} \frac{\delta \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2})}{\delta G(\mathbf{4}, \mathbf{5})} G(\mathbf{4}, \mathbf{6}) \frac{\delta G^{-1}(\mathbf{6}, \mathbf{7})}{\delta V(\mathbf{3})} G(\mathbf{7}, \mathbf{5}) \\ &= \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}) + \int d\mathbf{4}\mathbf{5}\mathbf{6}\mathbf{7} \frac{\delta \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2})}{\delta G(\mathbf{4}, \mathbf{5})} G(\mathbf{4}, \mathbf{6}) G(\mathbf{7}, \mathbf{5}) \Gamma(\mathbf{6}, \mathbf{7}; \mathbf{3}). \end{aligned} \quad (3.33)$$

We define the irreducible polarizability  $P$  as follows:

$$P(\mathbf{1}, \mathbf{2}) := \frac{\delta \langle n(\mathbf{1}) \rangle}{\delta V(\mathbf{2})} \quad (3.34)$$

$$\begin{aligned} &= i \int d\mathbf{3}\mathbf{4} G(\mathbf{1}, \mathbf{3}) \frac{\delta G^{-1}(\mathbf{3}, \mathbf{4})}{\delta V(\mathbf{2})} G(\mathbf{4}, \mathbf{1}^+) \\ &= -i \int d\mathbf{3}\mathbf{4} G(\mathbf{1}, \mathbf{3}) G(\mathbf{4}, \mathbf{1}^+) \Gamma(\mathbf{3}, \mathbf{4}; \mathbf{2}). \end{aligned} \quad (3.35)$$

We define the longitudinal dielectric function  $\epsilon$  as follows:

$$\epsilon^{-1}(\mathbf{1}, \mathbf{2}) := \frac{\delta V(\mathbf{1})}{\delta u(\mathbf{2})} \quad (3.36)$$

$$\begin{aligned} &= \delta(\mathbf{1}, \mathbf{2}) + \int d\mathbf{3} v(\mathbf{1}, \mathbf{3}) \frac{\delta \langle n(\mathbf{3}) \rangle}{\delta u(\mathbf{2})} \\ &=: \delta(\mathbf{1}, \mathbf{2}) + \int d\mathbf{3} v(\mathbf{1}, \mathbf{3}) \chi(\mathbf{3}, \mathbf{2}), \end{aligned} \quad (3.37)$$

where we defined the reducible polarizability  $\chi$ .  $\epsilon$  is a measure of the effect of shielding classical Coulomb interaction. By using the dielectric function  $\epsilon$ , we define the dynamically screened Coulomb interaction  $W$  as follows:

$$W(\mathbf{1}, \mathbf{2}) := \int d\mathbf{3} \epsilon^{-1}(\mathbf{1}, \mathbf{3}) v(\mathbf{3}, \mathbf{2}) \quad (3.38)$$

$$= v(\mathbf{1}, \mathbf{2}) + \int d\mathbf{3} d\mathbf{4} v(\mathbf{1}, \mathbf{4}) \frac{\delta \langle n(\mathbf{4}) \rangle}{\delta V(\mathbf{5})} \frac{\delta V(\mathbf{5})}{\delta u(\mathbf{3})} v(\mathbf{3}, \mathbf{2}) \quad (3.39)$$

$$= v(\mathbf{1}, \mathbf{2}) + \int d\mathbf{3} d\mathbf{4} v(\mathbf{1}, \mathbf{3}) P(\mathbf{3}, \mathbf{4}) W(\mathbf{4}, \mathbf{2}). \quad (3.40)$$

Finally, we can rewrite the xc self-energy operator  $\Sigma^{\text{xc}}$  without the infinitesimal potential  $u$

$$\begin{aligned} \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2}) &= i \int d\mathbf{3} d\mathbf{4} v(\mathbf{1}^+, \mathbf{3}) \frac{\delta G(\mathbf{1}, \mathbf{4})}{\delta u(\mathbf{3})} G^{-1}(\mathbf{4}, \mathbf{2}) \\ &= -i \int d\mathbf{3} d\mathbf{4} d\mathbf{5} d\mathbf{6} d\mathbf{7} v(\mathbf{1}^+, \mathbf{3}) \frac{\delta V(\mathbf{5})}{\delta u(\mathbf{3})} G(\mathbf{1}, \mathbf{6}) \frac{\delta G^{-1}(\mathbf{6}, \mathbf{7})}{\delta V(\mathbf{5})} G(\mathbf{7}, \mathbf{4}) G^{-1}(\mathbf{4}, \mathbf{2}) \\ &= i \int d\mathbf{5} d\mathbf{6} W(\mathbf{1}^+, \mathbf{5}) G(\mathbf{1}, \mathbf{6}) \Gamma(\mathbf{6}, \mathbf{2}; \mathbf{5}). \end{aligned} \quad (3.41)$$



Here we summarize the above results as the Hedin's equations and show those Feynman diagrams in Fig. 3.1.

$$G(\mathbf{1}, \mathbf{2}) = G^{(0)}(\mathbf{1}, \mathbf{2}) + \int d\mathbf{34} G^{(0)}(\mathbf{1}, \mathbf{3}) \Sigma(\mathbf{3}, \mathbf{4}) G(\mathbf{4}, \mathbf{2}) \quad (3.42a)$$

$$\Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2}) = i \int d\mathbf{34} W(\mathbf{1}^+, \mathbf{3}) G(\mathbf{1}, \mathbf{4}) \Gamma(\mathbf{4}, \mathbf{2}; \mathbf{3}) \quad (3.42b)$$

$$P(\mathbf{1}, \mathbf{2}) = -i \int d\mathbf{34} G(\mathbf{1}, \mathbf{3}) G(\mathbf{4}, \mathbf{1}^+) \Gamma(\mathbf{3}, \mathbf{4}; \mathbf{2}) \quad (3.42c)$$

$$W(\mathbf{1}, \mathbf{2}) = v(\mathbf{1}, \mathbf{2}) + \int d\mathbf{34} v(\mathbf{1}, \mathbf{3}) P(\mathbf{3}, \mathbf{4}) W(\mathbf{4}, \mathbf{2}) \quad (3.42d)$$

$$\Gamma(\mathbf{1}, \mathbf{2}; \mathbf{3}) = \delta(\mathbf{1}, \mathbf{2}) \delta(\mathbf{1}, \mathbf{3}) + \int d\mathbf{4567} \frac{\delta \Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2})}{\delta G(\mathbf{4}, \mathbf{5})} G(\mathbf{4}, \mathbf{6}) G(\mathbf{7}, \mathbf{5}) \Gamma(\mathbf{6}, \mathbf{7}; \mathbf{3}) \quad (3.42e)$$

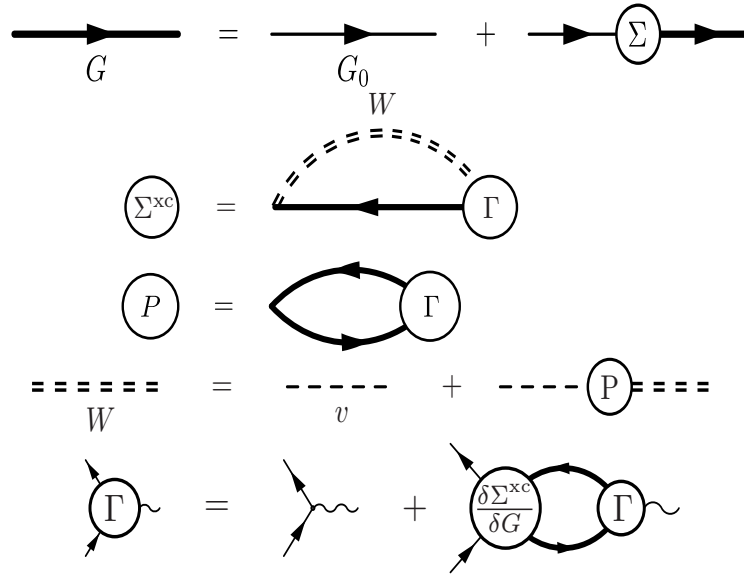


Figure 3.1: Feynman diagrams of the Hedin's equations

### 3.4 $GW$ approximation

We can, in principle, solve the Hedin's equations because they include five unknown functions and five equations. Firstly, setting the xc self-energy

operator  $\Sigma^{\text{xc}}$  equal to zero, the second term on r.h.s of Eq. (3.42e) is equal to zero, thus the irreducible vertex function  $\Gamma$  becomes

$$\Gamma(\mathbf{1}, \mathbf{2}; \mathbf{3}) = \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}). \quad (3.43)$$

Secondly, substituting the above equation into Eq. (3.42c), the polarization function  $P$  becomes

$$P(\mathbf{1}, \mathbf{2}) = -iG(\mathbf{1}, \mathbf{2})G(\mathbf{2}, \mathbf{1}^+). \quad (3.44)$$

Thirdly, substituting the above equation into Eq. (3.42d), we obtain the dynamical screened Coulomb interaction  $W$

$$W(\mathbf{1}, \mathbf{2}) = v(\mathbf{1}, \mathbf{2}) + \int d\mathbf{3}d\mathbf{4}v(\mathbf{1}, \mathbf{3})P(\mathbf{3}, \mathbf{4})W(\mathbf{4}, \mathbf{2}). \quad (3.45)$$

Finally, we obtain renewed xc self-energy operator  $\Sigma_{\text{xc}}$

$$\Sigma^{\text{xc}}(\mathbf{1}, \mathbf{2}) = iW(\mathbf{1}^+, \mathbf{2})G(\mathbf{1}, \mathbf{2}), \quad (3.46)$$

thus, we obtain renewed Green's function  $G$ . Iterating procedures mentioned above, in principles, we obtain exact Green's function  $G$ . This scheme is called the  $GW\Gamma$  scheme since  $\Sigma^{\text{xc}} = -iGW\Gamma$ . However, this scheme is not only highly complicated, but also specific expression of the vertex function  $\Gamma$  is still unknown. In general, the xc self-energy operator  $\Sigma^{\text{xc}}$  is calculated by the  $GW$  approximation ( $GWA$ )<sup>4-7,9)</sup>, which is simply given as a product of  $G$  and  $W$ , i.e.,  $\Sigma^{\text{xc}} = iGW$  or  $\Gamma = 1$ . Furthermore we call the one-shot  $GW$  or  $G_0W_0$ <sup>28,29)</sup> which truncates  $GWA$  with a single update and call it the self-consistent  $GW$  ( $scGW$ )<sup>30-34)</sup> to repeat it until convergence. The one-shot  $GW$  has been successfully applied to wide variety of materials to calculate (inverse) photoemission spectra. The  $scGW$  calculation does not always improve the one-shot  $GW$ , usually the QP energy gap is overestimated.<sup>35)</sup> However, it is advantageous that  $scGW$  allows to calculate the total energy of the system with the Luttinger-Ward (LW) functional<sup>36)</sup>.

From here on, we show the one-shot  $GW$  scheme in practice. We assume hamiltonian  $H$  conserves each spin of electrons so that Green's functions are diagonal for spin components;  $G(\mathbf{1}, \mathbf{1}') = G(\mathbf{1}, \mathbf{1}')\delta_{\sigma_1\sigma'_1}$ . We refer to  $|N \pm 1, n\mathbf{k}\sigma\rangle$  as  $n$ th eigenstates added or removed one-electron with spin  $\sigma$  to ground states of a  $N$  electron system. Substituting the completeness

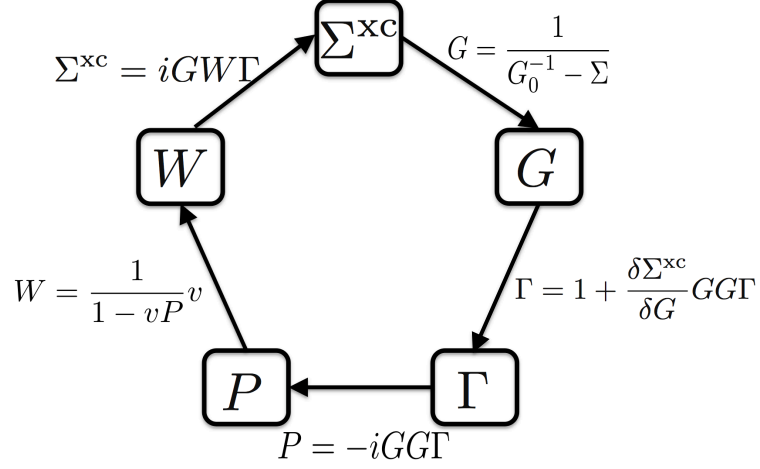


Figure 3.2: Symbolical representation of the practical solution of the Hedin's equations or  $GWT$  Scheme.

relation  $\sum_{n\mathbf{k}\sigma} |N \pm 1, n\mathbf{k}\sigma\rangle \langle N \pm 1, n\mathbf{k}\sigma|$  to Eq. (3.10), we obtain

$$\begin{aligned}
 G(\mathbf{1}, \mathbf{1}') &= -i\delta_{\sigma_1\sigma'_1} \sum_{n\mathbf{k}} \langle N, 0 | \psi(\mathbf{1}) | N+1, n\mathbf{k}\sigma_1 \rangle \langle N+1, n\mathbf{k}\sigma_1 | \psi^\dagger(\mathbf{1}') | N, 0 \rangle \theta(t_1 - t'_1) \\
 &\quad + i\delta_{\sigma_1\sigma'_1} \sum_{n\mathbf{k}} \langle N, 0 | \psi^\dagger(\mathbf{1}') | N-1, n\mathbf{k}\sigma_1 \rangle \langle N-1, n\mathbf{k}\sigma_1 | \psi(\mathbf{1}) | N, 0 \rangle \theta(t'_1 - t_1).
 \end{aligned} \tag{3.47}$$

Intermediate states of the first and second term correspond to a  $N+1$  and a  $N-1$  electron system, respectively. The former corresponds to adding one electron to empty states, while the latter corresponds to removing one electron from occupied states. That is, these quasiparticles correspond to “electron” and “hole”, respectively. By using  $\psi(\mathbf{1}) = e^{iHt_1}\psi(1)e^{-iHt_1}$ ,  $\psi^\dagger(\mathbf{1}') = e^{iHt'_1}\psi^\dagger(1')e^{-iHt'_1}$ ,  $H$  may be replaced by its eigenvalues

$$\begin{aligned}
 \langle N, 0 | \psi(\mathbf{1}) | N+1, n\mathbf{k}\sigma_1 \rangle &= \langle N, 0 | \psi(1) | N+1, n\mathbf{k}\sigma_1 \rangle e^{-i(E_{n\mathbf{k}\sigma_1}^{N+1} - E_0^N)t_1} \\
 \langle N-1, n\mathbf{k}\sigma_1 | \psi(\mathbf{1}) | N, 0 \rangle &= \langle N-1, n\mathbf{k}\sigma_1 | \psi(1) | N, 0 \rangle e^{-i(E_0^N - E_{n\mathbf{k}\sigma_1}^{N-1})t_1}.
 \end{aligned}$$

We define the QP wave functions  $\phi_n$  and the QP energy  $\epsilon_{n\mathbf{k}\sigma}$  of “electron” and “hole” as follows:

$$\phi_{n\mathbf{k}}(1) := \begin{cases} \langle N, 0 | \psi(1) | N+1, n\mathbf{k}\sigma_1 \rangle & (\text{emp}) \\ \langle N-1, n\mathbf{k}\sigma_1 | \psi(1) | N, 0 \rangle & (\text{occ}) \end{cases}, \tag{3.48}$$

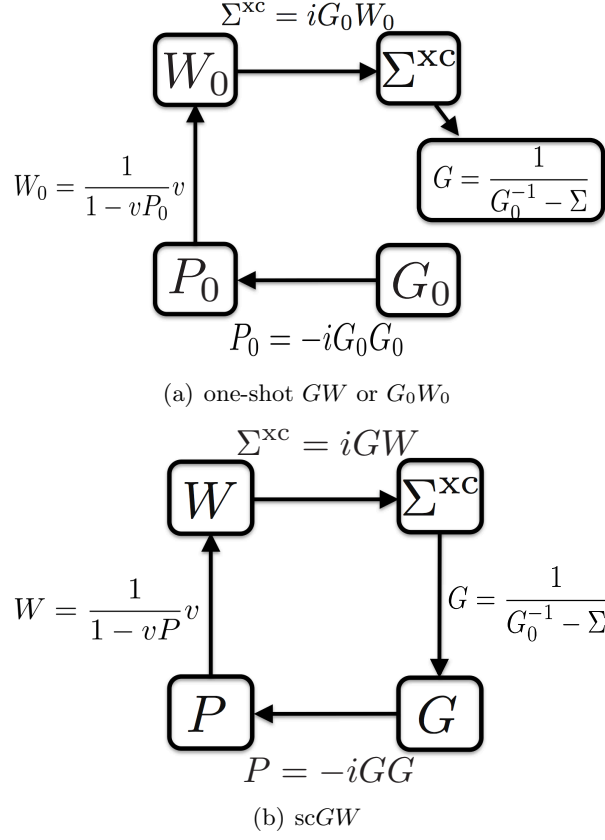


Figure 3.3: Symbolical GWA schemes are shown. (a) one-shot GW or  $G_0W_0$   
(b) self-consistent GW (scGW)

$$\epsilon_{n\mathbf{k}\sigma} := \begin{cases} E_{n\mathbf{k}\sigma}^{N+1} - E_0^N & (\text{emp}) \\ E_0^N - E_{n\mathbf{k}\sigma}^{N-1} & (\text{occ}) \end{cases}. \quad (3.49)$$

By using the above equations, we can rewrite Eq. (3.47) as follows:

$$\begin{aligned} G(\mathbf{1}, \mathbf{1}') = & - i\delta_{\sigma_1\sigma'_1} \sum_{c\mathbf{k}} e^{-i\epsilon_{c\mathbf{k}\sigma_1}(t_1-t'_1)} \phi_{c\mathbf{k}}(1) \phi_{c\mathbf{k}}^*(1') \theta(t_1 - t'_1) \\ & + i\delta_{\sigma_1\sigma'_1} \sum_{v\mathbf{k}} e^{-i\epsilon_{v\mathbf{k}\sigma_1}(t_1-t'_1)} \phi_{v\mathbf{k}}(1) \phi_{v\mathbf{k}}^*(1') \theta(t'_1 - t_1), \end{aligned} \quad (3.50)$$

where  $c$  and  $v$  are running for empty and occupied states, respectively. When

$G$  is Fourier transformed in time, we have

$$\begin{aligned} G(1, 1', \omega) &:= \int_{-\infty}^{\infty} d(t_1 - t'_1) e^{i\omega(t_1 - t'_1)} G(1, 1', t_1 - t'_1) \\ &= \delta_{\sigma_1 \sigma'_1} \sum_{n\mathbf{k}} \frac{\phi_{n\mathbf{k}}(1) \phi_{n\mathbf{k}}^*(1')}{\omega - \epsilon_{n\mathbf{k}\sigma_1} - i\delta_{n\mathbf{k}\sigma_1}}, \end{aligned} \quad (3.51)$$

where  $\delta_{n\mathbf{k}\sigma_1}$  is  $0^+(-0^+)$  for occupied (empty) states. The QP wavefunction also satisfies the following Dyson equation

$$H_0 \phi_{n\mathbf{k}}(1) + \int d\mathbf{r}_2 \Sigma^{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2; \epsilon_{n\mathbf{k}\sigma_1}) \phi_{n\mathbf{k}\sigma_1}(\mathbf{r}_2) = \epsilon_{n\mathbf{k}\sigma_1} \phi_{n\mathbf{k}}(1), \quad (3.52)$$

where  $H_0$  is the one-body part of the hamiltonian which includes the Hartree potential. By using Eqs. (3.44), (3.47), the polarizability  $P$  in GWA is given as follows:

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2; \omega) &= -i \sum_{\sigma} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} G_{\sigma}^0(\mathbf{r}_1, \mathbf{r}_2; \omega) G_{\sigma}^0(\mathbf{r}_2, \mathbf{r}_1; \omega' - \omega) \\ &= \sum_{\sigma} \sum_{n\mathbf{k}} \sum_{n'\mathbf{k}'} \frac{\phi_{n\mathbf{k}\sigma}(\mathbf{r}_1) \phi_{n'\mathbf{k}'\sigma}^*(\mathbf{r}_1) \phi_{n\mathbf{k}\sigma}^*(\mathbf{r}_2) \phi_{n'\mathbf{k}'\sigma}(\mathbf{r}_2)}{\omega - \epsilon_{n\mathbf{k}\sigma} + \epsilon_{n'\mathbf{k}'\sigma} - i\delta_{n\mathbf{k}\sigma}} (f_{n'\mathbf{k}'\sigma} - f_{n\mathbf{k}\sigma}), \end{aligned} \quad (3.53)$$

where  $f_{n\mathbf{k}\sigma}$  is the Fermi distribution function, and each term of the summation is non-zero if and only if one of  $n\mathbf{k}\sigma$  and  $n'\mathbf{k}'\sigma$  is occupied and the another one is unoccupied. Defining the Fourier transform for space-coordinates as follows:

$$P(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{\mathbf{q}} \sum_{\mathbf{G}\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_1} P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}_2}, \quad (3.54)$$

we obtain

$$P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \sum_{\sigma} \sum_{nn'\mathbf{k}} \frac{\langle n\mathbf{k}\sigma | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | n'\mathbf{k} + \mathbf{q}\sigma \rangle \langle n'\mathbf{k} + \mathbf{q}\sigma | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} | n\mathbf{k}\sigma \rangle}{\omega - \epsilon_{n\mathbf{k}\sigma} + \epsilon_{n'\mathbf{k}'\sigma} - i\delta_{n\mathbf{k}\sigma}} (f_{n'\mathbf{k}+\mathbf{q}\sigma} - f_{n\mathbf{k}\sigma}), \quad (3.55)$$

where  $\mathbf{G}$  and  $\mathbf{q}$  are the reciprocal lattice vector and the wave vector in the first Brillouin zone, respectively. Next we can calculate the dielectric function in the reciprocal space

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}\mathbf{G}'} - v(\mathbf{q} + \mathbf{G}) P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega). \quad (3.56)$$

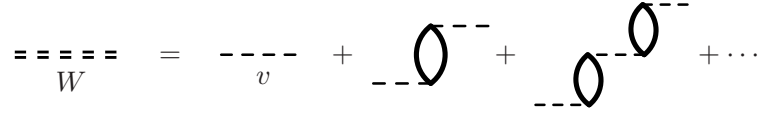
Next we can calculate the dynamically screened Coulomb interaction  $W$  as follows:

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = [\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)]^{-1} v(\mathbf{q} + \mathbf{G}'). \quad (3.57)$$

$W$  within  $GWA$  is equivalent to the random phase approximation (RPA) which is described by the sum of the ring diagrams shown in Fig. 3.4(a). The xc self-energy operator  $\Sigma^{\text{xc}}$  is given by the product of  $G$  and  $W$

$$\Sigma_{\sigma}^{\text{xc}}(\mathbf{r}, \mathbf{r}') = i \int \frac{d\omega'}{2\pi} e^{i\omega'0^+} G_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega'), \quad (3.58)$$

which corresponds to the diagrams shown in Fig. 3.4(b).



(a)  $W$  within RPA



(b)  $\Sigma^{\text{xc}}$  within  $GWA$

Figure 3.4: The Feynman diagrams of the dynamically screened Coulomb interaction  $W$  within RPA and xc self-energy operator  $\Sigma^{\text{xc}}$  within  $GWA$  are shown.

In practice, it is convenient to separate  $\Sigma^{\text{xc}}$  into the exchange part  $\Sigma^{\text{x}}$  and the correlation part  $\Sigma^{\text{c}}$

$$\Sigma_{\sigma}^{\text{x}}(\mathbf{r}, \mathbf{r}') = iv(\mathbf{r} - \mathbf{r}') \int \frac{d\omega'}{2\pi} e^{i\omega'0^+} G_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega'), \quad (3.59a)$$

$$\Sigma_{\sigma}^{\text{c}}(\mathbf{r}, \mathbf{r}'; \omega) = i \int \frac{d\omega'}{2\pi} e^{i\omega'0^+} G_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega + \omega') [W(\mathbf{r}, \mathbf{r}'; \omega') - v(\mathbf{r} - \mathbf{r}')]. \quad (3.59b)$$

We describe the matrix element sandwiched by the QP states

$$\begin{aligned}\langle n\mathbf{k}\sigma|\Sigma_\sigma^x|n'\mathbf{k}\sigma\rangle &= -\sum_{l,\mathbf{k}'}^{\text{occ}} \int d\mathbf{r}d\mathbf{r}' \frac{\phi_{n\mathbf{k}\sigma}^*(\mathbf{r})\phi_{l\mathbf{k}'\sigma}^*(\mathbf{r}')\phi_{l\mathbf{k}'\sigma}(\mathbf{r})\phi_{n\mathbf{k}\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &= -\frac{4\pi}{\Omega} \sum_l^{\text{occ}} \sum_{\mathbf{q}}^{\text{BZ}} \sum_{\mathbf{G}} \frac{\langle n\mathbf{k}\sigma|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|l\mathbf{k}-\mathbf{q}\sigma\rangle \langle l\mathbf{k}-\mathbf{q}\sigma|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n'\mathbf{k}\sigma\rangle}{|\mathbf{q}+\mathbf{G}|^2},\end{aligned}\quad (3.60a)$$

$$\begin{aligned}\langle n\mathbf{k}\sigma|\Sigma_\sigma^c|n'\mathbf{k}\sigma\rangle &= i \sum_l^{\text{occ}} \sum_{\mathbf{q}}^{\text{BZ}} \sum_{\mathbf{G}\mathbf{G}'} \int \frac{d\omega'}{2\pi} e^{i\omega'0+} \frac{[W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega') - v(\mathbf{q}+\mathbf{G})\delta_{\mathbf{G}\mathbf{G}'}]}{\omega+\omega'-\varepsilon_{l\mathbf{k}-\mathbf{q}\sigma}-i\delta_{l\mathbf{k}-\mathbf{q}\sigma}} \\ &\quad \times \langle n\mathbf{k}\sigma|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|l\mathbf{k}-\mathbf{q}\sigma\rangle \langle l\mathbf{k}-\mathbf{q}\sigma|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n'\mathbf{k}\sigma\rangle.\end{aligned}\quad (3.60b)$$

We find the  $\omega$  integral is necessary for only the correlation term. Generalized plasmon pole (GPP) models<sup>4,37,38</sup>) are often used to avoid this integral. In the GPP model, it is assumed that the energy dependence of the imaginary part of the dielectric function can be approximated well by one delta function corresponding to the plasma frequency  $\omega_p$ . For instance, the GPP model of Hypertsen and Louie<sup>4</sup>) is based on the  $f$  summation rule, which defines

$$\tilde{\omega}_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q}) := \frac{\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q})}{\delta_{\mathbf{G}\mathbf{G}'} - \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q};\omega=0)}, \quad (3.61a)$$

$$\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q}) := \omega_p^2 \frac{(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2} \frac{n(\mathbf{G}-\mathbf{G}')}{n(0)}, \quad (3.61b)$$

which is need to rewrite Eq. (3.60b) as

$$\begin{aligned}\langle n\mathbf{k}\sigma|\Sigma_\sigma^c|n'\mathbf{k}\sigma\rangle &= \sum_l \sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} v(\mathbf{q}+\mathbf{G}') \\ &\quad \times \frac{\Omega_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q}) \langle n\mathbf{k}\sigma|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|l\mathbf{k}-\mathbf{q}\sigma\rangle \langle l\mathbf{k}-\mathbf{q}\sigma|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n'\mathbf{k}\sigma\rangle}{2\tilde{\omega}_{\mathbf{G}\mathbf{G}'}^2(\mathbf{q})[\omega-\varepsilon_{l\mathbf{k}-\mathbf{q}\sigma}-\text{sgn}(\varepsilon_{l\mathbf{k}-\mathbf{q}\sigma})\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})]}.\end{aligned}\quad (3.62)$$

In actual  $GW$  calculation, choice of the initial QP wave function should be important<sup>39</sup>). Since the LDA wave function is considered reasonably close to the QP wave function, it is often chosen as the initial wave function. The QP spectrum within  $GW$  is obtained from the following equation

$$\varepsilon_{n\mathbf{k}\sigma}^{GW} = \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}} + \int d\mathbf{r}d\mathbf{r}' \phi_{n\mathbf{k}\sigma}^{\text{LDA}*}(\mathbf{r}) [\Sigma_\sigma(\mathbf{r},\mathbf{r}';\varepsilon_{n\mathbf{k}\sigma}^{GW}) - v_{\text{xc}\sigma}^{\text{LDA}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')] \phi_{n\mathbf{k}\sigma}^{\text{LDA}}(\mathbf{r}'). \quad (3.63)$$

In this equation, since the  $GW$  QP energy  $\varepsilon_{n\mathbf{k}\sigma}^{GW}$  to be solved is contained in the self energy, this dependency is numerically treated by using a linear extrapolation, which corresponds to so-called renormalization of energy. Then the above equation becomes

$$\varepsilon_{n\mathbf{k}\sigma}^{GW} = \varepsilon_{n\mathbf{k}\sigma}^0 + (\varepsilon_{n\mathbf{k}\sigma}^0 - \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}}) \frac{\partial \Sigma_{n\mathbf{k}\sigma}(\varepsilon)}{\partial \varepsilon} \bigg|_{\varepsilon = \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}}} Z_{n\mathbf{k}\sigma}, \quad (3.64a)$$

$$\varepsilon_{n\mathbf{k}\sigma}^0 := \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}} + \int d\mathbf{r} d\mathbf{r}' \phi_{n\mathbf{k}\sigma}^{\text{LDA}*}(\mathbf{r}) [\Sigma_{\sigma}(\mathbf{r}, \mathbf{r}'; \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}}) - v_{\text{xc}\sigma}^{\text{LDA}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')] \phi_{n\mathbf{k}\sigma}^{\text{LDA}}(\mathbf{r}'), \quad (3.64b)$$

$$Z_{n\mathbf{k}\sigma} := \left[ 1 - \frac{\partial \Sigma_{n\mathbf{k}\sigma}(\varepsilon)}{\partial \varepsilon} \bigg|_{\varepsilon = \varepsilon_{n\mathbf{k}\sigma}^{\text{LDA}}} \right]^{-1}, \quad (3.64c)$$

where  $Z_{n\mathbf{k}\sigma}$  is the renormalization factor, and we defined  $\Sigma_{n\mathbf{k}\sigma}(\varepsilon) := \langle n\mathbf{k}\sigma | \Sigma_{\sigma}(\varepsilon) | n\mathbf{k}\sigma \rangle$ .



## Chapter 4

# Optical spectra with Bethe-Salpeter equation

本章については5年以内に雑誌などで刊行予定のため、非公開。

## Chapter 5

# All-electron mixed basis approach

### 5.1 Feature

Our calculations are executed on our all-electron mixed basis program<sup>54–61</sup>, in which the KS wave function is expanded as a linear combination of plane waves (PWs) and atomic orbitals (AOs). In this study, the second-order correction in the dynamically screened Coulomb interaction was newly implemented. The *GW*+BSE method requires, in principle, all the information on electronic states including localized states in the core region and free electron states above the vacuum level. Our all-electron program can take those states into account.

The all-electron mixed basis approach has the following features:

1. The number of basis functions can be greatly reduced. For example, for the ethylene calculated in this study, the PW cutoff is sufficiently converged at about 18 Ry, whereas in the conventional pseudo-potential method, about 80 Ry is required.
2. AOs are numerically generated on the logarithmic mesh by using the Herman-Skillman technique<sup>62</sup>, which gives us accurate core electron states.
3. The algorithm is simpler than use of the norm-preserving<sup>63–66</sup> and ultrasoft<sup>67–69</sup> pseudopotentials.
4. Since the core AOs have values only in non-overlapping atomic spheres, there is no need to evaluate their overlap matrices and there is no basis-

set superposition error (BSSE). In addition, the over-completeness problem hardly occurs.

## 5.2 Outline of plane wave expansion method

Here, we briefly summarize the PW expansion approach which is a general method of band calculations.

We consider the following Schrödinger equation within an one-electron approximation in a crystal potential

$$H\phi_{i\mathbf{k}}(\mathbf{r}) = \epsilon_{i\mathbf{k}}\phi_{i\mathbf{k}}(\mathbf{r}), \quad (5.1)$$

where, the subscripts  $i$  and  $\mathbf{k}$  are a band index and a  $\mathbf{k}$  point in a first Brillouin zone (BZ), respectively. Let the potential be invariant to the translational vector  $\mathbf{R}$  of the crystal

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}). \quad (5.2)$$

According to Bloch's theorem, the electronic wave function  $\phi_{i\mathbf{k}}(\mathbf{r})$  in a periodic system can be written by the function  $u_{i\mathbf{k}}(\mathbf{r})$  having translational symmetry as follows:

$$\phi_{i\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{i\mathbf{k}}(\mathbf{r}), \quad (5.3)$$

$$u_{i\mathbf{k}}(\mathbf{r}) = u_{i\mathbf{k}}(\mathbf{r} + \mathbf{R}). \quad (5.4)$$

The Fourier expansion of  $u_{i\mathbf{k}}(\mathbf{r})$  is given by

$$\phi_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{i\mathbf{k}+\mathbf{G}} \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}), \quad (5.5)$$

where  $\mathbf{G}$  is a reciprocal vector and  $\Omega$  is the volume of the unit cell. We define the PW basis as follows:

$$\langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle = \frac{1}{\sqrt{\Omega}} \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}), \quad (5.6)$$

The PW basis satisfies the following orthonormality

$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\Omega} \int_{\Omega} \exp(-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}) d\mathbf{r} = \delta_{\mathbf{G}\mathbf{G}'}. \quad (5.7)$$

Consequently, the Fourier coefficient  $c_{i\mathbf{k}+\mathbf{G}}$  is given as follows:

$$c_{i\mathbf{k}+\mathbf{G}} = \frac{1}{\sqrt{\Omega}} \int_{\Omega} \psi_{i\mathbf{k}+\mathbf{G}}(\mathbf{r}) \exp(-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}). \quad (5.8)$$

In practice, the PW expansion is truncated at a finite number of terms, so that we introduce some cutoff wavenumber  $G_{\max}$  and expand within  $|\mathbf{k} + \mathbf{G}| < G_{\max}$ .  $G_{\max}/2\pi$  corresponds to the spatial resolution, and changes at smaller scale cannot be described.

Substituting Eq. (5.5) into the Schrödinger equation and using the orthonormality, we obtain the following eigenvalue equation

$$\sum_{\mathbf{G}'} \left[ \frac{1}{2} (\mathbf{k} + \mathbf{G})^2 \delta_{\mathbf{G}\mathbf{G}'} + \langle \mathbf{k} + \mathbf{G}' | V | \mathbf{k} + \mathbf{G} \rangle \right] c_{i\mathbf{k}+\mathbf{G}'} = \varepsilon_{i\mathbf{k}} c_{i\mathbf{k}+\mathbf{G}}, \quad (5.9)$$

where, the second term in parenthesis is the Fourier transform of the potential

$$V(\mathbf{G}-\mathbf{G}') := \langle \mathbf{k} + \mathbf{G}' | V | \mathbf{k} + \mathbf{G} \rangle = \frac{1}{\sqrt{\Omega}} \int_{\Omega} V(\mathbf{r}) \exp(i(\mathbf{G}-\mathbf{G}') \cdot \mathbf{r}) d\mathbf{r}. \quad (5.10)$$

Note that the KS equation in the reference system is formally equal to Schrödinger equation within the one-electron approximation. In practice, Calculations are performed using both the real and reciprocal space because the xc potential is easy to integrate in the real space, while kinetic energy is easy to integrate in the reciprocal space. This method is called “dual space formalism”. By combining this method with the fast Fourier transform (FFT), computational cost can be greatly reduced.

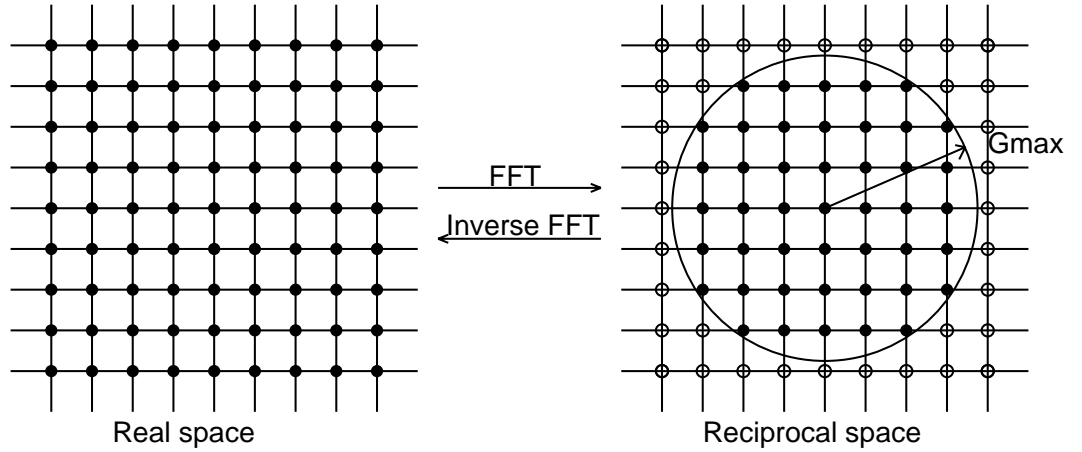


Figure 5.1: Dual space formalism. The real and reciprocal space mesh are transformed by FFT.

### 5.3 Electronic density and potential

We described the PW expansion approach above, here we introduce the basis function  $\phi_{jnlm}^{\text{AO}}$  for AOs, which is expressed as a product of radial function  $R_{jnl}(r)$  and spherical harmonics  $Y_{lm}(\hat{\mathbf{r}})$

$$\phi_{jnlm}^{\text{AO}}(\mathbf{r}) = Y_{lm}(\hat{\mathbf{r}})R_{jnl}(r). \quad (5.11)$$

Here,  $j, n, l$  and  $m$  are atomic species, principal quantum number, angular momentum quantum number and magnetic quantum number, respectively. Since an isolated atom has a spherical symmetry, the ordinary differential equation for  $R_{jnl}(r)$  is accurately solved over the logarithmic mesh.<sup>62)</sup> There is generally no overlap with the core AOs with other AOs, while the valence AOs overlap with other AOs. We avoid the overlap by restricting the amplitude of the valence AOs inside the non-overlapping atomic sphere with a cutoff radius  $r_c$ .

The total wavefunction is described as a linear combination of PWs and AOs as follows:

$$\phi_{\nu}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\nu}^{\text{PW}}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} + \sum_j \sum_{nlm} c_{\nu}^{\text{AO}}(jnlm) \phi_{jnlm}^{\text{AO}}(\mathbf{r} - \mathbf{R}_j) =: \sum_{\xi} c_{\nu, \xi} f_{\xi}(\mathbf{r}), \quad (5.12)$$

where,  $\nu$  denotes both the band index and the  $k$  point. Since the basis function  $f_{\xi}$  is not orthogonal to each other, we need to solve the following generalized eigenvalue equation for the KS equation

$$\sum_{\xi'} H_{\xi\xi'} c_{\nu, \xi'} = \varepsilon_{\nu} \sum_{\xi'} S_{\xi\xi'} c_{\nu, \xi'}, \quad (5.13)$$

where  $H_{\xi\xi'} := \langle f_{\xi} | H | f_{\xi'} \rangle$  and  $S_{\xi\xi'} := \langle f_{\xi} | f_{\xi'} \rangle$  are the Hamiltonian and overlap matrix elements, respectively. In our program, the above equation is transformed to the usual eigenvalue problem by using Choleski decomposition<sup>70)</sup>.

The electronic density consists of three kind of contributions (PW-PW, AO-PW and AO-AO)

$$n(\mathbf{r}) = n^{\text{PW-PW}}(\mathbf{r}) + \sum_j n_j^{\text{AO-PW}}(\mathbf{r}) + \sum_j n_j^{\text{AO-AO}}(\mathbf{r}), \quad (5.14)$$

these contributions are given, respectively, as

$$n^{\text{PW-PW}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\nu}^{\text{occ}} \sum_{\mathbf{G}} \sum_{\mathbf{G}'} c_{\nu}^{\text{PW}*} c_{\nu}^{\text{PW}} e^{i(\mathbf{G}-\mathbf{G}') \cdot \mathbf{r}}, \quad (5.15)$$

$$n_j^{\text{AO-PW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\nu}^{\text{occ}} \sum_{nlm} \sum_{\mathbf{G}} c_{\nu}^{\text{AO}*}(jnlm) c_{\nu}^{\text{PW}}(\mathbf{G}) \phi_{jnlm}^{\text{AO}}(\mathbf{r} - \mathbf{R}_j) e^{i\mathbf{G} \cdot \mathbf{r}} + \text{c.c.}, \quad (5.16)$$

$$n_j^{\text{AO-AO}}(\mathbf{r}) = \sum_{\nu}^{\text{occ}} \sum_{n'l'm'} \sum_{nlm} c_{\nu}^{\text{AO}*}(jn'l'm') c_{\nu}^{\text{AO}}(jnlm) \phi_{jn'l'm'}^{\text{AO}}(\mathbf{r} - \mathbf{R}_j) \phi_{jnlm}^{\text{AO}}(\mathbf{r} - \mathbf{R}_j). \quad (5.17)$$

Here,  $\sum_{\nu}^{\text{occ}}$  represents sum of all occupied states including spin degeneracy. It is convenient to treat the first contribution  $n^{\text{PW-PW}}$  in the reciprocal space at the grid points in the global mesh space (in our calculation, a unit cell is discretized into  $64 \times 64 \times 64$ ). We write together the rest two contributions involving AOs

$$n_j^{\text{AO}}(\mathbf{r}) := n_j^{\text{AO-PW}}(\mathbf{r}) + n_j^{\text{AO-AO}}(\mathbf{r}), \quad (5.18)$$

which is non-zero only inside the non-overlapping atomic sphere. We divide  $n_j^{\text{AO}}(\mathbf{r})$  into two parts; one of them is the spherical symmetric part  $\sigma_j(|\mathbf{r} - \mathbf{R}_j|)$ , which is given as the spherical average

$$\sigma_j(|\mathbf{r} - \mathbf{R}_j|) := \frac{1}{4\pi} \int n_j^{\text{AO}}(\mathbf{r}) d\Omega_j, \quad (5.19)$$

where  $\Omega_j$  is the solid angle around the  $j$ th atom. The another one is the asymmetric part, however, this term is generally negligible because  $n_j^{\text{AO}}(\mathbf{r})$  exhibits a high spherical symmetry within the atomic sphere. Consequently, we treat the total electronic density as follows:

$$n(\mathbf{r}) = n^{\text{PW-PW}}(\mathbf{r}) + \sum_j \sigma_j(|\mathbf{r} - \mathbf{R}_j|). \quad (5.20)$$

Once the electronic density is obtained both in the global mesh space and the radical mesh, we can evaluate the xc potential  $v_{\text{xc}}(\mathbf{r})$ . In the radical mesh, we construct the truncated potential  $v_j^{\text{xc}}(|\mathbf{r} - \mathbf{R}_j|)$  as well as the electronic density, which is easily Fourier transformed in the radical mesh. In order to evaluate the Fourier transform of  $v_{\text{xc}}(\mathbf{r})$  in the global mesh space,

we define the following global part

$$v^{\text{xc rest}}(\mathbf{r}) := v^{\text{xc}}(\mathbf{r}) - \sum_j v_j^{\text{xc}}(|\mathbf{r} - \mathbf{R}_j|), \quad (5.21)$$

which is a smooth function without cusp-like behavior.

In the PW-PW part, the Fourier transform of the external potential  $V^{\text{ext}}(\mathbf{G})$  is given as follows:

$$V^{\text{ext}}(\mathbf{G}) = -\frac{4\pi}{\Omega} \sum_j \frac{Z_j}{G^2} e^{-i\mathbf{G} \cdot \mathbf{R}_j}. \quad (5.22)$$

By using the Fourier transform of the electronic density  $n(\mathbf{G})$ , the Fourier transform of the Hartree potential  $v^{\text{H}}(\mathbf{G})$  is given as follows:

$$v^{\text{H}}(\mathbf{G}) = \frac{4\pi}{G^2} n(\mathbf{G}). \quad (5.23)$$

Other details and benchmark tests are given in Ref. [61]

## Chapter 6

# Quantitative characterization of exciton

本章については、5 年以内に雑誌などで刊行予定のため、非公開。



## Chapter 7

# Optical spectra of carbon nanocages

本章については、5年以内に雑誌などで刊行予定のため、非公開。

### 7.1 short introduction

## Chapter 8

# Effect of second-order kernel

本章については、5 年以内に雑誌などで刊行予定のため、非公開。

## Chapter 9

# Summary and conclusion

本章については、5年以内に雑誌などで刊行予定のため、非公開。

## Appendix A

# Schrödinger-Ritz variational principle

We prove the Schrödinger-Ritz variational principle. We consider the ground state of the following Schrödinger equation

$$H\Psi_0(\{\mathbf{r}_i\}, \{\mathbf{R}_J\}) = E_0\Psi_0(\{\mathbf{r}_i\}, \{\mathbf{R}_J\}),$$

and seek the lowest eigenvalue satisfying the above equation.

We define the following energy functional with respect to arbitrary wavefunctions  $\Psi$

$$E[\Psi] := \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

$E[\Psi]$  takes the stationary value at  $\Psi = \Psi_0$  and the following relation is satisfied

$$E[\Psi] \geq E_0.$$

**(proof)** If  $\Psi$  is varied from  $\Psi_0$  by  $\delta\Psi$ , then

$$\begin{aligned} E[\Psi] &= \frac{E_0(\langle \Psi_0 | \Psi_0 \rangle) + \langle \delta\Psi | \Psi_0 \rangle + \langle \Psi_0 | \delta\Psi \rangle + \langle \delta\Psi | \hat{H} | \delta\Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= \frac{E_0 \langle \Psi | \Psi \rangle + \langle \delta\Psi | \hat{H} - E_0 | \delta\Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= E_0 + O(\delta\Psi^2). \end{aligned}$$

Since there is no first order term of  $\delta\Psi$ ,  $E[\Psi]$  satisfies the stationary condition  $\delta E[\Psi]/\delta\Psi = 0$  as  $\delta\Psi \rightarrow 0$ . Furthermore, exploring  $\delta\Psi = \sum_n c_n \Psi_n$  by

eigenfunctions  $\{\Psi_n\}$  of  $H$ , we obtain

$$E[\Psi] = E_0 + \sum_n \frac{|c_n|^2}{\langle \Psi | \Psi \rangle} (E_n - E_0).$$

Since  $E_n - E_0 \geq 0$ , we can conclude  $E[\Psi] \geq E_0$ .

## Appendix B

# Functional derivative

We summarize some useful formulae of functional derivatives<sup>17)</sup> as follows:

- derivative for itself

$$\frac{\delta F(\mathbf{1})}{\delta F(\mathbf{2})} = \delta(\mathbf{1}, \mathbf{2}), \quad (\text{B.1})$$

- derivative of the product

$$\frac{\delta}{\delta H(\mathbf{2})}(F[H](\mathbf{1})G[H](\mathbf{1})) = \frac{\delta F[H](\mathbf{1})}{\delta H(\mathbf{2})}G[H](\mathbf{1}) + F[H](\mathbf{1})\frac{\delta G[H](\mathbf{1})}{\delta H(\mathbf{2})}, \quad (\text{B.2})$$

- derivative of the quotient

$$\frac{\delta}{\delta H(\mathbf{2})} \frac{F[H](\mathbf{1})}{G[H](\mathbf{1})} = \frac{1}{\{G[H](\mathbf{1})\}^2} \left[ \frac{\delta F[H](\mathbf{1})}{\delta H(\mathbf{2})} G[H](\mathbf{1}) - F[H](\mathbf{1}) \frac{\delta G[H](\mathbf{1})}{\delta H(\mathbf{2})} \right], \quad (\text{B.3})$$

- definition of the inverse

$$\int F^{-1}(\mathbf{1}, \mathbf{3}) F(\mathbf{3}, \mathbf{2}) d\mathbf{3} = \delta(\mathbf{1}, \mathbf{2}), \quad (\text{B.4})$$

- transformation of a derivative of a function to include its inverse

$$\frac{\delta F(\mathbf{1}, \mathbf{1}')}{\delta G(\mathbf{3})} = - \int F(\mathbf{1}, \mathbf{3}) \frac{\delta F^{-1}(\mathbf{3}, \mathbf{3}')}{\delta G(\mathbf{2})} F(\mathbf{3}', \mathbf{1}') d\mathbf{3}\mathbf{3}', \quad (\text{B.5})$$

- chain rule

$$\frac{\delta F[G[H]](\mathbf{1}, \mathbf{1}')}{\delta H(\mathbf{2}, \mathbf{2}')} = \int \frac{\delta F[G](\mathbf{1}, \mathbf{1}')}{\delta G(\mathbf{3}, \mathbf{3}')} \frac{\delta G[H](\mathbf{3}, \mathbf{3}')}{\delta H(\mathbf{2}, \mathbf{2}')} d\mathbf{3}\mathbf{3}'. \quad (\text{B.6})$$

## Appendix C

# Second-order correction without the static approximation

本章については、5年以内に雑誌などで刊行予定のため、非公開。

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