Appendix A

DENSITY FUNCTIONAL THEORY

The density functional theory (DFT) is one of the methods to derive properties of the interacting many-electron system such as solids and molecules. The DFT has been developed by Hohenberg and Kohn [89], and Kohn and Sham [90]. Within the DFT, the properties of the ground state are obtained only by a density distribution of electrons $\rho(\mathbf{r})$. Hohenberg and Kohn have shown that the total energy of many-electron system, including the exchange-correlation energy, is expressed as a functional of the electron density. The minimum value of the total energy functional is the energy of the ground state and the electron density which yields this total energy minimum is the exact single-particle ground state density.

However, this discussion is still in the level of the general theory. For the practical calculations, Kohn and Sham have introduced a set of the self-consistent one-electron equations (Kohn-Sham equations) which is equivalent to the many-electron problem. Kohn and Sham have also shown that the *local density approximation* (LDA) can be used to describe the exchange-correlation energy. The DFT is free from the empirical parameters. The great progress of the computational powers spreads the fields of DFT applications. Recently, the DFT becomes one of the major methods to describe the properties of the solids and molecules.

A.1 Hohenberg-Kohn Theorem

Hohenberg and Kohn have demonstrated that the ground state properties of the interacting many-electron system are expressed as functionals of the ground state electron density $\rho(\mathbf{r})$. The ground state is determined by the total number of the electrons N and the external potential $v(\mathbf{r})$. The first theorem of Hohenberg and Kohn states that the $v(\mathbf{r})$ is determined uniquely by the density $\rho(\mathbf{r})$. The $\rho(\mathbf{r})$ yields the total number of the electrons N. The N and $v(\mathbf{r})$ fix the Hamiltonian of the system. Therefore, the $\rho(\mathbf{r})$ which yields the N and $v(\mathbf{r})$ determines the ground state wave function Ψ and properties of the system.

We show how the $v(\mathbf{r})$ is determined uniquely by the $\rho(\mathbf{r})$. Here we prepare two different external

potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$. It is assumed that these two potentials give the same ground state density $\rho(\mathbf{r})$. From the two potential $v(\mathbf{r})$ and $v'(\mathbf{r})$, we would have two different Hamiltonian H and H'. These two Hamiltonians yield the same ground state densities. However, corresponding wave function Ψ and Ψ' are different. The eigenvalue equations are

$$H\Psi = E_0\Psi, \tag{A.1}$$

$$H'\Psi' = E_0'\Psi', \tag{A.2}$$

where E_0 and E_0' are the ground state energy for the H and H', respectively. We would have by definition of the E_0 and E_0'.

$$
\begin{aligned}
E_0 < \langle\Psi'|H|\Psi'\rangle &= \langle\Psi'|H'|\Psi'\rangle + \langle\Psi'|H - H'|\Psi'\rangle \\
&= E_0' + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r},
\end{aligned} \tag{A.3}
$$

and

$$
\begin{aligned}
E_0' < \langle\Psi|H'|\Psi\rangle &= \langle\Psi|H|\Psi\rangle + \langle\Psi|H' - H|\Psi\rangle \\
&= E_0 - \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d\mathbf{r}.
\end{aligned} \tag{A.4}
$$

Adding Eqs. (A.3) and (A.4), we obtain

$$E_0 + E_0' < E_0' + E_0. \tag{A.5}$$

This is contradiction. Therefore, the assumption that there are two different potentials that yield the same $\rho(\mathbf{r})$ is wrong. Thus, it is found that the $\rho(\mathbf{r})$ determines the $v(\mathbf{r})$ uniquely.

As discussed above, since both the N and $v(\mathbf{r})$ are determined by the $\rho(\mathbf{r})$, it is followed that the properties of the ground state are derived from the $\rho(\mathbf{r})$. We represent the total energy functional $E_v[\rho]$ as a summation of the kinetic energy $T[\rho]$, the potential energy $V_{ne}[\rho]$ and the electron-electron repulsion energy $V_{ee}[\rho]$, i.e.

$$
\begin{aligned}
E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\
&= \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[\rho],
\end{aligned} \tag{A.6}
$$

where

$$F[\rho] \equiv T[\rho] + V_{ee}[\rho]. \tag{A.7}$$

The second theorem of Hohenberg and Kohn states that the total energy of the ground state of the system E_0 is obtained by minimization of the total energy functional $E_v[\rho]$ with respect to the density $\rho(\mathbf{r})$ (the variational principle). For the trial density $\tilde{\rho}(\mathbf{r})$ which satisfies $\tilde{\rho}(\mathbf{r}) > 0$ and $\int \tilde{\rho}(\mathbf{r}) = N$,

$$E_0 \leq E_v[\tilde{\rho}(\mathbf{r})]. \tag{A.8}$$

We define a density to be *v-representable* if the density $\rho(\mathbf{r})$ uniquely determines the external potential $v(\mathbf{r})$. We discussed so far with assumption that the density is v-representable. However,

it is known that some reasonable electron density is not v-representable. Fortunately, the DFT can be formulated by the similar way with the weaker condition, that is N-*representable*. We define a density to be N-representable if the density can be obtained from some anti-symmetric wave function.

A.2 Levy Formalism

In this subsection, the DFT is formulated by using the N-representable density (Levy formalism) [96]. We define the Hamiltonian of the system as

$$H = T + V_{ee} + \sum_i^N v_{\text{ext}}(\mathbf{r}_i),$$ (A.9)

where the T is the kinetic enegy, V_{ee} is the interelectronic potential and the $v_{\text{ext}}(\mathbf{r})$ is the external field. The functional $F[\rho]$ of the N-representable ρ is defined as

$$F[\rho] \equiv \min_{\psi \to \rho} \langle \psi | T + V_{ee} | \psi \rangle.$$ (A.10)

The minimization is taken with respect to the ψ that gives ρ. This functional does not depend on the external field that specify the system. The total energy, wave function and density of the ground state of the system are denoted here by E_{GS}, ψ_{GS} and ρ_{GS}, respectively. Then the basic theorem in the DFT is

$$E[\rho] \equiv \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[\rho] \geq E_{\text{GS}}.$$ (A.11)

(The variational principle: The total energy of the ground state is the minimum value of the functional $E[\rho]$.) In addition, this E_{GS} is expressed by the ρ_{GS} as

$$\int \rho_{\text{GS}}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[\rho_{\text{GS}}] = E_{\text{GS}}.$$ (A.12)

We prove these two theorems in followings.

When we denote the wave function such that gives the $\rho(\mathbf{r})$ and minimizes the $\langle \psi | T + V_{ee} | \psi \rangle$ as ψ_{min}^{ρ}, we obtain from the definition of $F[\rho]$ (Eq. (A.10)),

$$F[\rho] = \langle \psi_{\text{min}}^{\rho} | T + V_{ee} | \psi_{\text{min}}^{\rho} \rangle.$$ (A.13)

Defining $V \equiv \sum_i v_{\text{ext}}(\mathbf{r}_i)$, we obtain

$$\int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} = \langle \psi_{\text{min}}^{\rho} | V | \psi_{\text{min}}^{\rho} \rangle.$$ (A.14)

Since the ground state should give the minimum total energy, we find

$$\int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[\rho] = \langle \psi_{\text{min}}^{\rho} | V + T + V_{ee} | \psi_{\text{min}}^{\rho} \rangle$$
$$\geq E_{\text{GS}}.$$ (A.15)

Thus, the first theorem (A.11) is proved.

On the other hand, the E_{GS} is represented by ψ_{GS} as

$$
\begin{aligned}
E_{GS} &= \langle \psi_{GS} | H | \psi_{GS} \rangle \\
&= \langle \psi_{GS} | V + T + V_{ee} | \psi_{GS} \rangle.
\end{aligned}
\tag{A.16}
$$

Therefore, we obtain

$$
\langle \psi_{GS} | V + T + V_{ee} | \psi_{GS} \rangle = E_{GS} \leq \langle \psi_{\min}^{\rho_{GS}} | V + T + V_{ee} | \psi_{\min}^{\rho_{GS}} \rangle.
\tag{A.17}
$$

Since the ψ_{GS} and $\psi_{\min}^{\rho_{GS}}$ yield the same density ρ_{GS}, the term of the external field can be rewritten as

$$
\langle \psi_{GS} | V | \psi_{GS} \rangle = \int \rho_{GS}(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} = \langle \psi_{\min}^{\rho_{GS}} | V | \psi_{\min}^{\rho_{GS}} \rangle.
\tag{A.18}
$$

When we subtract the external field from Eq. (A.17), we find,

$$
\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \leq \langle \psi_{\min}^{\rho_{GS}} | T + V_{ee} | \psi_{\min}^{\rho_{GS}} \rangle.
\tag{A.19}
$$

However, the right hand side of this equation is $F[\rho_{GS}]$ and we have from the definition of $\psi_{\min}^{\rho_{GS}}$,

$$
\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \geq \langle \psi_{\min}^{\rho_{GS}} | T + V_{ee} | \psi_{\min}^{\rho_{GS}} \rangle.
\tag{A.20}
$$

This relation is just inverse of Eq. (A.19). Therefore, the possible relation is

$$
\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle = \langle \psi_{\min}^{\rho_{GS}} | T + V_{ee} | \psi_{\min}^{\rho_{GS}} \rangle.
\tag{A.21}
$$

Then, from the discussion above, we obtain

$$
\begin{aligned}
E_{GS} &= \langle \psi_{GS} | V + T + V_{ee} | \psi_{GS} \rangle \\
&= \int \rho_{GS}(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + \langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \\
&= \int \rho_{GS}(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + \langle \psi_{\min}^{\rho_{GS}} | T + V_{ee} | \psi_{\min}^{\rho_{GS}} \rangle. \\
&= \int \rho_{GS}(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} + F[\rho_{GS}].
\end{aligned}
\tag{A.22}
$$

Thus, the theorem (A.12) is also proved.

A.3 Kohn-Sham Equation

Within the DFT, the total energy functional $E[\rho]$ is considered. The $E[\rho]$ is defined as

$$
E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[\rho],
\tag{A.23}
$$

where $v(\mathbf{r})$ is an external field (The subscript "ext" is omitted for simplicity) and $F[\rho]$ is represented by a summation of the kinetic energy $T[\rho]$ and the electron-electron repulsive energy $V_{ee}[\rho]$:

$$
F[\rho] = T[\rho] + V_{ee}[\rho].
\tag{A.24}
$$

The total energy of the ground state is the minimum value of the functional $E[\rho]$. Further, the density that yields the minimum value of $E[\rho]$ is the ground state density.

The ground state density that minimizes the total energy functional satisfies the Euler-Lagrange equation under the constraint that the total number of the electrons is kept constant:

$$\int \rho(\mathbf{r})d\mathbf{r} = N. \qquad (A.25)$$

Using the Lagrange mutiplier μ associated with this constraint, the Euler-Lagrange equation is,

$$\frac{\delta}{\delta\rho}\left\{E[\rho] - \mu\left(\int \rho(\mathbf{r})d\mathbf{r} - N\right)\right\} = 0 \qquad (A.26)$$

$$\Longleftrightarrow \qquad \mu = \frac{\delta E[\rho]}{\delta\rho} = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta\rho}. \qquad (A.27)$$

These discussions are the general theory of the DFT and do not show the scheme of practical calculations. To apply the DFT to the real system, the method developed by Kohn and Sham [90] is used. They have provided the set of self-consistent one-electron equations (Kohn-Sham equation).

At first, they have considered a hypothetical N-electron system without the electron-electron interactions. The Hamiltonian of this system H_s is

$$H_s = \sum_i^N (-\frac{1}{2}\nabla_i^2) + \sum_i^N v_s(\mathbf{r}_i). \qquad (A.28)$$

The ground state of this *non-interacting system* Ψ_s is given by the Slater determinant, *i.e.*

$$\Psi_s = \frac{1}{\sqrt{N!}} \det[\psi_1\psi_2\cdots\psi_N], \qquad (A.29)$$

where the ψ_i are the N lowest eigenstates of one-electron Hamiltonian $h_s = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r})$:

$$h_s\psi_i = \varepsilon_i\psi_i. \qquad (A.30)$$

The density in this system is obtained by

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2. \qquad (A.31)$$

The total energy of the non-interacting system H_s is represented by the functional:

$$\begin{aligned} E[\rho] &= \int \rho(\mathbf{r})v_s(\mathbf{r})d\mathbf{r} + F[\rho] \\ &= \int \rho(\mathbf{r})v_s(\mathbf{r})d\mathbf{r} + T_s[\rho]. \end{aligned} \qquad (A.32)$$

Since the there is no interaction between the electrons, $F[\rho]$ is equal to the kinetic energy $T_s[\rho]$:

$$\begin{aligned} T_s[\rho] &= \langle\Psi_s| \sum_i^N (-\frac{1}{2}\nabla_i^2)|\Psi_s\rangle \\ &= \sum_i^N \langle\psi_i| -\frac{1}{2}\nabla_i^2 |\psi_i\rangle. \end{aligned} \qquad (A.33)$$

In this system, the Euler-Lagrange equation (A.27) becomes

$$\mu = v_{\mathrm{s}}(\mathbf{r}) + \frac{\delta T_{\mathrm{s}}[\rho]}{\delta \rho}. \tag{A.34}$$

Keeping this discussion of the non-interacting system in mind, we get back to the general N-electron system with the electron-electron interactions. We divide the functional $F[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho]$ as following:

$$F[\rho] = T_{\mathrm{s}}[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\mathrm{xc}}[\rho], \tag{A.35}$$

where the $T_{\mathrm{s}}[\rho]$ in the right hand side is the kinetic energy of the non-interacting system, the second term is the classical Coulomb interaction for the electrons and the third term is referred as the *exchange-correlation energy*, which can be represented as,

$$E_{\mathrm{xc}}[\rho] \equiv \{T[\rho] - T_{\mathrm{s}}[\rho]\} + \left\{ V_{\mathrm{ee}}[\rho] - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right\}. \tag{A.36}$$

All the many-body effects are contained in this term.

From Eq. (A.35), the Euler-Lagrange equation is rewritten as,

$$\begin{aligned}
\mu &= v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho} \\
&= v(\mathbf{r}) + \frac{\delta}{\delta \rho}\left[T_{\mathrm{s}}[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r} + E_{\mathrm{xc}}[\rho] \right] \\
&= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\mathrm{xc}}(\mathbf{r}) + \frac{\delta T_{\mathrm{s}}[\rho]}{\delta \rho},
\end{aligned} \tag{A.37}$$

where the $v_{\mathrm{xc}}(\mathbf{r})$ is referred as the *exchange-correlation potential*, which is defined as

$$v_{\mathrm{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho}. \tag{A.38}$$

By setting

$$v_{\mathrm{eff}}(\mathbf{r}) \equiv v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\mathrm{xc}}(\mathbf{r}), \tag{A.39}$$

the Euler-Lagrange equation (A.37) becomes

$$\mu = v_{\mathrm{eff}}(\mathbf{r}) + \frac{\delta T_{\mathrm{s}}[\rho]}{\delta \rho}. \tag{A.40}$$

Comparing with Eq. (A.34), it is found that this system corresponds the non-interacting system with the external potential $v_{\mathrm{eff}}(\mathbf{r})$. Therefore, if $v_{\mathrm{eff}}(\mathbf{r})$ is given, by simply solving the Schrödinger equation

$$[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}]\psi_i = \varepsilon_i \psi_i, \tag{A.41}$$

the density of the ground state is obtained as

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2. \tag{A.42}$$

However, since the $v_{\mathrm{eff}}(\mathbf{r})$ depends on the $\rho(\mathbf{r})$, the Eqs. (A.39), (A.41) and (A.42) should be solved self-consistently. The set of these equations is termed as the *Kohn-Sham equations*.

A.4 Local Density Approximation

In the previous subsection, it is shown that the total energy of the interacting electrons system in the external field is derived by solving the single-particle equations, i.e. the Kohn-Sham equations. To solve the Kohn-Sham equations, we must know the exchange-correlation energy $E_{xc}[\rho]$. However, because of the many-body effects, the $E_{xc}[\rho]$ cannot be derived exactly. Therefore, a certain approximations are required for the $E_{xc}[\rho]$. The *local density approximation* (LDA) is one of such approximations. The LDA has been proposed by Kohn and Sham [90]. Within the LDA, the exchange-correlation energy at r is replaced by the exchange-correlation energy of a homogeneous electron gas of the density $\rho(r)$ i.e. $\varepsilon_{xc}(\rho(r))$. Therefore, the exchange-correlation energy and the exchange-correlation potential become

$$E_{xc}^{LDA}[\rho] \equiv \int \rho(r)\varepsilon_{xc}(\rho(r)) \tag{A.43}$$

and

$$v_{xc}^{LDA}(r) = \frac{\delta E_{xc}^{LDA}}{\delta\rho} = \varepsilon_{xc}(\rho(r)) + \rho(r) \left. \frac{\partial \varepsilon_{xc}(\rho)}{\partial\rho} \right|_{\rho=\rho(r)}, \tag{A.44}$$

respectively.

For the exchange-correlation energy $\varepsilon_{xc}(\rho(r))$, we can use the results by Ceperley and Alder [91]. Their results are based on Monte Carlo calculations of the interacting electron gas. Further, these results are parametrized in the low-density and high-density limit by Perdew and Zunger [92]. For the unporalized electron gas, the exchange-correlation energy is represented as

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c, \tag{A.45}$$

$$\varepsilon_x = -\frac{0.4582}{r_s}, \tag{A.46}$$

$$\varepsilon_c = \begin{cases} \dfrac{-0.1432}{1 + 1.0529\sqrt{r_s} + 0.3334 r_s} & (r_s \geq 1) \\ -0.0480 + 0.0311 \ln r_s - 0.0116 r_s + 0.0020 r_s \ln r_s & (r_s < 1) \end{cases}, \tag{A.47}$$

where the r_s is the average distance between the electrons and calculated by

$$\frac{1}{\rho} = \frac{4\pi}{3} r_s^3. \tag{A.48}$$

The large (small) r_s corresponds to the low (high) density.

We can calculate the exchange-correlation potential v_{xc} from these parametrized representations:

$$\begin{aligned} v_{xc} &= \varepsilon_{xc} + \rho \frac{\partial \varepsilon_{xc}}{\partial \rho} \\ &= \varepsilon_{xc} + \frac{dr_s}{d\rho} \cdot \frac{d\varepsilon_{xc}}{dr_s} \\ &= \varepsilon_{xc} - \frac{r_s}{3} \cdot \frac{d\varepsilon_{xc}}{dr_s}. \end{aligned} \tag{A.49}$$

We must obtain the derivative of ε_{xc} with respect to the r_s:

$$\frac{d\varepsilon_{xc}}{dr_s} = \frac{d\varepsilon_x}{dr_s} + \frac{d\varepsilon_c}{dr_s}. \tag{A.50}$$

Inserting Eqs. (A.46) and (A.47) into the right hand side, we find

$$\frac{d\varepsilon_x}{dr_s} = \frac{0.4582}{r_s^2}, \tag{A.51}$$

$$\frac{d\varepsilon_c}{dr_s} = \begin{cases} \dfrac{0.1432\left(\frac{1.0529}{2}r_s\sqrt{r_s}+0.3334\right)}{\left(1+1.0529\sqrt{r_s}+0.3334r_s\right)^2} & (r_s \geq 1) \\[4mm] \dfrac{0.0311}{r_s} - 0.0116 + 0.0020(\ln r_s + 1) & (r_s < 1) \end{cases} \tag{A.52}$$

Therefore, we obtain following results for the exchange-correlation potential.

$$\begin{aligned} v_{xc} &= \varepsilon_{xc} - \frac{r_s}{3}\cdot\frac{d\varepsilon_{xc}}{dr_s} \\ &= \left(\varepsilon_x - \frac{r_s}{3}\cdot\frac{d\varepsilon_x}{dr_s}\right) + \left(\varepsilon_c - \frac{r_s}{3}\cdot\frac{d\varepsilon_c}{dr_s}\right) \\ &= \frac{4}{3}\cdot\frac{0.4582}{r_s} + \varepsilon_c - \frac{r_s}{3}\cdot\frac{d\varepsilon_c}{dr_s}. \end{aligned} \tag{A.53}$$

Consequently, the v_{eff} in the Kohn-Sham equation can be calculated approximately.