

Density Functional Theory through Legendre Transformation

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Theoretical foundation of density functional theory in terms of field theoretical Legendre transformation is presented. The ground state energy is first written as a functional of local probe coupled to the density operator. The density functional is then defined by the functional Legendre transformation, which leads to a systematic formulation of density functional theory. Excitation spectrum is also determined within the same formalism in a unified way. The diagrammatic evaluation is most conveniently done by using auxiliary field method. Several generalizations of the formalism and extension to the case other than the density operator are also discussed.

§ 1. Introduction

The density functional theory is now one of the most commonly used methods in discussing various many particle systems.¹⁾ In this formalism the energy of the system is written as a functional of the density which is a function of single variable x instead of N coordinates $x_1 \sim x_N$ of N particles. In spite of the usefulness, its theoretical formulation is rather involved and sometimes difficult to achieve a systematic approximation scheme.

The purpose of this paper is to present a clear formulation of the density functional theory in terms of full use of the Legendre transformation applied to the quantum system, especially to the system described by the second quantized field theory.²⁾ It presents a theoretical basis of the density functional formalism which is both exact and systematic. These can be achieved by a straightforward application of our technique called on-shell expansion.

The discussion is organized as follows:

1. Ground state
2. Excited states
3. Generalization to the case other than the density operator
4. Finite temperature case (equilibrium and non-equilibrium), etc.

They are all formulated in terms of the field theoretical Legendre transformation in a unified way. We have in mind, in the following, atomic system with N electrons but the arguments can be applied to any many particle system with minor modifications. The essential feature of the formulation of the density functional theory in terms of Legendre transformation is the following. In the usual approach the ground state wave function Ψ is used to connect the potential v and the density n ;

$$v \rightarrow \Psi \rightarrow n.$$

The problem is then to find the inverse $n \rightarrow v$ of the product of the above two mappings. Legendre transformation is, however, the process of the inversion of the direct mapping

$$v \rightarrow n$$

without recourse to Ψ . This is done by a diagrammatic consideration and the mapping $n \rightarrow v$ is given by the graphical rule. The information contained in Ψ can be extracted by introducing the probe into the theory and after Legendre transformation from v to n we can simply differentiate by the probe to get the ground state expectation value of the desired operator as a functional of n .

In this paper the general formalism is presented and we do not attempt at any numerical evaluation which is postponed to the forthcoming paper but we believe that the present scheme helps us to perform a systematic approximation to get actual numerical values.

In §2, after defining Legendre transformation in quantum mechanical system, functional Legendre transformation between local probe and density is introduced for atomic system described by the second quantized field theory. Section 3 is devoted to the discussion on the relation of our approach to the Hohenberg-Kohn theorem.³⁾ One of the advantages of the present formalism is that the excitation spectrum can be handled in a transparent way by the method of Legendre transformation, which is the subject of §4. The crucial point is how to calculate the density functional in our approach. It is performed in the form of expansion in the electron repulsion, using the diagrammatic solution of the Legendre transformation. The density functional is then evaluated in two ways; auxiliary field method or Stratonovich-Hubbard transformation⁴⁾ §5 and inversion method⁵⁾ §7. For the diagrammatic evaluation, the use of auxiliary field is most convenient. In §5 we introduce the auxiliary field operator $\bar{\sigma}(x)$ for the density $\hat{\psi}^\dagger(x)\hat{\psi}(x)$ and explain how to use $\bar{\sigma}(x)$ in the actual calculation. Section 6 deals with the generalization of our method, which is achieved by coupling local probe not only to the density operator but to any other operators. We thus get an equation determining the ionization (or affinity) energy, or get the Schrödinger equation itself. In §7 we present a generalization of Legendre transformation called inversion method⁵⁾ which is also powerful in diagrammatic study of the density functional. It is formulated by extracting the most essential part of the Legendre transformation; the inversion of the relation which expresses the density as a functional of probe. We thus get a probe as a functional of the density. After extending in §8 our formalism to the case of finite temperature, both equilibrium and non-equilibrium, we discuss in the final section the local density approximation scheme in our terminology.

§2. Density functional by functional Legendre transformation

2.1. Legendre transformation in quantum mechanics

Let us first explain the definition of the Legendre transformation²⁾ which is used throughout our discussion below. The Hamiltonian of the system is denoted by \hat{H} ,

with hat indicating that it is an operator. Suppose that we are interested in the expectation value of some operator \hat{O} , the density in the present case. As a probe we insert the external c -number source J coupled to \hat{O} and change the Hamiltonian \hat{H} to $\hat{H}_J = \hat{H} - J\hat{O}$. Now calculate the ground state energy $-W(J)$ as a function of J and make a Legendre transformation from $W(J)$ to $E(\phi)$,

$$-E(\phi) = W(J) - J \frac{\partial W}{\partial J}, \quad (2.1)$$

$$\phi \equiv \frac{\partial W}{\partial J}. \quad (2.2)$$

The key point of the Legendre transformation is the inversion process in (2.2) where it is solved in favor of J to get $J = J(\phi)$ which is inserted into (2.1). It is known that $E(\phi)$ is the minimum energy of the system under the constraint that the expectation value of \hat{O} is fixed to be ϕ . Note here that ϕ defined in (2.2) is the expectation value $\langle \hat{O} \rangle_J$ of \hat{O} in the ground state $|0\rangle_J$ of H_J . In the following we take the case where the ground state is non-degenerate. If $|0\rangle_J$ is degenerate, it is assumed that a weak external field, the magnetic field for example, is present to lift the degeneracy. In the end of calculation such a field is reduced to zero. Such an external field has to be chosen depending on the difference of the symmetry of the degenerate states. Now the solution to the whole minimization problem without any constraint is given by looking for the minimum of $E(\phi)$ as a function of ϕ . But we have an identity of the Legendre transformation

$$\frac{\partial E(\phi)}{\partial \phi} = -J. \quad (2.3)$$

Therefore to extrematize $E(\phi)$ is equivalent to make the external probe J vanish, thus getting back to the original theory. If we assume that $E(\phi)$ is minimized by $\phi = \phi^{(0)}$ then $E(\phi^{(0)})$ is the true ground state energy.

2.2. Atomic system with N electrons

Let us take an atomic system whose Hamiltonian is given by using the second quantized electron field $\hat{\psi}(\mathbf{x})$ as follows:

$$\begin{aligned} \hat{H} = & \int d^3\mathbf{x} \hat{\psi}_a^\dagger(\mathbf{x}) \left(-\frac{\nabla^2}{2m} - v(\mathbf{x}) - \mu \right) \hat{\psi}_a(\mathbf{x}) \\ & + \frac{e^2}{2} \int d^3\mathbf{x} \int d^3\mathbf{y} \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_\beta^\dagger(\mathbf{y}) \frac{1}{|\mathbf{x} - \mathbf{y}|} \hat{\psi}_\beta(\mathbf{y}) \hat{\psi}_a(\mathbf{x}), \end{aligned} \quad (2.4)$$

$$\hat{H}_J = \hat{H} - \int d^3\mathbf{x} J(\mathbf{x}, t) \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_a(\mathbf{x}), \quad (2.5)$$

$$v(\mathbf{x}) = \frac{Ze^2}{|\mathbf{x}|}. \quad (2.6)$$

Here μ is the chemical potential and $v(\mathbf{x})$ the potential by the nucleus with atomic number Z and the sum over the repeated spin indexes α, β is implied. We have added the time dependent source term $J(\mathbf{x}, t)$ coupled to density operator in order to discuss

later the excitation levels. Note that the probe is inserted locally at every point x therefore the Legendre transformation becomes a functional one.

It is only for convenience that we have introduced both μ and $J(x, t)$. The total number is either obtained by differentiating by μ or by functionally differentiating through $J(x, t)$ which is then integrated over whole space, see (2.11) below.

More detailed Hamiltonian with relativistic corrections such as L - S coupling can be treated in a similar way therefore we restrict ourselves to the form (2.4) in the following.

For the field theoretical case $W[J]$ is most conveniently evaluated through the time evolution kernel K . Consider the case where J is time independent then the kernel defined in the time interval $t_F - t_I \equiv T$ is given by

$$K = {}_J \langle 0 | \exp(-iH_J T) | 0 \rangle_J \equiv {}_J \langle \exp(-iH_J T) \rangle_J \equiv \exp(iW[J]). \quad (2.7)$$

We assume in the following that the ground state $|0\rangle_J$ is not degenerate.

Taking the limit $t_I \rightarrow -\infty$, $t_F \rightarrow +\infty$, we get the path integral formula which is particularly suited for the diagrammatical expansion. As stated in §2.1, non-degeneracy of ground state is assumed here. Below we give the general expression which holds even when the source J is time dependent. In case the source J is time dependent, K is defined by the time ordered form;

$$\begin{aligned} K &= {}_J \left\langle \text{Texp} \left(-i \int_{-\infty}^{\infty} dt H_J \right) \right\rangle_J \\ &= \int [d\psi^\dagger d\psi] \exp \left(i \int_{-\infty}^{\infty} dt L_J \right) \equiv \exp(iW[J]), \end{aligned} \quad (2.8)$$

where L_J is the Lagrangian derived from H_J and $\int [d\psi^\dagger d\psi]$ implies of course the Grassmannian functional path integral. As is well-known we have to sum over paths in functional space with the weight $\exp i(\text{action})$. Explicit form of L_J is shown below for ease of reference;

$$\begin{aligned} L &= i \int d^3x \psi_a^\dagger(x) \dot{\psi}_a(x) - \int d^3x \psi_a^\dagger(x) \left(-\frac{\nabla^2}{2m} - v(x) - \mu \right) \psi_a(x) \\ &\quad - \frac{e^2}{2} \int d^3x \int d^3y \psi_a^\dagger(x) \psi_\beta^\dagger(y) \frac{1}{|\mathbf{x}-\mathbf{y}|} \psi_\beta(y) \psi_a(x), \end{aligned} \quad (2.9)$$

$$L_J = L + \int d^3x J(x) \psi_a^\dagger(x) \psi_a(x), \quad (2.10)$$

where $\dot{\psi} \equiv d\psi/dt$ and the notation $x = (x, t)$ is also introduced; $J(x) \equiv J(x, t)$ for example. Note that in (2.9), y stands for $y = (y, t)$. Strictly speaking, the ground state $|0\rangle_J$ in the presence of time dependent source J is not definable but we always set J to be zero after taking the (functional) derivative with respect to J . Therefore the notation $|0\rangle_J$ does not cause any ambiguities. Or we can alternatively assume that J vanishes sufficiently fast and smoothly as $t \rightarrow \pm\infty$.

$W[J]$ as defined above is a functional of $J(x)$. Let us make functional Legendre transformation by introducing the expectation value of the density $n(x)$ and introduce the action functional $\Gamma[n]$,

$$n(x) = \frac{\delta W[J]}{\delta J(x)} = \langle \psi_a^\dagger(x) \psi_a(x) \rangle_J. \quad (2.11)$$

Here the functional derivative is defined through

$$\frac{\delta J(x)}{\delta J(y)} = \delta^4(x-y), \quad (2.12)$$

where the right-hand side represents the four dimensional Dirac δ -function. Now the functional $\Gamma[n]$ called effective action is defined as

$$\Gamma[n] = W[J] - \int d^4x J(x) \frac{\delta W[J]}{\delta J(x)}. \quad (2.13)$$

Here as in (2.2) J has to be written as a functional of n by solving (2.11). The question whether $E[n]$ exists as the density functional is the question about the possibility of inverting (2.11), which is discussed later in connection with the Hohenberg-Kohn theorem.³⁾

The density $n(x)$ is determined by the stationarity requirement

$$\frac{\delta \Gamma[n]}{\delta n(x)} = -J(x) = 0. \quad (2.14)$$

Since the ground state is stationary, we look for the time independent solution $n(x) = n^{(0)}(x)$ of (2.14) which represents the density of the ground state in the absence of the source J ,

$$n^{(0)}(x) = \langle 0 | \psi_a^\dagger(x) \psi_a(x) | 0 \rangle, \quad (2.15)$$

where $|0\rangle = |0\rangle_{J=0}$.

The energy $E[n]$ as a density functional is obtained by assuming that $n(x)$ is a function of the space variables x only. In this case $\Gamma[n]$ acquires a factor corresponding to the whole time interval $t_f - t_i = \int_{-\infty}^{\infty} dt$ with the coefficient $E[n]$;

$$\Gamma[n] = -E[n] \times \int_{-\infty}^{\infty} dt. \quad (2.16)$$

The above static solution $n^{(0)}(x)$ can also be found by solving

$$\frac{\delta E[n]}{\delta n(x)} = 0. \quad (2.17)$$

If a time dependent external field is actually present, the solution $n(x)$ to (2.14) is also time dependent which describes time dependence of the density in such a situation. In this case our $\Gamma[n]$ is the time dependent density functional defined in a different way from Ref. 6), see also Ref. 1).

2.3. Kinetic energy as a functional of n

It is an important subject to have a rigorous expression for the kinetic energy $T[n]$ written in terms of n . This can be done quite easily in the present formalism. As stated in the Introduction, we first insert a c -number field $j(x)$ to probe (locally) the kinetic energy operator;

$$\hat{H}_{j,j} = \hat{H}_j - \int d^3x j(x) \hat{\psi}^\dagger(x) \left(-\frac{\nabla^2}{2m} \right) \hat{\psi}(x).$$

Here \hat{H}_j is given by (2.5). Now we make Legendre transform from J to n as in (2.13) regarding j as a fixed parameter and get $\Gamma[n, j]$. Then $T[n]$ is given by

$$T[n](x) = \langle \hat{\psi}^\dagger(x) \left(-\frac{\nabla^2}{2m} \right) \hat{\psi}(x) \rangle = \frac{\delta \Gamma[n, j]}{\delta j(x)} \Big|_{j=0}.$$

The diagrammatical rule for $T[n]$ is also obtainable in a straightforward manner.

2.4. Spin density functional

All the above discussion is applicable to the spin density functional $\Gamma[n_\alpha]$ or $E[J_\alpha]$ ($\alpha = \uparrow, \downarrow$). We have only to introduce two independent sources $J_\uparrow(x)$ and $J_\downarrow(x)$ in \hat{H}_j of (2.5);

$$\hat{H}_{j_\alpha} = \hat{H} - \int d^3x \sum_{\alpha=\uparrow, \downarrow} J_\alpha(x) \hat{\psi}_\alpha^\dagger(x) \hat{\psi}_\alpha(x).$$

Then $W[J_\alpha]$ is defined as in (2.8) and $\Gamma[n_\alpha]$ by

$$\Gamma[n_\alpha] = W[J_\alpha] - \int d^4x \sum_{\beta=\uparrow, \downarrow} J_\beta(x) \frac{\delta W[J_\alpha]}{\delta J_\beta(x)},$$

$$n_\beta(x) = \frac{\delta W[J_\alpha]}{\delta J_\beta(x)}.$$

The spin density is determined by solving

$$\frac{\delta \Gamma[n_\alpha]}{\delta n_\beta(x)} = 0. \quad (\beta = \uparrow, \downarrow) \tag{2.18}$$

§ 3. Hohenberg-Kohn theorem

The relation of our approach to the Hohenberg-Kohn theorem³⁾ is pointed out here. We discuss two theorems below which are the fundamental starting points of their approach.

3.1. Existence theorem

The theorem states that the density functional $E[n]$ exists. As has been pointed out the validity of this theorem is converted, in our case, to the invertibility of the defining equation of $n(x)$ as a functional of $J(x)$. If this is possible the Legendre transformation from $W[J]$ to $\Gamma[n]$ can be done and hence $E[n]$ exists. In the quantized field theory the above inversion process has been extensively studied in diagrammatical terms. For the case of density variable the introduction of the auxiliary field corresponding to the density operator by Stratonovich-Hubbard transformation⁴⁾ is particularly convenient. Then as a result of the Legendre transformation the concept of one particle irreducible (1PI) vacuum diagrams naturally appears. Note here that the diagrammatical expansion in our case is the expansion in powers of the electron repulsion. These are explained in §5 below. The density functional

$E[n]$ therefore exists in diagrammatical sense and the diagrams are characterized by 1PI.

3.2. Universality theorem

The second theorem states that $E[n]$ can be written as a sum of two terms, $E[n] = E^0[n] + E^1[n]$ where $E^0[n]$ is a universal functional independent of the nuclear potential v and $E^1[n]$ is given explicitly by

$$E^1[n] = \int d^3x v(x)n(x). \quad (3.1)$$

The proof of this theorem is rather trivial in our formalism since it is a well-known consequence of the Legendre transformation. We discuss the problem using the Hamiltonian (2.4) and the definition (2.7). Recall here that $W[J]$ is a functional of $v+J$ therefore, writing $\int_{-\infty}^{\infty} dt = T$,

$$\begin{aligned} -E[n]T &= W[v+J] - \int d^3x J(x) \frac{\delta W[v+J]}{\delta J(x)} \\ &= W[v+J] - \int d^3x (J(x) + v(x)) \frac{\delta W[v+J]}{\delta J(x)} + \int d^3x v(x) \frac{\delta W[v+J]}{\delta J(x)}. \end{aligned} \quad (3.2)$$

However if we invert the relation

$$n(x)T = \frac{\delta W[v+J]}{\delta J(x)}, \quad (3.3)$$

$v+J$ is given as a functional of n which is independent of v . Since the first and second terms on the right-hand side of (3.2) is written by n only, the theorem is proved;

$$E[n] = E[n]_{v=0} - \int d^3x v(x)n(x).$$

Recall here that the mapping between $v(x)$ and $n(x)$ itself is fixed *after* solving the stationary equation,

$$\frac{\delta E[n]_{v=0}}{\delta n(x)} = v(x).$$

Now the question of whether a given n corresponds to some v , v -representability, is in the affirmative if $E[n]$ exists at all; v is given by the expression on the left-hand side of the above equation.

§ 4. Excitation Spectrum

One of the great advantages of the present formalism is that it provides a unified way of studying the excitation spectrum as opposed to the usual density functional theory. This is achieved by on-shell expansion scheme which is reproduced below restricting ourselves to the density variable.

Let $n^{(0)}(x)$ be a solution to the stationarity equation (2·14) and assume that $n^{(0)}(x)$ is independent of time since it corresponds to the ground state. In order to discuss the excitation levels above the ground state thus determined, we look for another solution of (2·14) in the vicinity of $n^{(0)}(x)$ by writing

$$n(x) = n^{(0)}(x) + \Delta n(x).$$

Then, up to the first order in $\Delta n(x)$, we get

$$\begin{aligned} 0 &= \left. \frac{\delta \Gamma[n]}{\delta n(x)} \right|_{n=n^{(0)}+\Delta n} \\ &= \left(\frac{\delta \Gamma[n]}{\delta n(x)} \right)_0 + \int d^4 y \left(\frac{\delta^2 \Gamma[n]}{\delta n(x) \delta n(y)} \right)_0 \Delta n(y) + \dots \end{aligned} \quad (4.1)$$

Here $(\dots)_0$ implies the value of (\dots) evaluated at $n = n^{(0)}(x)$. Since the first term on the right-hand side of (4.1) vanishes by the definition of $n^{(0)}$, we arrive at the following result which we call the mode determining equation or the on-shell condition in the terminology of relativistic field theory;⁷⁾

$$\begin{aligned} \int d^4 y \Gamma^{(2)}(x, y)_0 \Delta n(y) &= 0, \\ \Gamma^{(2)}(x, y) &\equiv \frac{\delta^2 \Gamma[n]}{\delta n(x) \delta n(y)}. \end{aligned} \quad (4.2)$$

Regarding x and y as indices specifying rows and columns, Eq. (4.2) has the form of zero eigenvalue equation of the matrix of the second derivative of Γ . As an equation of the excitation energy ω , it is a non-linear eigenvalue equation which is seen as follows. The second derivative of Γ , if it is evaluated at the static solution $n^{(0)}$, is a function of difference $t - t'$ of the time coordinate of x and y , therefore Eq. (4.2) takes the form

$$\int d^3 y dt' \Gamma^{(2)}(\mathbf{x}, \mathbf{y}, t - t') \Delta n(\mathbf{y}, t') = 0. \quad (4.3)$$

In Fourier space it becomes

$$\int d^3 \mathbf{y} \Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega) \Delta n(\mathbf{y}, \omega) = 0. \quad (4.4)$$

In this form it is easy to see that a non-trivial solution to Δn exists only for such values of ω for which the matrix $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, \omega)$ has the zero eigenvalue. Let one of such ω be ω_i , assuming that it lies in the discrete spectrum, then Eq. (4.4) determines both eigenvalue ω and the wave function $\Delta n(\mathbf{y}, \omega)$ corresponding to that mode. It is easy to see⁷⁾ that ω_i is the excitation energy $\pm |E_i - E_0|$ of the i -th excited state $|i\rangle$ where E_i or E_0 is the energy eigenvalue of the state $|i\rangle$ or $|0\rangle$ respectively and Δn is given by

$$\Delta n(\mathbf{x}, \omega_i) = \begin{cases} \langle i | \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_a(\mathbf{x}) | 0 \rangle & \text{if } \omega_i = E_i - E_0, \\ \langle 0 | \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_a(\mathbf{x}) | i \rangle & \text{if } \omega_i = -(E_i - E_0). \end{cases} \quad (4.5)$$

Another way of deriving (4.2) is given as follows. We first note the following identity of the Legendre transformation,

$$\int d^4y \frac{\delta^2 \Gamma[n]}{\delta n(x) \delta n(y)} \frac{\delta^2 W[J]}{\delta J(y) \delta J(z)} = -\delta^4(x-z). \quad (4.6)$$

We see that, by looking for the zero of the second derivative of Γ , we are at the same time searching for the pole of the second derivative of W , which is the connected part of the causal correlation function of the densities;

$$\frac{\delta^2 W[J]}{\delta J(x) \delta J(y)} = \langle 0 | T \hat{\psi}_\alpha^\dagger(x) \hat{\psi}_\alpha(x) \hat{\psi}_\beta^\dagger(y) \hat{\psi}_\beta(y) | 0 \rangle. \quad (4.7)$$

Let us rewrite (4.6) in Fourier representation in the time difference $t_x - t_y$ after setting $J=0$;

$$\int d^3y \Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega) W^{(2)}(\mathbf{y}, \mathbf{z}, \omega) = -\delta^3(\mathbf{x}-\mathbf{z}). \quad (4.8)$$

Now, by inserting the complete set $|j\rangle$ as usual, $W^{(2)}$ has the representation

$$W^{(2)}(\mathbf{y}, \mathbf{z}, \omega) = i \sum_j \left(\frac{n_j^*(\mathbf{y}) n_j(\mathbf{z})}{\omega + \omega_j + i\varepsilon} + \frac{n_j^*(\mathbf{z}) n_j(\mathbf{y})}{\omega - \omega_j + i\varepsilon} \right), \quad (4.9)$$

$$n_j(\mathbf{y}) \equiv \langle j | \hat{\psi}_\alpha^\dagger(\mathbf{y}, 0) \hat{\psi}_\alpha(\mathbf{y}, 0) | 0 \rangle.$$

Here $*$ denotes the complex conjugation and ε is the positive infinitesimal quantity. Selecting particular ω_i we multiply $\omega - \omega_i$ on both side of (4.8) and take the limit $\omega \rightarrow \omega_i$. Then using (4.9) we get

$$\int d^3y \Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega_i) n_i(\mathbf{y}) = 0. \quad (4.10)$$

Here we have assumed that the level ω_i is not degenerate or if it is degenerate each state can be characterized by different symmetry. If we multiply $\omega + \omega_i$ and take the limit $\omega \rightarrow -\omega_i$, the results (4.4), (4.5) together with the identification $\Delta n(\mathbf{y}, \omega_i) = n_i(\mathbf{y})$ or $n_i^*(\mathbf{y})$ are obtained. (Here Heisenberg and Schrödinger representations are assumed to coincide at $t=0$.)

Note that in order to study the excitation levels the time dependent probe is required. In this sense the energy functional $E[n]$, which is obtained by a static probe, does not contain any information of the excitation; we have to use the effective action $\Gamma[n]$. Since our formalism enables us to determine both the ground state, by (2.14), and the excited state, by (4.2), in a systematic way, both of them can be studied by the same approximation scheme because once the starting $\Gamma[n]$ is fixed every calculation goes through according to the above guideline.

It is straightforward to generalize above arguments to the spin density functional. After solving (2.18), the excitation spectrum with the spin content specified is given by solving the following 2×2 (in spin space) coupled zero eigenvalue equation;

$$\sum_\beta \int d^4y \left(\frac{\delta^2 \Gamma[n_\uparrow, n_\downarrow]}{\delta n_\alpha(x) \delta n_\beta(y)} \right)_0 \Delta n_\beta(y) = 0. \quad (4.11)$$

We have discussed in (4·1) up to the term which is linear in Δn . Higher order terms are known to correspond to the scattering matrix elements among the modes determined by (4·2).⁸⁾ We are not going into details of these higher terms here.

§ 5. The method of the auxiliary field

The most important ingredient in Legendre transformation is the inversion process to get v as a functional of n . Usually this is done in a graphical terminology but the operator \hat{n} is a local composite operator and the diagrammatical rule for such an operator is hard to obtain. It is only recently that the corresponding rule is established starting from the inversion method.⁹⁾ We will briefly discuss inversion method in §7 but here another way of performing Legendre transformation is explained.

Legendre transformation for the density variable can most conveniently be done by introducing the auxiliary operator field $\bar{\sigma}(x)$ for the density $\hat{n}(x)$. The auxiliary field method, known as the Stratonovich-Hubbard transformation⁴⁾ enables us to treat the density operator as if it is an elementary (not composite) field variable. This is done as follows. Consider the Lagrangian (2·9) and multiply the following identity to (2·8):

$$1 = \frac{\int [d\sigma] \exp i \frac{e^2}{2} \int d^4x \int d^4y [\sigma(x) - \psi_a^\dagger(x) \psi_a(x)] U_0(x-y) [\sigma(y) - \psi_\beta^\dagger(y) \psi_\beta(y)]}{\int [d\sigma] \exp i \frac{e^2}{2} \int d^4x \int d^4y \sigma(x) U_0(x-y) \sigma(y)}, \quad (5.1)$$

where

$$\int d^4x = \int d^3x dt$$

and

$$U_0(x-y) = \frac{1}{|\mathbf{x}-\mathbf{y}|} \delta(t_x - t_y).$$

Then Eq. (2·8) becomes, apart from irrelevant constant factor,

$$\begin{aligned} \exp i W[J] &= \int [d\psi d\psi^\dagger] \exp \left(i \int_{-\infty}^{+\infty} dt L_J \right) \times 1 \\ &= \int [d\psi d\psi^\dagger d\sigma] \exp i \left\{ \int dt L_J \right. \\ &\quad \left. + \frac{e^2}{2} \int d^4x d^4y [\sigma(x) - \psi_a^\dagger(x) \psi_a(x)] U_0(x-y) [\sigma(y) - \psi_\beta^\dagger(y) \psi_\beta(y)] \right\} \\ &\quad \times \left[\text{Det} \left\{ -\frac{ie^2}{2} U_0(x-y) \right\} \right]^{1/2} \\ &\equiv \int [d\psi d\psi^\dagger d\sigma] \exp i I, \end{aligned} \quad (5.2)$$

where $\text{Det } F(x-y)$ with some function F implies the functional determinant which is taken by regarding x and y as the indices of rows and columns. The functional I has the expression

$$I = \int d^4x \left\{ \psi_a^\dagger(x) \left[i\partial_t + \frac{\nabla^2}{2m} + \mu + v(x) \right] \psi_a(x) - e^2 \psi_a^\dagger(x) \int d^4y U_0(x-y) \sigma(y) \psi_a(x) + \frac{e^2}{2} \sigma(x) \int d^4y U_0(x-y) \sigma(y) + J(x) \psi_a^\dagger(x) \psi_a(x) \right\} + \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0 \right\}. \quad (5.3)$$

Here Tr implies the functional trace operation. The Euler-Lagrange equation in the operator form can be obtained by requiring that I is stationary as an operator in functional sense;

$$0 = \frac{\delta \tilde{I}}{\delta \bar{\sigma}(x)} = e^2 \int d^4y U_0(x-y) [\bar{\sigma}(y) - \hat{\psi}_a^\dagger(y) \hat{\psi}_a(y)].$$

Therefore

$$\bar{\sigma}(x) = \hat{\psi}_a^\dagger(x) \hat{\psi}_a(x).$$

The system described by the action I in (5.3) is physically equivalent to the one described by the original action $\int L_J dt$.

Now we set $J=0$ in (5.3) and the term $J\sigma$ is newly introduced later in order to probe the density. Recall that the expression (5.3) is bilinear in ψ^\dagger and ψ and it has the form that the nuclear potential $v(x)$ is modified to

$$v(x) - e^2 \int d^4y U_0(x-y) \sigma(y), \quad (5.4)$$

which is the shielded nuclear potential due to Coulomb repulsion in the presence electron charge density $\sigma(y)$. Integrating by ψ , ψ^\dagger , we get

$$\begin{aligned} \exp iW &= \int [d\sigma] \exp i \left\{ \frac{2}{i} \text{Tr} \ln \left[D_0(x-y) - \int d^4z e^2 U_0(x-z) \sigma(z) \delta^4(x-y) \right] \right. \\ &\quad \left. + \int d^4x d^4y \sigma(x) \frac{e^2}{2} U_0(x-y) \sigma(y) + \frac{1}{2i} \text{Tr} \ln \left[-\frac{ie^2}{2} U_0(x-y) \right] \right\} \\ &\equiv \int [d\sigma] \exp i \int d^4x I[\sigma], \end{aligned} \quad (5.5)$$

where

$$D_0(x-y) = \left[i\partial_t + \frac{\nabla_x^2}{2m} + \mu + v(x) \right] \delta^4(x-y). \quad (5.6)$$

Recall here that we have not explicitly introduced the magnetic field so that the factor 2 comes into (5.5) from the functional integration over $\psi_{\uparrow, \downarrow}$ and $\psi_{\uparrow, \downarrow}^\dagger$. Such a restriction can easily be removed however. Now the functional $I[\sigma]$ is the action functional of σ variable. As stated above, we introduce here the source $J(x)$ coupled to $\sigma(x)$ and make Legendre transformation from $W[J]$ to $\Gamma[\sigma_c]$;

$$\exp(iW[J]) = \int [d\sigma] \exp i\{I[\sigma] + J \cdot \sigma\},$$

$$J \cdot \sigma \equiv \int d^4x J(x) \sigma(x), \quad (5.7)$$

$$\Gamma[\sigma_c] = W[J] - J \cdot \sigma_c,$$

$$\sigma_c(x) \equiv \frac{\delta W[J]}{\delta J(x)} = \langle \bar{\sigma}(x) \rangle_J. \quad (5.8)$$

Here σ_c represents the expectation value of $\bar{\sigma}$ in the presence of the source J and it plays the role of $n(x)$ given in (2.11). Once $W[J]$ is written in the form of (5.5), the rule of the diagrammatical expansion of $\Gamma[\sigma_c]$ is obtained by applying the well-known rule of the Legendre transformation of the elementary field. It is the expansion in powers of the size of fluctuation of the density. For this purpose, we first write σ as $\sigma_c + \sigma'$, where σ' represents the fluctuating part of the density operator, and expand $I[\sigma]$ functionally in powers of σ' .

$$\begin{aligned} I[\sigma] &= I[\sigma_c + \sigma'] \\ &= I[\sigma_c] + I'[\sigma_c] \cdot \sigma' + \frac{1}{2!} I''[\sigma_c] \cdot \sigma' \cdot \sigma' + \frac{1}{3!} I'''[\sigma_c] \cdot \sigma' \cdot \sigma' \cdot \sigma' + \dots, \end{aligned} \quad (5.9)$$

where we have used the notation, for example,

$$I''[\sigma_c] \cdot \sigma' \cdot \sigma' = \iint \left(\frac{\delta^2 I[\sigma]}{\delta \sigma(x) \delta \sigma(y)} \right)_{\sigma=\sigma_c} \sigma'(x) \sigma'(y) d^4x d^4y.$$

In (5.9), we have to throw away the second term, because it is known to be cancelled in the process of Legendre transformation. The propagator of σ' field is symbolically given by $I''[\sigma_c]^{-1}$. It is the functional inverse of the matrix $I''[\sigma_c]_{xy} \equiv (\delta^2 I[\sigma] / \delta \sigma(x) \delta \sigma(y))_{\sigma=\sigma_c}$. The remaining terms are the interaction vertices of field σ' . They are given by

$$I[\sigma_c + \sigma'] - I[\sigma_c] - I'[\sigma_c] \cdot \sigma' - \frac{1}{2} I''[\sigma_c] \cdot \sigma' \cdot \sigma'. \quad (5.10)$$

Upshot of these manipulations is^{2),10)}

$$\Gamma[\sigma_c] = I[\sigma_c] + \frac{i}{2} \text{Tr} \ln I''[\sigma_c] + (\text{1PI vacuum graphs}). \quad (5.11)$$

The first term represents tree diagrams. The second one is the sum of the contributions of one-loop diagrams and it is given by the functional trace of $\ln I''[\sigma_c]$. In (5.11), 1PI vacuum graphs imply the one particle irreducible connected vacuum diagrams of the σ' field. They are defined as the sum of vacuum graphs which are not separated into disconnected two pieces if one of σ' -propagators is cut. The construction rule of 1PI vacuum graphs is now obvious; sum up all the 1PI vacuum diagrams of σ' field with the propagator $I''[\sigma_c]^{-1}$ and vertex given by (5.10). They are necessarily diagrams with more than two loops. If the source J is time independent ($J(x) = J(x)$), $\sigma_c(x)$ is also time independent. Then $\Gamma[\sigma_c]$ has the form,

$$\Gamma[\sigma_c] = - \int dt E[\sigma_c],$$

and $E[\sigma_c]$ is the energy as a density functional by the method of auxiliary field. In order to see the diagrammatic structure of $\Gamma[\sigma_c]$, we write down explicitly the expansion (5.9) by writing $\sigma = \sigma_c + \sigma'$ in (5.5),

$$\begin{aligned} I[\sigma] = & \frac{2}{i} \left[\text{Tr} \ln D_c(x-y) \right. \\ & - \sum_{n=1}^{\infty} \frac{(-1)^n e^{2n}}{n} \int d^4 X_1 d^4 X_2 \cdots d^4 X_n \text{Tr} \{ D_c^{-1} D_{X_1} D_c^{-1} D_{X_2} \cdots \\ & \times D_c^{-1} D_{X_n} \} \sigma'(X_1) \sigma'(X_2) \cdots \sigma'(X_n) \left. \right] \\ & + \int d^4 x d^4 y \frac{e^2}{2} U_0(x-y) (\sigma_c(x) \sigma_c(y) + 2\sigma_c(x) \sigma'(y) + \sigma'(x) \sigma'(y)) \\ & + \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(x-y) \right\}, \end{aligned}$$

where Tr in the second term on the right-hand side is taken with the matrix elements,

$$(D_X)_{x,y} \equiv D_X(x,y) = -\delta^4(x-y) U_0(y-X),$$

$$(D_{1c})_{x,y} \equiv D_{1c}(x,y) = -\int d^4 z e^2 U_0(x-z) \sigma_c(z) \delta^4(x-y),$$

$$D_c = D_0 + D_{1c}.$$

In what follows we write D_c^{-1} and $e^2 U_0$ graphically as shown in Fig. 1. With this $I[\sigma]$, $\Gamma[\sigma_c]$ is represented as

$$\begin{aligned} \Gamma[\sigma_c] = & \frac{2}{i} \text{Tr} \ln D_c + \frac{e^2}{2} \int d^4 x d^4 y \sigma_c(x) U_0(x-y) \sigma_c(y) + \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(x-y) \right\} \\ & - \frac{1}{2i} \text{Tr} \ln \left\{ +2e^4 \int d^4 x d^4 y D_c^{-1}(x,y) U_0(y-X_1) D_c^{-1}(y,x) U_0(x-X_2) \right. \\ & \left. - \frac{ie^2}{2} U_0(X_1-X_2) \right\} \\ & + \frac{1}{i} \sum_{n=1}^{\infty} \frac{1}{n!} \left\langle \left[-\sum_{m=3}^{\infty} \frac{2e^{2m}}{m} \int d^4 X_1 \cdots d^4 X_m d^4 x_1 \cdots d^4 x_m \right. \right. \\ & \times D_c^{-1}(x_m, x_1) U_0(x_1-X_1) \cdots D_c^{-1}(x_{m-1}, x_m) U_0(x_m-X_m) \\ & \left. \left. \times \sigma'(X_1) \cdots \sigma'(X_m) \right]^n \right\rangle_{\text{conn.1PI}}, \end{aligned} \quad (5.12)$$

where the Tr operation in the third line on the right-hand side is taken in X -space, i.e., in X_1 and X_2 . The notation $\langle \cdots \rangle_{\text{conn.1PI}}$ implies the connected 1PI diagrams of the σ' -field. The first three terms of (5.12) correspond to tree diagrams in the auxiliary field method and they include the Thomas-Fermi term and Hartree term as explained later. The fourth term is the sum of the contributions of one-loop diagrams and the

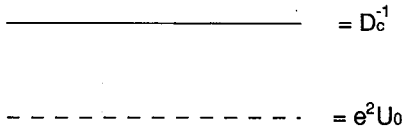


Fig. 1. Definitions in the diagram. The electron propagator D_c^{-1} is denoted by a solid line. The Coulomb potential $e^2 U_0$ between electrons is represented by a dashed line.

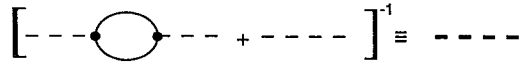


Fig. 2. Diagrammatic representation of the propagator of σ' field. It is denoted by thick broken line.

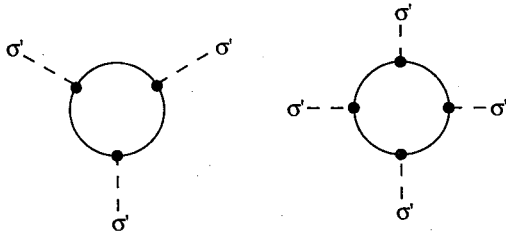


Fig. 3. Some examples of the vertex of σ' . The left figure represents three point vertex which is created by third derivative of I . The right figure is four point vertex, created by fourth derivative.

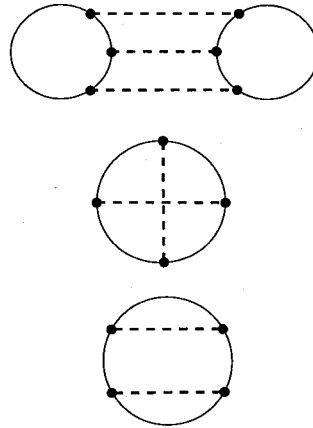


Fig. 4. Some examples of 1PI vacuum graphs contributing to $\Gamma[\sigma_c]$.

other terms, after a straightforward application of the contraction theorem to σ' field, produce 1PI vacuum diagrams which have more than two-loops. The propagator $\mathcal{A}(X_1, X_2)$ of these diagrams is

$$\left[2e^4 \int d^4x d^4y D_c^{-1}(x, y) U_0(y - X_1) D_c^{-1}(y, x) U_0(x - X_2) - ie^2 U_0(X_1 - X_2) \right]^{-1}. \tag{5.13}$$

This again has the physical meaning that the Coulomb interaction U_0 between electrons is shielded by the other electrons. Therefore, remembering (5.4), both the shielding of the nuclear potential and that of Coulomb repulsion of electrons are automatically taken into account in our expansion scheme. The propagator $\mathcal{A}(X_1, X_2)$ is represented diagrammatically in Fig. 2. The lowest two interaction vertices among σ' are shown in Fig. 3 and some examples of 1PI vacuum diagrams are also given in Fig. 4.

Let us illustrate some lower order contributions to $\Gamma[\sigma_c]$ regarding Γ as a function(al) of σ_c and e^2 . For instance, up to the order e^2 , we get from (5.12)

$$\begin{aligned} \Gamma[\sigma_c] \cong & \frac{2}{i} [\text{Tr} \ln D_0 + \text{Tr}(D_0^{-1} D_{1c})] + \frac{e^2}{2} \int d^4x d^4y \sigma_c(x) U_0(x - y) \sigma_c(y) \\ & + \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(X_1 - X_2) \right\} - \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(X_1 - X_2) \right\} \\ & + 2e^4 \int d^4x d^4y D_0^{-1}(x, y) U_0(y - X_1) D_0^{-1}(y, x) U_0(x - X_2) \Big\}. \end{aligned}$$

If we solve the stationary equation

$$0 = \frac{\delta \Gamma}{\delta \sigma_c(x)} (= -J(x)), \quad (5.14)$$

the solution is given by, for small e^2 ,

$$\sigma_c(x) = -2iD_0^{-1}(x, x) + \mathcal{O}(e^2).$$

So we get, at the solution,

$$\begin{aligned} \Gamma[\sigma_c] \cong & -2i \text{Tr} \ln D_0 - \frac{e^2}{2} \int d^4x d^4y \sigma_c(x) U_0(x-y) \sigma_c(y) \\ & + \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(X_1 - X_2) \right\} - \frac{1}{2i} \text{Tr} \ln \left\{ -\frac{ie^2}{2} U_0(X_1 - X_2) \right. \\ & \left. + 2e^4 \int d^4x d^4y D_0^{-1}(x, y) U_0(y - X_1) D_0^{-1}(y, x) U_0(x - X_2) \right\}. \end{aligned}$$

If we make local approximation, it can be shown by an explicit calculation that the first term reduces to Thomas-Fermi energy, and the second term is the Hartree term. The remaining $\text{Tr} \ln$ term can be expanded in power series of e^2 starting from the term of e^2 . The lowest term is the Fock term.

In case of the electron gas in a uniform positive charge background, $U_0(\mathbf{q}=0)$ is cancelled by the background, therefore the relation $U_0(\mathbf{q}=0)=0$ can be used. In the local density approximation (LDA), we set $\sigma_c(x)$ to be a constant ($\sigma_c(x)=\sigma_c$) but if this is done $D_{1c}=0$ so that $\Gamma[\sigma_c]$ is independent of σ_c : we cannot make LDA in the presence of uniform background. The reason why the auxiliary field method does not work for LDA in this case is that the total number variable $\int \psi^\dagger(x)\psi(x)d^3x$ has no interaction in (2.4) because of the condition $U_0(\mathbf{q}=0)=0$. By the same reason the auxiliary field can be introduced only for the sum of the spin density $\sum_{\alpha=\uparrow, \downarrow} \psi_\alpha^\dagger(x)\psi_\alpha(x)$ not for each spin density variable $\psi_\uparrow^\dagger(x)\psi_\uparrow(x)$ or $\psi_\downarrow^\dagger(x)\psi_\downarrow(x)$. In such a case, however, we can utilize the dependence of Γ on the chemical potential μ to get the energy as a function of the average electron number \bar{n} . Explicitly Γ is written as, assuming $v=0$, $\Gamma = -\int d^4x \varepsilon(\mu)$ where $\varepsilon(\mu)$ is the energy density which has the property that

$$\bar{n} = \frac{N}{V} = -\frac{\partial \varepsilon}{\partial \mu} = \langle \psi^\dagger(x)\psi(x) \rangle_\mu, \quad (5.15)$$

where V is the volume of the system. If the energy density is required to be expressed by \bar{n} , we solve (5.15), writing μ as a function of \bar{n} and we make Legendre transformation once more to get $\tilde{\varepsilon}(\bar{n}) = \varepsilon(\mu) + \mu\bar{n}$. However in most cases it is convenient to keep μ as an independent variable and, without performing explicit Legendre transformation, to consider the defining relation $N/V = -(\partial \varepsilon / \partial \mu)$ as a function of μ . It is clear that the diagram expansion for $\varepsilon(\mu)$ in the presence of uniform positive charge background is obtained by setting $\sigma_c=0$ in (5.12). For example, if we assume $\sigma_c = \text{constant}$, then $D_{1c}=0$ because $U_0(\mathbf{q}=0)=0$ which is equivalent to set $\sigma_c=0$. By the replacement $D \rightarrow D_0$, the tree diagram brings us the usual Thomas-Fermi

term and 1-loop diagram, i.e., $\text{Tr} \ln$ term, equals the sum of the exchange term and ring diagrams. They all agree with the known results, see for example Ref. 11). The higher diagrams represent the term what is called the correlation energy. For uniform density, details of calculations are found in many literatures.¹⁾

Relation between $\Gamma[n]$ and $\Gamma[\sigma_c]$

Now we discuss the difference between $\Gamma[n]$ of (2·13) and $\Gamma[\sigma_c]$ of (5·8). The conclusion is that, although both are different quantities, all the physical observable informations derived from them are the same. Let us use the notation $\Gamma_1[n] \equiv \Gamma[n]$, $\Gamma_2[\sigma_c] \equiv \Gamma[\sigma_c]$ in order to clarify that two functionals are different quantities. Their relationship is easily seen if we start from $W_{1,2}[J]$, where $W_1[J]$ is $W[J]$ of (2·8) and $W_2[J]$ is that of (5·7). The starting observation is that $W_1[J]$ has another representation which is obtained by using

$$\sigma(x) - \phi^\dagger(x)\phi(x) + \int d^4z J(z) U_0^{-1}(z-x) \quad (5.16)$$

instead of $\sigma(x) - \phi^\dagger(x)\phi(x)$ in the numerator of (5·1). With this replacement the right-hand side of (5·1) is still unity. Then $W_1[J]$ becomes $W[J]$ of (5·7) with the extra term which is proportional to the square of the third term of (5·16). Thus we arrive at the relation;

$$W_1[J] = W_2[J] + \frac{e^2}{2} \iint d^4x d^4y J(x) U_0^{-1}(x-y) J(y). \quad (5.17)$$

Therefore $n(x) = \delta W_1 / \delta J(x)$ and $\sigma_c(x) = \delta W_2 / \delta J(x)$ are related through

$$n(x) = \sigma_c(x) + e^2 \int d^4y U_0^{-1}(x-y) J(y), \quad (5.18)$$

and the relation between $\Gamma_1[n]$ and $\Gamma_2[\sigma_c]$ is

$$\begin{aligned} \Gamma_1[n] &= W_1[J] - \int d^4x \frac{\delta W_1[J]}{\delta J(x)} J(x) \\ &= W_2[J] - \int d^4x \frac{\delta W_2[J]}{\delta J(x)} J(x) - \frac{e^2}{2} \iint d^4x d^4y J(x) U_0^{-1}(x-y) J(y) \\ &= \Gamma_2[\sigma_c] - \frac{e^2}{2} \iint d^4x d^4y J(x) U_0^{-1}(x-y) J(y). \end{aligned} \quad (5.19)$$

In (5·19) $J(x)$ has to be expressed by n or σ_c . As long as $J=0$, there is no difference between two formalisms as is seen from (5·17), (5·18) and (5·19), namely $W_1[0] = W_2[0]$, $n = \sigma_c$, $\Gamma_1[n] = \Gamma_2[\sigma_c]$. Recall here that we have always kept $J=0$; the stationary equation (2·14) or (2·17) is nothing but the requirement $J=0$ and also the excitation is determined by the condition $J=0$, see (4·2). Therefore all the results coming from our equations are the same for both schemes. This is because, stated in more general terms, removing the artificial probe by setting $J=0$, the original theory is recovered and we are just determining the eigenstates of the true Hamiltonian of the system—the ground state by (2·17) and the excited states by (4·2). These are the concepts which are independent how one probes the system.

The universality in terms of $\Gamma[\sigma_c]$

The universality theorem of Hohenberg-Kohn in the language of $\Gamma[\sigma_c]$ goes as follows. Let us change the numerator of (5.1) from $\sigma(x) - \phi^\dagger(x)\phi(x)$ to

$$\sigma(x) - \phi^\dagger(x)\phi(x) + \frac{1}{e^2} \int d^4y v(y) U_0^{-1}(y-x), \tag{5.20}$$

which states that the operator $\bar{\sigma}(x)$ is not given by $\hat{\phi}^\dagger(x)\hat{\phi}(x)$ but by

$$\hat{\phi}^\dagger(x)\hat{\phi}(x) - \frac{1}{e^2} \int d^4y v(y) U_0^{-1}(y-x).$$

Then, after adding $J \cdot \sigma$ and making Legendre transformation it is easy to see the relation

$$\Gamma[\sigma_c] = \Gamma_0[\sigma_c] + \int d^4x v(x) \sigma_c(x) + \frac{1}{e^2} \iint d^4x d^4y v(x) U_0^{-1}(x-y) v(y), \tag{5.21}$$

where $\Gamma_0[\sigma_c]$ is $\Gamma[\sigma_c]$ evaluated by setting $v=0$ — a universal functional of σ_c independent of v . We have only to solve

$$\frac{\delta \Gamma_0[\sigma_c]}{\delta \sigma_c(x)} = -v(x) \tag{5.22}$$

and, from (5.20), the density is known to be given by

$$n(x) = \langle \phi^\dagger(x)\phi(x) \rangle = \sigma_c^0(x) + \frac{1}{e^2} \int d^4y v(y) U_0^{-1}(y-x),$$

where $\sigma_c^0(x)$ is a solution to (5.22).

§ 6. Generalization

In our formalism, the operator \hat{O} which is probed by introducing the source term $J\hat{O}$ into the Hamiltonian is completely arbitrary. Therefore we can take not only $\int d^3\mathbf{x} J(x) \hat{\phi}_\alpha^\dagger(\mathbf{x}) \hat{\phi}_\alpha(\mathbf{x})$ as a probe of the density but also any other operator $J\hat{O}$ as long as \hat{O} does not change the electron number. Even if the operator \hat{O} changes the electron number, all the procedures presented above go through. For instance we arrive at the equation of the type (4.4) with Δn replaced by $\langle i|\hat{O}|0\rangle$. This is the equation of the excitation spectrum determining the energy difference of the excited states $|i\rangle$ and $|0\rangle$ which differ in electron number. Furthermore the operator \hat{O} can be non-local in the sense that it refers to two different space-time points. These examples are given below. The following discussion is based on the general formalism developed in Ref. 7).

6.1. Ionization (affinity) energy

As an example, let us consider an atom with N electrons and add two source terms $-\int d^3\mathbf{x} \eta_\alpha^\dagger(\mathbf{x}, t) \hat{\phi}_\alpha(\mathbf{x})$ and $-\int d^3\mathbf{x} \hat{\phi}_\alpha^\dagger(\mathbf{x}) \eta_\alpha(\mathbf{x}, t)$ to the Hamiltonian with $\eta_\alpha, \eta_\alpha^\dagger$ being c -number Grassmann variables. These operators change the electron number by unity. Let us consider

$$\begin{aligned} \widehat{H}_{J,\eta,\eta^\dagger} = & \widehat{H} - \int d^3x J(x,t) \widehat{\psi}_a^\dagger(x) \widehat{\psi}_a(x) \\ & - \int d^3x \eta \eta_a^\dagger(x,t) \widehat{\psi}_a(x) - \int d^3x \widehat{\psi}_a^\dagger(x) \eta_a(x,t). \end{aligned} \quad (6.1)$$

Then $W[J,\eta,\eta^\dagger]$ is defined as

$$\exp(iW[J,\eta,\eta^\dagger]) \equiv \int [d\psi^\dagger d\psi] \exp\left(i \int_{-\infty}^{\infty} dt L_{J,\eta,\eta^\dagger}\right), \quad (6.2)$$

where L_{J,η,η^\dagger} is the Lagrangian derived from H_{J,η,η^\dagger} ;

$$L_{J,\eta,\eta^\dagger} = L + \int d^3x J(x) \psi_a^\dagger(x) \psi_a(x) + \int d^3x \eta \eta_a^\dagger(x) \psi_a(x) + \int d^3x \psi_a^\dagger(x) \eta_a(x). \quad (6.3)$$

Now we introduce the expectation values

$$n(x) = -\frac{\delta W}{\delta J(x)} = \langle \widehat{\psi}_a^\dagger(x) \widehat{\psi}_a(x) \rangle_{J,\eta,\eta^\dagger}, \quad (6.4)$$

$$\Psi_a(x) = \frac{\overrightarrow{\delta} W}{\delta \eta_a^\dagger(x)} = \langle \widehat{\psi}_a(x) \rangle_{J,\eta,\eta^\dagger}, \quad \Psi_a^\dagger(x) = \frac{\overleftarrow{\delta} W}{\delta \eta_a(x)} = \langle \widehat{\psi}_a^\dagger(x) \rangle_{J,\eta,\eta^\dagger}. \quad (6.5)$$

Since the probes η_a, η_a^\dagger (and also Ψ_a, Ψ_a^\dagger) are the Grassmann variables, we have to distinguish the left and right derivatives. The definitions of them are given for any Grassmann variable ξ by

$$F[\xi + \delta\xi] - F[\xi] \equiv \delta\xi \frac{\overrightarrow{\delta} F[\xi]}{\delta\xi} \equiv \frac{\overleftarrow{\delta} F[\xi]}{\delta\xi} \delta\xi. \quad (6.6)$$

Then the effective action defined in (2.13) is extended to the case of three variables;

$$\begin{aligned} \Gamma[n, \Psi^\dagger, \Psi] = & W[J, \eta^\dagger, \eta] - \int d^4x J(x) n(x) - \int d^4x \eta \eta_a^\dagger(x) \Psi_a(x) \\ & - \int d^4x \Psi_a^\dagger(x) \eta_a(x). \end{aligned} \quad (6.7)$$

Because the chemical potential μ is kept fixed in the above Legendre transformation, we have the relation, which relates μ to the total electron number N ,

$$\frac{\partial \Gamma}{\partial \mu} = \frac{\partial W}{\partial \mu} = \int d^4x \langle \widehat{\psi}^\dagger(x) \widehat{\psi}(x) \rangle_{J,\eta^\dagger,\eta} \rightarrow \int dt N. \quad (\text{as } J, \eta^\dagger, \eta \rightarrow 0) \quad (6.8)$$

This condition determines μ as a function of N and the vacuum state $|0\rangle$ becomes the ground state of the system with N electrons; $\mu = \mu(N)$, $|0\rangle = |N\rangle$. There are now three stationary requirements

$$\frac{\delta \Gamma}{\delta n(x)} = -J(x) = 0, \quad (6.9)$$

$$\frac{\overleftarrow{\delta} \Gamma}{\delta \Psi_a^\dagger(x)} = -\eta_a^\dagger(x) = 0, \quad \frac{\overrightarrow{\delta} \Gamma}{\delta \Psi_a(x)} = -\eta_a(x) = 0, \quad (6.10)$$

and we write the solutions as

$$n(x) = n^{(0)}(x) = \langle N | \hat{\phi}_\alpha^\dagger(x) \hat{\phi}_\alpha(x) | N \rangle, \quad (6.11)$$

$$\Psi_\alpha(x) = \Psi_\alpha^{(0)}(x) = \langle N | \hat{\phi}_\alpha(x) | N \rangle = 0, \quad \Psi_\alpha^\dagger(x) = \Psi_\alpha^{\dagger(0)}(x) = \langle N | \hat{\phi}_\alpha^\dagger(x) | N \rangle = 0. \quad (6.12)$$

As in §4, we look for other solutions to (6.9) and (6.10) in the vicinity of $n^{(0)}(x)$, $\Psi_\alpha^{(0)}(x)$ and $\Psi_\alpha^{\dagger(0)}(x)$ by writing $n(x) = n^{(0)}(x) + \Delta n(x)$, $\Psi_\alpha(x) = \Psi_\alpha^{(0)}(x) + \Delta \Psi_\alpha(x)$, $\Psi_\alpha^\dagger(x) = \Psi_\alpha^{\dagger(0)}(x) + \Delta \Psi_\alpha^\dagger(x)$.⁷⁾ Taking into account the electron number conservation law, which states for instance that

$$\left(\frac{\overleftarrow{\delta}}{\delta \Psi_\beta(y)} \left(\frac{\delta \Gamma}{\delta n(x)} \right) \right)_0 = 0,$$

we get three mode determining equations; one of them is identical to (4.2) and the other two take the form,

$$\int d^4 y \left(\frac{\overrightarrow{\delta}}{\delta \Psi_\beta^\dagger(y)} \left(\frac{\overleftarrow{\delta} \Gamma}{\delta \Psi_\alpha(x)} \right) \right)_0 \Delta \Psi_\beta^\dagger(y) = 0, \quad (6.13)$$

$$\int d^4 y \left(\frac{\overleftarrow{\delta}}{\delta \Psi_\beta(y)} \left(\frac{\overrightarrow{\delta} \Gamma}{\delta \Psi_\alpha^\dagger(x)} \right) \right)_0 \Delta \Psi_\beta(y) = 0, \quad (6.14)$$

where $(\dots)_0$ implies the value of (\dots) evaluated at the stationary solutions (6.11) and (6.12).

Now let us investigate the meaning of these wave equations. Using simple extension of the identity of the Legendre transformation (4.6), Eqs (4.2), (6.13), and (6.14) can be seen to be the equations determining the poles of the Green's functions ${}_0 \langle N | T \hat{n}(x) \hat{n}(y) | N \rangle_0$, ${}_0 \langle N | T \hat{\phi}_\alpha(x) \hat{\phi}_\beta^\dagger(y) | N \rangle_0$ and ${}_0 \langle N | T \hat{\phi}_\alpha^\dagger(x) \hat{\phi}_\beta(y) | N \rangle_0$ respectively. Inserting the complete set between $\hat{n}(x)$ and $\hat{n}(y)$ of ${}_0 \langle N | T \hat{n}(x) \hat{n}(y) | N \rangle_0$, we see that only the states with N electrons contribute. So the eigenvalues of (4.2) are given as the difference of the energy between arbitrary excited levels and the ground state both with the same number N of the electrons. On the other hand, if we insert the complete set between $\hat{\phi}_\alpha(x)$ and $\hat{\phi}_\beta^\dagger(y)$ of ${}_0 \langle N | T \hat{\phi}_\alpha(x) \hat{\phi}_\beta^\dagger(y) | N \rangle_0$, only the states with $N \pm 1$ (for $t_x \geq t_y$) electrons contribute. So the eigenvalues of (6.13) are equal to the differences between the energy of the excited levels $|N \pm 1\rangle$ of the system with $N \pm 1$ electrons and the ground state energy of the system with N electrons. This is the ionization or the affinity energy. Equation (6.13) or (6.14) separately yields two different sets of mode each of which belongs to the channel defined by different electron number. However we can easily distinguish between the affinity energy and the ionization energy, if we keep track of the sign of the time difference $t_x - t_y$ in (6.13) in the course of calculation. Equation (6.14), of course, gives the same eigenvalues as in (6.13), but there is a difference between $\Delta \Psi_\alpha^\dagger(y)$ and $\Delta \Psi_\alpha(y)$. By the arguments leading to (4.10), the wave function $\Delta \Psi_\alpha^\dagger(y)$ can be written as^{7),8)}

$$\Delta \Psi_\alpha^\dagger(y) = \langle N+1 | \hat{\phi}_\alpha^\dagger(y) | N \rangle_0 \quad \text{or} \quad {}_0 \langle N | \hat{\phi}_\alpha^\dagger(y) | N-1 \rangle, \quad (6.15)$$

while $\Delta \Psi(y)$ has the form

$$\Delta\Psi_a(y) = \langle N-1 | \hat{\phi}_a(y) | N \rangle_0 \text{ or } \langle N | \hat{\phi}_a(y) | N+1 \rangle. \tag{6.16}$$

In the following the explicit form of the mode determining equation is examined. We have already discussed the case of density variable in §5 by auxiliary field method. Here we take up Eq. (6.14). Let us consider, for simplicity, the case where we do not perform Legendre transformation with regard to J or disregard the J dependence altogether. The effective action in such a case is well-known,^{2),10)}

$$\Gamma[\Psi, \Psi^\dagger] = \int d^4x \Psi_a^\dagger(x) \left(i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + v(x) + \mu \right) \Psi_a(x) - \frac{e^2}{2} \int d^4x \int d^4y \Psi_a^\dagger(x) \Psi_b^\dagger(y) U_0(x-y) \Psi_b(y) \Psi_a(x) - i\kappa^{(1)}, \tag{6.17}$$

where $\kappa^{(1)}$ represents all the one-particle irreducible vacuum graphs. In the above formula, we have included in $\kappa^{(1)}$ the one-loop vacuum diagrams represented by $\text{Tr} \ln$. So Eq. (6.14) becomes

$$\int d^4y \left[\left(i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + v(x) + \mu(N) \right) \delta^4(x-y) \delta_{\alpha,\beta} - i \left(\frac{\overleftarrow{\delta}}{\delta\Psi_\beta(y)} \left(\frac{\overrightarrow{\delta}}{\delta\Psi_a^\dagger(x)} \right) \right)_0 \right] \Delta\Psi_\beta(y) = 0. \tag{6.18}$$

This is the wave equation which determines the ionization or the affinity energy. In Fig. 5, we write down the last term in (6.18) up to the second order in e^2 . The first or second term in Fig. 5 corresponds to Fock or Hartree term respectively.

Loosely speaking, $\Delta\Psi_a(y)$ or $\Delta\Psi_a^\dagger(y)$ is the wave function of the electron which is deleted or added. However such a picture does not hold in a strict sense, of course, since all the electrons are identical quantum mechanically. Combining (4.2), (6.13) and (6.14) and surveying all the atomic number Z , we can obtain in principle any of

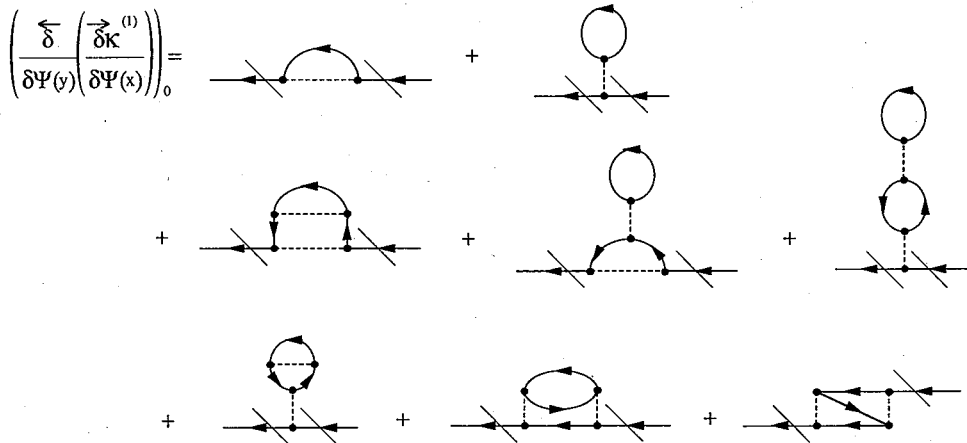


Fig. 5. Diagrams contributing to the last term of (6.18) up to e^4 . Solid line here represents the electron propagator; $i(i\partial/\partial t) + (\nabla^2/2m) + v(x) + \mu(N)^{-1} \delta^4(x-y) \delta_{\alpha\beta}$. The potential between electrons is denoted by broken line. The slashes indicate the amputation of the corresponding propagator lines.

the levels of atomic system. Detailed study of (6·18) is an interesting subject which will be given in a forthcoming paper.

6.2. Multiple ionization (affinity) energy and Schrödinger equation

The above arguments can be generalized by adding the following source term to the Hamiltonian \hat{H} (for notational clarity, the spin indices will be suppressed),

$$-\int d^3x_1 \cdots \int d^3x_k \eta^\dagger(x_1, x_2, \dots, x_k) \hat{\psi}(x_1) \hat{\psi}(x_2) \cdots \hat{\psi}(x_k) + \text{c.c.},$$

where c.c. implies the complex conjugation and the notation $x_j = (x_j, t)$ is used. The c -number function η or η^\dagger is completely antisymmetric in its arguments and it is a Grassmann number if k is odd. This term corresponds to the source term,

$$\int d^4x_1 \cdots \int d^4x_k \eta^\dagger(x_1, x_2, \dots, x_k) \phi(x_1) \phi(x_2) \cdots \phi(x_k) + \text{c.c.},$$

which is to be added to L of (2·9). In this form, we are probing the operator $\hat{\psi}(x_1) \hat{\psi}(x_2) \cdots \hat{\psi}(x_k)$ where $\hat{\psi}(x_j)$ is the electron field operator in Heisenberg representation. Now $W[\eta^\dagger, \eta]$ is defined as usual and $\Gamma[\Psi^\dagger, \Psi]$ is introduced as follows:

$$\Gamma[\Psi^\dagger, \Psi] = W[\eta^\dagger, \eta] - \int d^4x_1 \cdots \int d^4x_k \{ \eta^\dagger(x_1, \dots, x_k) \Psi(x_1, \dots, x_k) + \Psi^\dagger(x_1, \dots, x_k) \eta(x_1, \dots, x_k) \},$$

$$\Psi(x_1, \dots, x_k) = \frac{\overrightarrow{\delta} W[\eta^\dagger, \eta]}{\delta \eta^\dagger(x_1, \dots, x_k)},$$

$$\Psi^\dagger(x_1, \dots, x_k) = \frac{\overleftarrow{\delta} W[\eta^\dagger, \eta]}{\delta \eta(x_1, \dots, x_k)}.$$

The ground state is characterized of course by $\Psi^{(0)} = \Psi^{\dagger(0)} = 0$ and the excitation levels are determined by

$$\int d^4y_1, \dots, \int d^4y_k \left(\frac{\overleftarrow{\delta}}{\delta \Psi(y_1, \dots, y_k)} \left(\frac{\overrightarrow{\delta} \Gamma}{\delta \Psi^\dagger(x_1, \dots, x_k)} \right) \right)_0 \Delta \Psi(y_1, \dots, y_k) = 0 \quad (6\cdot19)$$

and its conjugate equation. The total energy $\omega = \sum_{i=1}^k \omega_i$, where ω_i is the energy Fourier component in the channel specified by x_i , is determined as an eigenvalue of (6·19). It is the ionization (affinity) energy where k electrons are removed from (added to) the N -electrons atom (N comes in through the chemical potential μ).

The Schrödinger equation itself for N -electrons system is derived in our formalism as follows. Take $k=N$ in (6·19) and $\mu=0$. Then it can be shown¹²⁾ that Eq. (6·19) is nothing but the Schrödinger equation if we identify $\Delta \Psi(x_1, x_2, \dots, x_N) \equiv \Delta \Psi(x_1, t, x_2, t, \dots, x_N, t)$ with the Schrödinger wave function $\Psi(x_1, \dots, x_N, t)$;

$$\begin{aligned} \Delta \Psi(x_1, t, x_2, t, \dots, x_N, t) &= \Psi(x_1, x_2, \dots, x_N, t) \\ &= \langle 0 | \hat{\psi}(x_1, t) \hat{\psi}(x_2, t) \cdots \hat{\psi}(x_N, t) | N \rangle. \end{aligned}$$

In this sense the energy eigenvalue of N -electron system is viewed in our formalism as the ionization energy required in the process of removing N -electrons from

N -electron system.

6.3. Non-local density

As an electron number conserving operator, we can generalize the local density operator $\hat{n}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x)$ to "non-local density" operator $\hat{n}(x, y) = \hat{\psi}^\dagger(x)\hat{\psi}(y)$. This operator can equally be used in place of $\hat{n}(x)$ since $\hat{n}(x, y)$ has the same quantum number, i.e., zero-electron number as $\hat{n}(x)$. Or we can generalize still further to consider the operator $\hat{n}(x, y) = \hat{\psi}^\dagger(x)\hat{\psi}(y)$ which is non-local in time also. Here $\hat{\psi}(x) = \hat{\psi}(x, t)$ is the Heisenberg field operator of the electron at time t . In order to get the effective action of $\hat{n}(x, y)$, we add the term $\int d^4x \int d^4y J(x, y) \hat{\psi}^\dagger(x)\hat{\psi}(y)$ to (2.9) and $W[J]$ is defined as in (2.8). Then as an argument of the effective action $\Gamma[n]$, we define

$$n(x, y) \equiv \frac{\delta W[J]}{\delta J(x, y)} = \langle \psi^\dagger(x)\psi(y) \rangle_J$$

and $\Gamma[n]$ is given by

$$\Gamma[n] = W[J] - \int d^4x \int d^4y J(x, y)n(x, y).$$

The stationary solution $n^{(0)}(x, y)$ to the equation $\delta\Gamma/\delta n(x, y) = 0$ is the propagator function in this case;

$$n^{(0)}(x, y) = {}_0\langle N | T \psi^\dagger(x)\psi(y) | N \rangle_0$$

and the mode determining equation has the form,

$$\int d^4x' \int d^4y' \left(\frac{\delta^2 \Gamma[n]}{\delta n(x, y) \delta n(x', y')} \right)_0 \Delta n(x', y') = 0, \quad (6.20)$$

which determines the exnergy $\omega = \sum_{i=1}^2 \omega_i$ corresponding to the sum of energy of the channel specified by x and y (or x' and y'). The energy ω thus determined is the same as is given by using the local density operator $\hat{n}(x)$.

Although $n(x, y)$ formalism looks more complicated than $n(x)$ it has an advantage that the Feynman rule of Γ using $n(x, y)$ is more transparent than $n(x)$. It is known that $\Gamma[n]$ is given by the formula¹⁰⁾

$$\Gamma[n] = \text{Tr} D_0(x-y)n(x, y) - \text{Tr} \ln n(x, y) + \kappa^{(2)}[n],$$

where $D_0(x-y)$ is given in (5.6), Tr implies the functional trace and $\kappa^{(2)}[n]$ is the sum of all 2PI (two particle irreducible) vacuum diagrams where the propagator is $n(x, y)$ and the vertices are dictated from the Lagrangian (2.9). Here 2PI means that the diagram is not separated into two disconnected parts if two propagator lines (each represented by $n(x, y)$) are cut at the same time. Examples are shown in Fig. 6.

Equation (6.20) is the BS-type equation in relativistic field theory and various techniques developed there will be useful in solving (6.20). Another advantage of using $n(x, y)$ is that, since the probe $J(x, y)$ depends on x and y independently, we get more information about the ground state and excited levels. For example, the i -th level $|i\rangle$ corresponds to $\Delta n(x, y) \simeq {}_i\langle N | T \psi^\dagger(x)\psi(y) | N \rangle_0$ therefore it contains the infor-

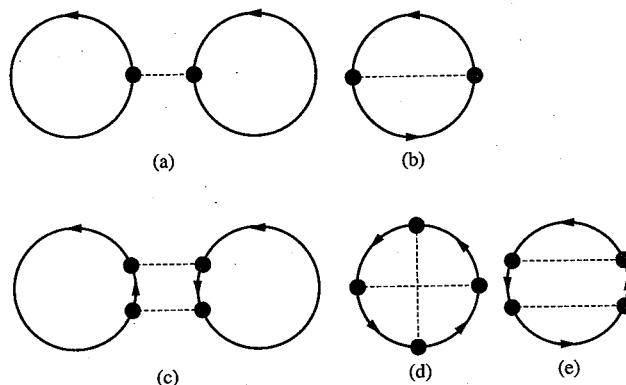


Fig. 6. Diagrams for $\Gamma[n]$ of non-local density. (a)~(d) are the examples of 2PI diagram. The solid line represents the propagator $n(x, y)$. (e) is one of the examples of the two particle reducible graphs which is excluded.

mation about the dependence of the wave function on the relative co-ordinate of the particle-hole pair.

§ 7. Inversion method—Generalization of Legendre transformation

The central problem is of course how to calculate $\Gamma[n]$. In case the auxiliary field σ can be introduced, the diagrammatic rule of $\Gamma[n]$ has been discussed in §5. Here we investigate the general situation without using σ . It includes the case where the auxiliary field method does not work. Even for the case σ can be used, we can make Legendre transformation without using σ . The merit of such a procedure is that the variable introduced in this way has a direct relation to the observed physical quantity. It turns out that the newly introduced method is a generalization of Legendre transformation. This method has already been applied to many examples⁵⁾ and the diagrammatic full order rule is now available for the local composite operators such as the density operator.⁹⁾

As has been stressed, the essential ingredient of the Legendre transformation is the *inversion*⁵⁾ of the relation between the artificially introduced probe J (we assume here single J for simplicity) and the expectation value of the quantity we are interested in, which is usually the force variable X conjugate to J . It is straightforward to calculate X as a function of J in a diagrammatic expansion and, solving (i.e., inverting) this relation $X[J]$ in terms of J , we are led in some cases to a compact diagrammatical rule for $\Gamma[X]$, i.e., 1PI or 2PI vacuum diagrams, for example. However a simple diagrammatical rule is not always possible for all X .

The inversion method is applicable for any X including the case where X is not the conjugate force of J or even the case where X is not necessarily the expectation value of any operator. Suppose we have an expansion parameter g . In case of diagrammatic expansion, for example, g is the strength of Coulomb repulsion e^2 . Then the rule of the inversion method is summarized in three steps.

1. Calculate X as a power series of g , up to some finite order N ;

$$X = \sum_{n=0}^N g^n f_n[J], \quad (7.1)$$

where f_i is a calculable function of J in a diagrammatic series.

2. Invert (7.1) to get

$$J = \sum_{n=0}^M g^n h_n[X]. \quad (7.2)$$

Recall here that $h_j (0 \leq j \leq N)$ is calculable as a functional of X by using $f_i (0 \leq i \leq N)$ appearing in (7.1). Therefore in (7.2) we take $M=N$.

3. Solve the equation $J=0$ which ensures that the artificial source is absent;

$$0 = \sum_{n=0}^N g^n h_n[X], \quad (7.3)$$

which is the equation determining X . The solution has been denoted by $X^{(0)}$ in the previous sections.

The important difference between (7.1) and (7.2) is that in (7.1) J is regarded as the quantity of order g^0 , i.e., unity, while X is order unity in (7.2). If X is to be used as a variable of the theory, as in the case of density functional theory, the second choice has to be adopted. Choosing X as a variable has the effect of summing up an infinite number of terms of the original series (7.1) even if we cut off the inverted series (7.2) at finite M . Because of this situation, the solution to (7.3) with $M=N$ usually produces better results than (7.1).

In practical use of the inversion method the following inversion formulas are used, which are obtained by the identity $X = \sum_{n=0}^{\infty} g^n f_n[\sum_{m=0}^{\infty} g^m h_m[X]]$;

$$h_0[X] = f_0^{-1}[X],$$

$$h_1[X] = -\frac{f_1[h_0[X]]}{f_0'[h_0[X]]},$$

$$h_2[X] = -\frac{f_2[h_0[X]] + f_1'[h_0[X]]h_1[X] + \frac{1}{2}f_0''[h_0[X]]h_1^2[X]}{f_0'[h_0[X]]},$$

⋮

Here $f_0^{-1}[X]$ is the inverse function of $f_0[X]$. Note that the inverse function is required only for the lowest function $f_0[X]$. The generalization of the above formulas to the case where we have several sources J_k or the function $J(x)$ as in the density functional theory is straightforward. The following important observations have to be noted here.

1) If we set $J=0$ in the original series, we are calculating X just perturbatively. Therefore, in the case where X is the order parameter which breaks the symmetry of the Hamiltonian in the limit $J=0$, we get only a trivial solution $X=0$ for all order of g ; $f_i[J=0]=0$ for any i . On the other hand the non-trivial symmetry breaking solution is found, if it is a solution at all, in (7.3) besides a trivial one. The reason

why such a solution can be found in a perturbative series of (7.3) is that, as has been pointed out already, by changing the variable from J to X through inversion an infinite number of subdiagrams are summed up in (7.3). Indeed for any model the lowest non-trivial equation of (7.3) agrees with the self-consistent mean-field approximation.

2) Excitation spectrum is obtained by inversion method following the same procedure as in §5. Let one of the solution to (7.3) be $X^{(0)}(x)$ recovering the space-time argument x . We have to replace $J \rightarrow J(x)$, $h_n[X] \rightarrow h_n[x, X]$ in (7.3). Then another solution $X^{(0)}(x) + \Delta X(x)$ is substituted into (7.3) which becomes for small ΔX ,

$$\int d^4y \left\{ \sum_{n=0}^N g^n \left(\frac{\delta h_n[x, X]}{\delta X(y)} \right)_0 \right\} \Delta X(y) = 0.$$

This is the generalization of (4.2) determining the excitation energy ω in the channel x or y .

3) As has been pointed out, X can be any quantity in the inversion method. However if X is written as a derivative of certain functional $W[J]$ as

$$X(x) = \frac{\delta W[J]}{\delta J(x)}, \quad (7.4)$$

then the inverted relation $J(x) = J[x, X]$ can also be represented by using a functional $\Gamma[X]$ through

$$-J(x) = \frac{\delta \Gamma[X]}{\delta X(x)},$$

where $\Gamma[X]$ is the Legendre transformation of $W[J]$;

$$\Gamma[X] = W[J] - \int d^4x J(x) \frac{\delta W[J]}{\delta J(x)}.$$

In this sense the inversion method is a generalization of Legendre transformation. If (7.4) does not hold, $\Gamma[X]$ cannot be obtained by our method but this does not cause any trouble. We can determine the ground state solution $X^{(0)}$ and excitation modes and scattering among modes⁸⁾ thus determined. The only quantity that cannot be calculated is the numerical value $\Gamma[X^{(0)}]$ which is related to the energy of ground state. Note that the absolute value of the ground state energy is not a physical quantity except for the case where we want to compare the energy of two ground states (if they exist) in the case of field theoretical systems.

§ 8. Finite temperature—Equilibrium and non-equilibrium

The system of finite temperature is studied in a similar way. We first discuss the equilibrium case and then proceed to the non-equilibrium process where the initial density matrix ρ is arbitrarily given. The form of ρ can be an equilibrium one but we assume a time dependent Hamiltonian which brings the system into a non-equilibrium state. The discussions are given in a brief manner since they are quite straightforward.

Equilibrium case

Let us define $W[J]$ for the system of temperature T ;

$$\exp(-\beta W[J]) = \text{Tr} \exp(-\beta \hat{H}_J),$$

where $\beta = 1/kT$ and \hat{H}_J is given in (2.5) with $J(\mathbf{x}, t)$ replaced by $J(\mathbf{x})$. Then the expectation value of the density at temperature T is written as

$$\begin{aligned} n(\mathbf{x}) &\equiv \frac{\delta W[J]}{\delta J(\mathbf{x})} = \frac{\text{Tr}\{\exp(-\beta \hat{H}_J) \hat{n}(\mathbf{x})\}}{\text{Tr} \exp(-\beta \hat{H}_J)} \\ &= \langle \hat{n}(\mathbf{x}) \rangle_\beta. \end{aligned}$$

The Legendre transformation of $W[J]$ is usually called the free energy $F[n]$;

$$F[n] = W[J] - \int d^3 \mathbf{x} J(\mathbf{x}) \frac{\delta W[J]}{\delta J(\mathbf{x})}.$$

The density $n(\mathbf{x})$ is determined by the equation,

$$0 = \frac{\delta F[n]}{\delta n(\mathbf{x})} = -J(\mathbf{x}). \quad (8.1)$$

All the previous discussion about auxiliary field method, inversion method, etc., can be applied of course to the finite temperature case.

Non-equilibrium process

The time dependent phenomenon is discussed by introducing a time dependent source $J(x) = J(\mathbf{x}, t)$. We assume here that the system is described at initial time $t = t_i$ by an arbitrary density matrix ρ including the case $\rho = \exp(-\beta \hat{H})$. The probe is introduced starting from t_i assuming that $J(\mathbf{x}, t_i) = 0$. The expectation value $n(x) = n(\mathbf{x}, t)$ of the density at any time $t > t_i$ is given by

$$n(x) = \langle \hat{n}(x) \rangle_{t_i} = \frac{\text{Tr} \rho U_J^*(t, t_i) \hat{n}(x) U_J(t, t_i)}{\text{Tr} \rho}, \quad (8.2)$$

where $U_J(t_2, t_1)$, is the time evolution operator in time ordered form,

$$U_J(t_2, t_1) = \text{Texp} \left(-i \int_{t_1}^{t_2} dt' \hat{H}_J(t') \right)$$

with $\hat{H}_J(t')$ given in (2.5) and U_J^* is the Hermite conjugate of U_J . Now we define the generating functional corresponding to $W[J]$. In order to do this we need two kinds of probe $J_1(x)$ and $J_2(x)$ and define $W[J_1, J_2]$ as

$$\exp i W[J_1, J_2] = \text{Tr} \{ \rho U_{J_2}^*(\infty, t_i) U_{J_1}(\infty, t_i) \}.$$

Then $n(x)$ can be obtained in two ways,

$$n(x) = \left. \frac{\delta W[J_1, J_2]}{\delta J_1(x)} \right|_{J_1=J_2=J} = - \left. \frac{\delta W[J_1, J_2]}{\delta J_2(x)} \right|_{J_1=J_2=J}.$$

Let us introduce $\Gamma[n_1, n_2]$ by

$$\Gamma[n_1, n_2] = W[J_1, J_2] - \int d^4x \left(J_1(x) \frac{\delta W[J_1, J_2]}{\delta J_1(x)} + J_2(x) \frac{\delta W[J_1, J_2]}{\delta J_2(x)} \right),$$

where

$$n_i(x) = (-1)^{i+1} \frac{\delta W[J_1, J_2]}{\delta J_i(x)}. \quad (i=1, 2)$$

Then we have the identity

$$J_i(x) = (-1)^i \frac{\delta \Gamma[n_1, n_2]}{\delta n_i(x)} \quad (i=1, 2)$$

from which two sets of equation of motion determining $n_i(x)$ is obtained;

$$\frac{\delta \Gamma[n_1, n_2]}{\delta n_i(x)} = 0. \quad (i=1, 2) \quad (8.3)$$

However through the symmetry property of Γ under $n_1 \leftrightarrow n_2$, the solution always satisfies $n_1(x) = n_2(x)$ (corresponding to $J_1(x) = J_2(x)$) therefore (8.3) is equivalent to

$$\left. \frac{\delta \Gamma[n_1, n_2]}{\delta n_i(x)} \right|_{n_1=n_2=n} = 0, \quad (8.4)$$

which is the equation of motion determining the physically observed $n(x)$. In the equilibrium limit, Eq. (8.4) is known¹³⁾ to reduce to (8.1). However, for general situation, Eq. (8.4) is not of variational form in a strict sense; in contrast to the zero temperature case it does not take the form $\delta \Gamma / \delta n(x) = 0$ with some functional $\Gamma[n]$ of $n(x)$. This is because of the non-conservative phenomenon such as dissipation which is present in a general non-equilibrium processes.

The excitation spectrum is studied by inserting $n(x) = n^{(0)}(x) + \Delta n(x)$ to (8.4) where $n^{(0)}(x)$ is one of the solutions to (8.4). We get in this case

$$\int d^4y (\Gamma_{1x,1y}^{(2)} + \Gamma_{1x,2y}^{(2)})_0 \Delta n(y) = 0, \quad (8.5)$$

where

$$\Gamma_{ix,jy}^{(2)} \equiv \frac{\delta^2 \Gamma[n_1, n_2]}{\delta n_i(x) \delta n_j(y)}.$$

It turns out that¹³⁾ $\Gamma_{1x,1y}^{(2)} + \Gamma_{1x,2y}^{(2)}$ is the inverse of the retarded thermal Green's function $\Delta_R(x, y)$,

$$\Delta_R(x, y) = \text{Tr} \{ \rho \theta(t_x - t_y) [\bar{n}(x), \bar{n}(y)] \},$$

therefore solving (8.5) amounts to the fact that we are looking for the pole of $\Delta_R(x, y)$. It is also known that Fourier transform of $\Delta_R(x, y)$ is analytic in frequency ω and that the discrete eigenvalue ω determined by (8.5) is the same as that determined by (4.2) since ω is the eigenvalue of the Hamiltonian of the system.

$\Gamma[n_1, n_2]$ is the most general density functional in the sense that Eq. (8.4) reduces to (8.1) in the equilibrium limit and to (2.14) in the zero temperature limit which in turn reduces to (2.17) in the static limit.

Detailed discussion of Γ of general non-equilibrium processes has been given in Refs. 13) and 14).

§ 9. Discussion

We have discussed density functional theory which is formulated by the field theoretical functional Legendre transformation. Recall here that in any physical system we have to use the energy function which is written by the most convenient variable according to the situation we are considering. Such a variable is sometimes called the natural variable as we know many examples in equilibrium statistical physics. The natural variable can be introduced through Legendre transformation. The density $n(x)$ has been taken as a natural variable in this paper.

The density functional theory presented here is a most systematic formulation of the problem in the following sense. Consider the zero temperature case. We start from the effective action $\Gamma[n]$ and;

- 1) Determine the ground state by solving the first derivative equation;

$$\frac{\delta\Gamma[n]}{\delta n(x)}=0$$

and find the solution $n^{(0)}(x)=\langle 0|\hat{n}(x)|0\rangle$.

- 2) Solve the second derivative equation

$$\int d^4y \left(\frac{\delta^2\Gamma[n]}{\delta n(x)\delta n(y)} \right)_0 \Delta n(y) = 0,$$

where $(\dots)_0$ is evaluated by the solution $n^{(0)}(x)$ determined in 1). This is the eigenvalue equation which determines the excitation energy ω_i .

- 3) The third derivative or higher gives the scattering matrix (S-matrix) element among the excitation modes obtained in 2).

The point 3) has not been discussed in this paper. See Ref. 8) for details. The important point that should be stressed here is that once $\Gamma[n]$ is calculated with some approximation scheme, then the ground state, excited states and even the scattering among the excited levels are determined by the same approximation. This is an important property required for any approximation scheme.

In the body of the text we have not discussed the local density approximation (LDA) but it can straightforwardly be discussed in our formalism. Let us take $\Gamma[n]$ of (2·13) ($E[n]$ of (2·16) can similarly be discussed), and expand it around some constant $n(x)=n$, which is taken to be zero for simplicity below. Then $\Gamma[n]$ is expanded in functional Taylor series,

$$\Gamma[n] = \sum_{n=0}^{\infty} \frac{1}{n!} \int d^4x_1 \cdots \int d^4x_n \Gamma^{(n)}(x_1, \dots, x_n) n(x_1) n(x_2) \cdots n(x_n). \quad (9\cdot1)$$

If we use auxiliary field method, $n(x)$ is replaced by $\sigma_c(x)$ and above $\Gamma^{(n)}(x_1, \dots, x_n)$ is related to the sum of 1PI n -point Green's functions. In the homogeneous case, $\Gamma^{(n)}(x_1,$

\dots, x_n) is a function of the difference of the co-ordinates $x_i - x_j (1 \leq i, j \leq n)$. The local density approximation is obtained in a systematic way by expanding each x_i around some fixed point x , say the center co-ordinate $x = (\sum_{i=1}^n x_i)/n$. But since x is arbitrary, we take for convenience $x = x_1$ and expand $n(x_j) (j \geq 2)$ as

$$n(x_j) = n(x_1) + (x_j - x_1)_\mu \partial^\mu n(x_1) + \frac{1}{2!} (x_j - x_1)_\mu (x_j - x_1)_\nu \partial^\mu \partial^\nu n(x_1) + \dots, \quad (9.2)$$

where $\partial^\mu \equiv (\nabla, \partial/\partial t)$, $x_\mu \equiv (\mathbf{x}, t)$. Inserting (9.2) into (9.1) and collecting the terms with the same number of derivatives we get the local expansion of $\Gamma[n]$ which in general takes the form,

$$\Gamma[n] = \int d^4x \left(\Gamma^{(0)}(n(x)) + \Gamma_\mu^{(1)}(n(x)) \partial^\mu n(x) + \frac{1}{2!} \Gamma_{\mu\nu}^{(2)}(n(x)) \partial^\mu \partial^\nu n(x) + \dots \right).$$

Each co-efficient $\Gamma_{\mu\nu}^{(k)} (k=0, 1, 2, \dots)$ is now a function of $n(x)$. We have checked that in the case of electron gas with uniform positive background our expansion formula reproduces the known results of LDA ($\Gamma_\mu^{(1)} = 0$ in this case).

Here we want to stress once more that our formalism is again systematic and straightforward in obtaining LDA since a diagrammatic evaluation of $\Gamma[n]$ is straightforward.

As has been stated in the introduction, the arguments presented in this paper constitute a basis of our numerical study which is expected to provide a systematic scheme of approximation. We believe that a firm theoretical foundation is highly required before any approximation can be done.

We have not discussed the equation based on the single particle picture like Kohn-Sham equation.¹⁵⁾ Such an equation can be written down in our scheme but its physical interpretation is not so clear; it is not possible, for example, to derive a single particle equation for which the sum of single particle energy ϵ_i equals to the total energy E and at the same time the sum of the single particle density $\psi_i^\dagger(\mathbf{x})\psi_i(\mathbf{x})$ gives the correct density $n(\mathbf{x})$. It has to be regarded as the equation which is helpful when we try to get actual numerical values by solving the stationary equation of the density functional. The situation is the same as in the case of Kohn-Sham equation.

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