Theorems on ground-state phase transitions in Kohn–Sham models given by the Coulomb density functional

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Received 7 December 2010, in final form 7 February 2011
Published 1 March 2011
Online at stacks.iop.org/JPhysA/44/135305

Abstract
Some theorems on derivatives of the Coulomb density functional with respect to the coupling constant $\lambda$ are given. A model Fermion system with the reduced coupling constant, $\lambda < 1$, is defined to reproduce a ground-state electron density $n_{GS}(r)$ and the ground state energy. Fixing the charge density, possible phase transitions as level crossings occur only at discrete points along the $\lambda$ axis. We prove that Dini’s $\lambda$ derivatives of the reduced energy density functional are given by expectation values of the Coulomb interaction with respect to two-state vectors at the crossing point. If the density is $v$-representable also for $\lambda < 1$, the accumulation of phase transition points is forbidden when $\lambda \to 1$. Our theorems ensure the existence of a converging series of models defined by the multi-reference density functional theory.

PACS numbers: 02.30.Sa, 31.15.ec, 71.15.Mb

1. Introduction
Density functional theory (DFT) [1, 2] is one of the successful frameworks in the theory of electron systems. For a present standard scheme of this theory, the universal energy density functional $F[n]$ defined by the constrained minimization method [3–6] is used as a key quantity. Lieb has analyzed $F[n]$, which is often cited as the Levy–Lieb functional [7]. This functional connects a Fermion density $n(r)$ to a variational energy of an electron wavefunction $\Psi$ showing the same density. Here the density is given as a function of $r \in \mathbb{R}^3$. Let $N$ be the electron number in a system considered. To specify a Fermion density, a set $\mathcal{I}_N$ of the density was introduced, where $n(r) \in \mathcal{I}_N$ satisfies $\int n(r) \, d^3r = N$, and that $\nabla \sqrt{n(r)}$ is square integrable [7]. Thus, $\mathcal{I}_N$ is a subspace of the Sobolev space $H^1(\mathbb{R}^3)$ [8]. The density in this
special space is called \( N \)-representable. Correspondence between \( n(\mathbf{r}) \) and the minimizing state vector \( |\Psi\rangle \) was shown to exist [7], which is a basic principle in DFT.

A continuous modification of the Coulomb operator appearing in the definition of \( F[n] \) is one of the relevant techniques to analyze this functional [5, 6, 9, 10]. The idea is similar to the ordinal perturbation theory of electron systems [11, 12]. To have an exact expression of the so-called exchange-correlation functional, people fixed the charge density and considered continuous reduction of the coupling constant by multiplying a factor \( \lambda \) to the Coulomb operator in the energy density functional [9, 10].

We re-analyze this modified functional, which is called \( F_\lambda[n] \) in this paper, to consider phase transition points appearing in a generalized Kohn–Sham scheme [13]. We have two main purposes for this analysis. The first is to study a parameter differentiability of this \( \lambda \)-modified \( F[n] \). Fixing a density at an \( N \)-representable density in \( \mathcal{I}_N \) [7], the parameter derivative of \( F_\lambda[n] \) is shown to be well defined. Namely, the existence of state vectors giving Dini’s derivatives is shown. As the second purpose, a condition on phase transitions around the \( \nu \)-representable density is derived from the theorems on \( F_\lambda[n] \). A set of \( \nu \)-representable densities is called \( \mathcal{A}_N \) [7]. The existence of level-crossing points in the lowest level, i.e. quantum phase transition points, is known as exemplified by the paramagnetic–ferromagnetic transition in the electron gas system, when one introduces change in the interaction strength [11, 14]. We address the existence of an \( \varepsilon \)-vicinity around the true solution of the many-electron system. In this finite region, no level crossing point is found provided that the density of the Coulomb system is also \( \nu \)-representable with a model given by \( F_\lambda[n] \). The definition of the model is given in section 6. The relevance of this \( \varepsilon \)-vicinity for a general Kohn–Sham scheme is discussed in section 8.

2. The setup of the problem

We consider a static state of a material. The number of electrons \( N \) is fixed to be a finite integer. We apply the Born–Oppenheimer approximation (BOA), in which the motion of nuclei is separated from the motion of electrons. To find a stable state, we consider a classical state of nuclei and fix the coordinates of nuclei, whose number is \( M \). The motion of the electron system is determined for this classical configuration of nuclei, which gives a static electric potential for electrons.

Let \( |0\rangle \) be the electron vacuum. The electronic state in an external scalar potential is symbolically written by a state vector \( |\Psi\rangle \). This electron state is described by Fermion field operators \( \psi_\sigma^\dagger(\mathbf{r}) \) and \( \psi_\sigma(\mathbf{r}) \). Here, \( \psi_\sigma^\dagger(\mathbf{r}) \) creates (\( \psi_\sigma(\mathbf{r}) \) annihilates) an electron with the spin \( \sigma = \pm 1 \) at a position \( \mathbf{r} \in \mathbb{R}^3 \). Thus, \( \psi_\sigma(\mathbf{r})|0\rangle = 0 \). These operators satisfy the canonical anti-commutation relations as

\[
[\psi_\sigma^\dagger(\mathbf{r}), \psi_\sigma(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}')\delta_{\sigma,\sigma'}.
\]

Considering a position basis \( |\{\mathbf{r}_i, \sigma_i\}\rangle = \prod_{i=1}^N \psi_\sigma^\dagger(\mathbf{r}_i)|0\rangle \), we have a wavefunction as an inner product between this position vector and \( |\Psi\rangle \):

\[
\Psi(|\{\mathbf{r}_i, \sigma_i\}\rangle) = \langle |\{\mathbf{r}_i, \sigma_i\}| |\Psi\rangle.
\]  

(1)

The number operator \( \hat{n}(\mathbf{r}) \) probing existence of an electron at a point \( \mathbf{r} \) is defined as

\[
\hat{n}(\mathbf{r}) \equiv \sum_\sigma \psi_\sigma^\dagger(\mathbf{r})\psi_\sigma(\mathbf{r}),
\]

(2)
while the density of $|\Psi\rangle$ is given as $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$. The kinetic energy operator $\hat{T}$ for electrons is assumed to be

$$
\hat{T} = -\frac{\hbar^2}{2m} \int d^3r \sum_\sigma \lim_{\mathbf{r}' \to \mathbf{r}} \psi_\sigma^\dagger(\mathbf{r}') \Delta_r \psi_\sigma(\mathbf{r}),
$$

with the electron mass $m$.

Owing to BOA, we have an external scalar potential $v_{\text{ext}}(\mathbf{r})$ given by the charge of nuclei. Using position vectors $\mathbf{R}_I$ ($I = 1, \ldots, M$) of fixed nuclei, the potential $v_{\text{ext}}(\mathbf{r})$ is given as

$$
v_{\text{ext}}(\mathbf{r}) = -\sum_{I=1}^M \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}|},
$$

Here, the charge of the $I$th nucleus is $Z_I e$. The potential term for the Hamiltonian of electrons is given by the next operator:

$$
\hat{V}_{\text{ext}} = \int d^3r v_{\text{ext}}(\mathbf{r}) \hat{n}(\mathbf{r}).
$$

In the following discussion, we omit a constant Coulomb energy coming from the ion–ion interaction

$$
\hat{V}_{ii} = \sum_{\langle I,J \rangle} Z_I Z_J e^2 |\mathbf{R}_I - \mathbf{R}_J|,
$$

although this term is important for the charge neutrality condition. Hereafter, the symbol $\langle I, J \rangle$ denotes a pair of two different integers ranging from 1 to a finite integer (here it is $M$), and the summation with respect to these pairs are written as $\sum_{\langle I,J \rangle}$.

If we have more than two electrons, the electron–electron interaction always takes place. In a static state, the inter-electron interaction is described by the next operator:

$$
\hat{V}_{ee} = \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \sum_{\sigma,\sigma'} \psi_\sigma^\dagger(\mathbf{r}) \psi_\sigma^\dagger(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r})
$$

$$
= \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} : \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') :.
$$

The symbol $: O :$ for an operator $O$ denotes the normal ordering of the field operators. In $: O :$, the order of $\psi$ and $\psi^\dagger$ is reorganized so that the creation operators come to the left of the annihilation operators by interchanging operators. If interchange of two field operators is made $m$ times, the sign of $(-1)^m$ is multiplied to the reordered operator.

We consider an isolated electron system having $N \geq 2$ in an equilibrium. Competition between the Coulomb interaction $\hat{V}_{ee}$ and other single-particle parts, $\hat{T} + \hat{V}_{\text{ext}}$, causes various phase transitions in the electron systems. We search for the minimum energy allowed for the electron system. Thus, any state vector, which has an anti-symmetric property for the spin-$1/2$ Fermion system, has to be normalizable and has to have a finite kinetic energy. Thus, wavefunctions for the allowed state vectors has a form classified in $H^1(\mathbb{R}^{3N})$. For a function $f((\mathbf{r}_i))$ ($i = 1, \ldots, N$), a $p$-norm is defined by

$$
||f||_p = \left( \int_1^N \prod_{i=1}^N d^3r_i |f((\mathbf{r}_i)))|^p \right)^{1/p}.
$$

A complex function $f$ in $H^1(\mathbb{R}^{3N})$ has a finite 2-norm and $\nabla_i f$ is also square measurable, i.e. $\sum_i \int \prod_{j \neq i} d^3r_j \nabla_i f^* \cdot \nabla_i f < \infty$. Thus, $f \in H^1(\mathbb{R}^n)$ is $f \in L^2(\mathbb{R}^n)$ and $\nabla_i f \in L^2(\mathbb{R}^n)$ for
an integer \( n \). Besides, as a Fermion wavefunction, \( \Psi ([r_i, \sigma_i]) \) is anti-symmetric when two coordinates \( (r_i, \sigma_i) \) and \( (r_j, \sigma_j) \) are interchanged.

For any state vector \( |\Psi\rangle \) of an \( N \) electron state with \( N \geq 2 \), we have \( |\Psi\rangle \equiv \psi_{\sigma_1}^*(\mathbf{r}_1)\psi_{\sigma_2}^*(\mathbf{r}_2)|\Psi\rangle \), and the quantum state \( |\Psi\rangle \) has a positive semidefinite norm \( |\Psi\rangle : \hat{\Psi}(\mathbf{r}_1)\hat{\Psi}(\mathbf{r}_2) : |\Psi\rangle = \langle \Psi|\Psi\rangle \geq 0 \). If we assume that \( \langle \Psi|\hat{V}_{\text{ee}}|\Psi\rangle = 0 \), positivity of the Coulomb kernel requires that \( \forall \mathbf{r} \) and \( \forall \mathbf{r}' \), \( \langle \Psi|\hat{\Psi}(\mathbf{r})\hat{\Psi}(\mathbf{r}') : |\Psi\rangle = 0 \). But then we have zero of the integral

\[
\int d^3\mathbf{r} d^3\mathbf{r}'\langle \Psi|\hat{\Psi}(\mathbf{r})\hat{\Psi}(\mathbf{r}') : |\Psi\rangle = \frac{N(N - 1)}{2} = 0,
\]

which yields \( N = 0 \) or \( N = 1 \).

The expectation value of \( \hat{V}_{\text{ee}} \) by \( \Psi \in H^1(\mathbb{R}^3) \) is known to be finite [7], which is shown using three inequalities: the Hölder, Sobolev and triangular inequality. Actually, the Hölder inequality for \( f \in L^p(\mathbb{R}^n) \) and \( g \in L^q(\mathbb{R}^n) \), with two indices \( p, q \) satisfying \( 1/p + 1/q = 1 \) and \( 1 \leq p \leq \infty \), is written as

\[
\left| \int d^n\mathbf{r} f|g| \right| \leq \int d^n\mathbf{r}|f||g| \leq ||f||_p ||g||_q.
\]

The Sobolev inequality for a function \( h \in L^2(\mathbb{R}^3) \) with \( \nabla h \in L^2(\mathbb{R}^3) \) is written as

\[
||\nabla h||^2_2 \geq 3 \left( \frac{\pi}{2} \right)^{4/3} ||h||^2_6.
\]

Then, using three inequalities, the finiteness of the kinetic energy expectation value of \( \Psi \) shows that

\[
\langle \Psi|\hat{V}_{\text{ee}}|\Psi\rangle = \sum_{(i,j)} \prod_{i=1}^{N} \int d^3\mathbf{r}_i \sum_{\sigma_i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi^*(\mathbf{r}_i, \sigma_i)\Psi(\mathbf{r}_j, \sigma_j)
\]

\[
= \sum_{(i,j)} \prod_{i=1}^{N} \int d^3\mathbf{r}_i \sum_{\sigma_i} \frac{e^2\theta(|\mathbf{r}_i|) + e^2[1 - \theta(|\mathbf{r}_i|)]}{|\mathbf{r}_i|} |\Psi^*(\mathbf{r}_i, \sigma_i)|^2
\]

\[
\leq \sum_{(i,j)} \left\{ \prod_{i=1}^{N} \int d^3\mathbf{r}_i \sum_{\sigma_i} \frac{e^2\theta(|\mathbf{r}_i|)}{|\mathbf{r}_i|} |\Psi(\mathbf{r}_i, \sigma_i)|^2
\]

\[
+ \prod_{i=1}^{N} \int d^3\mathbf{r}_i \sum_{\sigma_i} e^2[1 - \theta(|\mathbf{r}_i|)] |\Psi(\mathbf{r}_i, \sigma_i)|^2 \right\}
\]

\[
\leq e^2(N - 1) \sum_{\mathbf{r}_i} \left\{ \left( \frac{2^4}{3\pi^2} \right)^{1/3} ||\nabla\Psi||^2_2 + ||\Psi||^2_2 \right\} < \infty.
\]

Here, we write \( \mathbf{r}_1 - \mathbf{r}_j = \mathbf{r}_ij \) and \( \theta(x) = 1 \) if \( |x| \leq 1 \), \( \theta(x) = 0 \) if \( |x| > 1 \). In equation (11), we use a symbol for the 2-norm as \( ||\Psi||^2_2 = \int \prod_{i=1}^{N} d^3\mathbf{r}_i \sum_{\sigma_i} |\Psi(\mathbf{r}_i, \sigma_i)|^2 \). We considered that \( \Psi([\mathbf{r}_i, \sigma_i]) \) is a Fermionic anti-symmetric function and \( (\nabla\Psi)^2 \leq |\nabla\Psi|^2 \). Thus, for \( N \geq 2 \), we have

\[
0 < \langle \Psi|\hat{V}_{\text{ee}}|\Psi\rangle < \infty.
\]

3. The charge density being the primary order parameter

The electron system is characterized by the electron charge density \( n_{\Psi}(\mathbf{r}) \equiv \langle \Psi|\hat{\Psi}(\mathbf{r})|\Psi\rangle \). This physical quantity is observable by x-ray diffraction measurements. Since the wavefunction \( \Psi([\mathbf{r}_i, \sigma_i]) \) is given as a function in the space \( L^2 \) of integrable functions, and since we assume
that the kinetic energy is finite for $\Psi$, $n_{\Psi}(\mathbf{r})^{1/2}$ and $\nabla n_{\Psi}(\mathbf{r})^{1/2}$ are in $L^{2}$. Then, $n_{\Psi}(\mathbf{r})$ is also known to be in $L^{3}$ [7]. The space $L^{3/2} + L^{\infty}$ is a dual of the $L^{1} + L^{3}$ space. Since the Coulomb potential is in $L^{3/2} + L^{\infty}$, $v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r})$ is integrable.

The Hamiltonian of this electron system is given as

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}.$$  \hspace{1cm} (13)

The total energy $E[\Psi, v_{\text{ext}}]$ of this electron system is given by

$$E[\Psi, v_{\text{ext}}] \equiv \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} | \Psi \rangle + \int d^{3}r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}).$$  \hspace{1cm} (14)

The lowest steady state is given by minimizing this energy in the space of wavefunctions:

$$E_{0}[v_{\text{ext}}] = \min_{\Psi} E[\Psi, v_{\text{ext}}] = \min_{\Psi} \left[ \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} | \Psi \rangle + \int d^{3}r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right]. \hspace{1cm} (15)$$

A definition of the order parameter is given by a derivative of the total energy with respect to the external field. For the electron system, this external degree of freedom is given by $v_{\text{ext}}(\mathbf{r})$. Let us consider a stable electronic state $|\Psi\rangle$ without degeneracy. We may assume that $\langle \Psi | \Psi \rangle = 1$. This state has an energy $E_{0}[v_{\text{ext}}] = \langle \Psi | \hat{H} | \Psi \rangle$. If an infinitesimal variation of $v_{\text{ext}}(\mathbf{r})$ is given in $L^{3/2} + L^{\infty}$, the wavefunction minimizing $E[\Psi, v_{\text{ext}} + \delta v_{\text{ext}}]$ exists. This minimizing wavefunction may be given as

$$|\Psi + \delta \Psi \rangle = e^{\delta \hat{H}} (|\Psi\rangle + |\delta \Psi \rangle).$$

A complex phase factor $e^{i\phi}$ represents a gauge degree of freedom. We also use the notation

$$\delta \hat{H} = \int d^{3}r \delta v_{\text{ext}}(\mathbf{r}) \hat{h}(\mathbf{r}).$$  \hspace{1cm} (16)

When $||\delta v_{\text{ext}}|| = \delta \to 0$, the norm of $|\delta \Psi \rangle$ goes to zero, and $\langle \delta \Psi | \delta \Psi \rangle = O(\delta^{2})$. The state $|\delta \Psi \rangle$ may be chosen to be orthogonal to $|\Psi\rangle$ so that $\langle \Psi | \delta \Psi \rangle = 0$. We note that

$$\hat{H}|\Psi\rangle = E_{0}[v_{\text{ext}}]|\Psi\rangle,$$

$$\langle \hat{H} + \delta \hat{H} | \Psi + \delta \Psi \rangle = E_{0}[v_{\text{ext}} + \delta v_{\text{ext}}]|\Psi + \delta \Psi \rangle.$$ Multiplying $\langle \Psi |$ to the above equation from the left, we have

$$E_{0}[v_{\text{ext}} + \delta v_{\text{ext}}] = \frac{\langle \Psi | \hat{H} + \delta \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle}.$$  \hspace{1cm} (17)

Similarly, we also have

$$E_{0}[v_{\text{ext}}] = \frac{\langle \Psi + \delta \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi + \delta \Psi | \Psi + \delta \Psi \rangle} = \frac{\langle \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle} = \frac{\langle \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle}.$$  \hspace{1cm} (18)

Then, we have a derivative of $E_{0}[v_{\text{ext}}]$:

$$E_{0}[v_{\text{ext}} + \delta v_{\text{ext}}] - E_{0}[v_{\text{ext}}]$$

$$= \frac{\langle \Psi | \hat{H} + \delta \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle} - \frac{\langle \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle} = \frac{\langle \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle} - \frac{\langle \Psi | \hat{H} | \Psi + \delta \Psi \rangle}{\langle \Psi | \Psi + \delta \Psi \rangle}$$

$$= \langle \Psi | \delta \hat{H} | \Psi \rangle + \langle \Psi | \delta \hat{H} | \delta \Psi \rangle + \langle \Psi | \delta \hat{H} | \delta \Psi \rangle = O(\delta^{2})$$

$$= \int d^{3}r \delta v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) + O(\delta^{2}) = \int d^{3}r \frac{\delta^{2}E_{0}[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})} \delta v_{\text{ext}}(\mathbf{r}) + O(\delta^{2}).$$  \hspace{1cm} (17)

This derivation follows a proof of the force theorem by Parr [15].

For the Hamiltonian, equation (13), in the BOA, $v_{\text{ext}}(\mathbf{r})$ behaves as a unique external field. The coefficient of the functional derivative $\frac{\delta E_{0}[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})} = n_{\Psi}(\mathbf{r})$ is the primary order parameter of the electron system.
When $\delta v_{\text{ext}}(r)$ is introduced, if we have a jump in $n/\Psi_1(r)$, a level crossing in the lowest energy state $|\Psi_1\rangle$ occurs. This is regarded as a first-order ground-state phase transition. In such a special point, only the directed derivatives may be defined. However, this jump is detected as a jump in the charge density. In this sense, the electron charge density, which is shown to be a directed derivative of the energy functional $E_0[v_{\text{ext}}]$, is regarded as the primary order parameter.

In section 5, we will define another first-order phase transition without a jump in $n(r)$. This transition can occur in electron systems owing to internal degrees of freedom, e.g. the electron spin. The transition without change in $n(r)$ can occur much frequently, when the interaction strength or the form of the inter-particle interaction are modified. Once the interaction strength is shifted from that of the Coulomb interaction, the resulting Hamiltonian describes a model system. The model can be identical to the Kohn–Sham model [2]. Thus, for the analysis of the Kohn–Sham scheme, it is important to analyze these second-type phase transitions in an abstract model space.

4. The density functional theory as a Landau theory

To define the universal energy density functional, a Sobolev space $\mathcal{I}_N$ of functions in $\mathbb{R}^3$ was introduced in DFT. For a function $n(r)$ in the set $\mathcal{I}_N$, $n(r) \geq 0$ and $n^{1/2}(r)$ is square integrable. Its gradient $\nabla n^{1/2}(r)$ is also square integrable. In addition, $n(r)$ satisfies

$$\int d^3r n(r) = N. \quad (18)$$

We use the theorem 3.3 of [7] stating that if $n(r) \in \mathcal{I}_N$, $F[n]$ given by the next definition exists:

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle. \quad (19)$$

The symbol $\Psi \to n$ represents that a minimizing state $|\Psi\rangle$ is searched with a constraint $\langle \Psi | \hat{n}(r) | \Psi \rangle = n(r)$. Then, the existence of the minimizing $\Psi$ is relevant.

We have the next constrained minimization process

$$E_0[v_{\text{ext}}] = \min_{n} \min_{\Psi \to n} E[\Psi, v_{\text{ext}}] = \min_{n} \left[ F[n] + \int d^3r v_{\text{ext}}(r)n(r) \right]. \quad (20)$$

Here, $F[n]$ behaves as a free energy of the electron system.

If we have a well-defined description of the free energy of the system as a functional of the primary order parameter, we have a complete expression of the Landau free energy. DFT actually gives an example. In an $N$-representable form of the energy density functional, the Landau free energy of the system is given as a summation of the so-called universal energy density functional and the energy of the external scalar potential. The latter, $\int d^3r v_{\text{ext}}(r)n(r)$, is linear in the order parameter.

5. The $\lambda$ modified functional

Let $\lambda$ be a real parameter in $[0, 1]$. We now consider a reduced energy density functional $E_\lambda[n]$ defined by

$$E_\lambda[n] = \min_{\Psi \to n} \langle \Psi' | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi' \rangle. \quad (21)$$

Existence of the minimizing $\Psi'$ is also given by theorem 3.3 of [7]. We would like to address a next statement.
Theorem 1. If \( 0 \leq \lambda \leq 1 \), and if \( n(r) \in \mathcal{I}_N \), \( F_\lambda[n] \) is a monotone increasing continuous function of \( \lambda \). \( F_\lambda[n] \) is concave as a function of \( \lambda \).

First, choose \( 0 \leq \lambda_1 < \lambda_2 \leq 1 \). Assume that \( F_{\lambda_1}[n] \geq F_{\lambda_2}[n] \). Choose a minimizing state \( |\Psi_0\rangle \rightarrow n \) of the expectation value \( \langle \Psi' | \hat{T} + \lambda_2 \hat{V}_{\text{ee}} | \Psi' \rangle \). Then, we have

\[
F_{\lambda_1}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda_1 \hat{V}_{\text{ee}} | \Psi \rangle \\
\geq \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda_2 \hat{V}_{\text{ee}} | \Psi \rangle = \langle \Psi_0 | \hat{T} + \lambda_2 \hat{V}_{\text{ee}} | \Psi_0 \rangle \\
= \langle \Psi_0 | \hat{T} + \lambda_1 \hat{V}_{\text{ee}} | \Psi_0 \rangle + (\lambda_2 - \lambda_1) \times \langle \Psi_0 | \hat{V}_{\text{ee}} | \Psi_0 \rangle \\
> \langle \Psi_0 | \hat{T} + \lambda_1 \hat{V}_{\text{ee}} | \Psi_0 \rangle.
\]

This inequality contradicts the definition of \( F_{\lambda_2}[n] \). Thus, \( F_{\lambda_2}[n] \) is a monotone increasing function of \( \lambda \). Next, assume that \( F_{\lambda}[n] \) is not continuous when \( \lambda = \lambda_0 \geq 0 \). This is equivalent to the statement that \( \exists \epsilon > 0, \forall \delta > 0, \exists \lambda > 0 \), such that \( |\lambda - \lambda_0| < \delta \) and \( |F_{\lambda}[n] - F_{\lambda_0}[n]| > \epsilon \).

For simplicity, let us further assume that \( 0 < \lambda - \lambda_0 < \delta \) and then \( F_{\lambda}[n] - F_{\lambda_0}[n] > \epsilon \). If \( n(r) \in \mathcal{I}_N \), for any minimizing state vector \( |\Psi_0\rangle \) of \( F_{\lambda_0}[n] \), the wavefunction of \( \Psi_0 \rightarrow n(r) \) is in \( H_0 \), and

\[
0 < \langle \Psi_0 | \hat{V}_{\text{ee}} | \Psi_0 \rangle < \exists C_0 < \infty.
\]

If we let \( \delta = \epsilon/(2C_0) \), we have

\[
\min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi \rangle > \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda_0 \hat{V}_{\text{ee}} | \Psi \rangle + \epsilon \\
= \langle \Psi_0 | \hat{T} + \lambda_0 \hat{V}_{\text{ee}} | \Psi_0 \rangle + \epsilon \\
\geq \langle \Psi_0 | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi_0 \rangle + (\lambda_0 - \lambda)C_0 + \epsilon \\
> \langle \Psi_0 | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi_0 \rangle - \delta C_0 + \epsilon \\
= \langle \Psi_0 | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi_0 \rangle + \frac{\epsilon}{2}.
\]

This inequality contradicts the definition of the minimum.

Consider \( 0 \leq \lambda_1 < \lambda_2 \leq 1 \), \( 0 < \xi < 1 \), and \( \lambda_\xi \equiv \xi \lambda_1 + (1-\xi)\lambda_2 \). We call a state \( \Psi_{\lambda_\xi} \rightarrow n(r) \), which minimizes \( \langle \Psi | \hat{T} + \lambda_\xi \hat{V}_{\text{ee}} | \Psi \rangle \). Then, we have

\[
F_{\lambda_\xi[1+\xi]}[n] = \xi \langle \Psi_{\lambda_1} | \hat{T} + \lambda_1 \hat{V}_{\text{ee}} | \Psi_{\lambda_1} \rangle + (1-\xi) \langle \Psi_{\lambda_2} | \hat{T} + \lambda_2 \hat{V}_{\text{ee}} | \Psi_{\lambda_2} \rangle \\
\geq \xi F_{\lambda_1}[n] + (1-\xi) F_{\lambda_2}[n].
\]

This inequality ensures concavity of \( F_{\lambda}[n] \) as a function of \( \lambda \).

Following knowledge on the monotone increasing continuous functions and the convex (concave) functions, we immediately obtain results on derivatives and an integral of the derivative [16]. Let us define Dini’s derivatives of \( F_{\lambda}[n] \):

\[
\begin{align*}
D^- (\lambda) &= \lim_{y \rightarrow 0^-} \sup_{y < h < 0} \frac{F_{\lambda+h}[n] - F_\lambda[n]}{h}, \\
D_+ (\lambda) &= \lim_{y \rightarrow 0^+} \inf_{0 < h < y} \frac{F_{\lambda+h}[n] - F_\lambda[n]}{h}.
\end{align*}
\]

When \( \lambda = 1 \), we formally define \( D_+ (\lambda) \) by considering \( F_1[n] \) for \( \lambda > 1 \). In practical simulation, however, \( D_+ (\lambda) \) is not required at \( \lambda = 1 \).

Corollary 2. For \( n(r) \in \mathcal{I}_N \), the monotone increasing concave function \( F_{\lambda}[n] \) of \( \lambda \) has a directed derivative at \( \forall \lambda \in (0, 1] \) and \( D^- (\lambda) \geq D_+ (\lambda) \).
When $D^-(\lambda) = D_\lambda(\lambda)$, we have the derivative $\frac{d}{d\lambda} F_\lambda[n]$ of the monotone increasing function of $F_\lambda[n]$. The differentiability of a monotone increasing function is given by Lebesgue. Besides, the next statement holds.

**Corollary 3.** If $0 \leq \lambda \leq 1$, for $n(r) \in \mathcal{I}_N$, $F_\lambda[n]$ is differentiable a.e. The derivative $\frac{d}{d\lambda} F_\lambda[n]$ is integrable in $[0, 1]$.

Next, consider the case with $N \geq 2$. A set of state vectors $|\Psi\rangle$ reproducing $n(r)$ is denoted as $Q_n$. Fix $\lambda \in (0, 1]$. We consider a subset of $|\Psi\rangle \in Q_n$ minimizing $\langle \Psi|T + \lambda \hat{V}_{ee}|\Psi\rangle$ and call it $P_n(\lambda)$. For any $|\Psi\rangle \in P_n(\lambda)$, $0 < \langle \Psi|\hat{V}_{ee}|\Psi\rangle < \infty$. Thus, we have a finite range including values of $\langle \Psi|\hat{V}_{ee}|\Psi\rangle$ for $|\Psi\rangle \in P_n(\lambda)$. The maximum of this range is given by a state vector in $P_n(\lambda)$ and the minimum is given by another vector. They might be different with each other. Thus, they are denoted as $|\Psi^-\rangle \in P_n(\lambda)$ and $|\Psi^+\rangle \in P_n(\lambda)$. The very definitions of $P_n(\lambda)$ and these vectors ensure that

$$F_\lambda[n] = \langle \Psi^-|\hat{T} + \lambda \hat{V}_{ee}|\Psi^-\rangle = \langle \Psi^+|\hat{T} + \lambda \hat{V}_{ee}|\Psi^+\rangle$$

and that

$$\langle \Psi^+|\hat{V}_{ee}|\Psi^+\rangle \leq \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle.$$  

Now we prove the existence of a vector giving the directed derivative of $F_\lambda[n]$.

**Lemma 4.** For $\lambda \in (0, 1]$, we have $D_\lambda(\lambda) = \langle \Psi^+|\hat{V}_{ee}|\Psi^+\rangle$ and $D^-(\lambda) = \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle$.

For $0 < \lambda < \lambda' = \lambda - \delta < \lambda$ and

$$F_\lambda[n] \leq \langle \Psi^-|\hat{T} + \lambda' \hat{V}_{ee}|\Psi^-\rangle = \langle \Psi^-|\hat{T} + \lambda \hat{V}_{ee}|\Psi^-\rangle - \delta \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle$$

$$\leq \langle \Psi^+|\hat{T} + \lambda \hat{V}_{ee}|\Psi^+\rangle - \delta \langle \Psi^+|\hat{V}_{ee}|\Psi^+\rangle = \langle \Psi^+|\hat{T} + \lambda \hat{V}_{ee}|\Psi^+\rangle.$$  

Thus,

$$D^-(\lambda) = \lim_{\lambda' \rightarrow 0^+} \sup_{0 < \delta < \lambda} \frac{F_\lambda[n] - F_{\lambda-h}[n]}{h}$$

$$\geq \lim_{\lambda' \rightarrow 0^+} \sup_{0 < \delta < \lambda} \frac{F_\lambda[n] - \langle \Psi^-|\hat{T} + \lambda \hat{V}_{ee}|\Psi^-\rangle + \delta \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle}{h}$$

$$= \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle.$$  

Similarly, we have

$$D_\lambda(\lambda) \leq \langle \Psi^+|\hat{V}_{ee}|\Psi^+\rangle.$$

These inequalities together with equation (28) give just another proof of corollary 2.

Let us assume that $D^-(\lambda) > \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle$. Then, we have

$$0 < \lim_{\lambda' \rightarrow 0^+} \sup_{0 < \delta < \lambda} \frac{F_\lambda[n] - F_{\lambda-h}[n] - \delta \langle \Psi^-|\hat{V}_{ee}|\Psi^-\rangle}{h}$$

$$= \lim_{\lambda' \rightarrow 0^+} \sup_{0 < \delta < \lambda} \frac{\langle \Psi^-|\hat{T} + \lambda \hat{V}_{ee}|\Psi^-\rangle - F_{\lambda-h}[n]}{h}.$$  

Independently, we have a next inequality by the definition of $F_{\lambda-h}[n]$:

$$\langle \Psi^+|\hat{T} + (\lambda - h) \hat{V}_{ee}|\Psi^+\rangle \geq F_{\lambda-h}[n],$$

which yields $\forall h \in [0, y]$:
\[ f(h) \equiv \langle \Psi^-_\lambda | \hat{T} + (\lambda - h) \hat{V}_{ee} | \Psi^-_\lambda \rangle - F_{\lambda-h}[n] \geq 0. \]  

(34)

By equation (27), \( f(0) = 0 \).

We show that \( f(h)/h \) is also a monotone increasing function. Actually, if we assume that \( 0 < D\kappa_0 < y \), and that \( \frac{D\kappa_0}{y} > \frac{D\kappa_0}{y} \), we have a next inequality

\[
1 - \frac{D\kappa_0}{y} F_2[n] + \frac{D\kappa_0}{y} F_{\lambda-\gamma}[n] > F_{\lambda-h_0}[n].
\]

This contradicts the concavity of \( F_\gamma[n] \) given by equation (24). Thus, equation (32) shows that

\[
0 < \lim_{y \rightarrow 0^+} \frac{\langle \Psi^-_\lambda | \hat{T} + (\lambda - y) \hat{V}_{ee} | \Psi^-_\lambda \rangle - F_{\lambda-\gamma}[n]}{y}.
\]

(35)

We call a state vector, which is in \( \mathcal{P}_n(\lambda - y) \) and maximizes the expectation value of \( \hat{V}_{ee}, \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle \). Then the above expression yields

\[
\lim_{y \rightarrow 0^+} \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle > \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle + \lim_{y \rightarrow 0^+} \frac{1}{y} [\langle \Psi^-_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi^-_\lambda \rangle - \langle \Psi^-_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi^-_\lambda \rangle]
\]

(36)

We note that \( \lim_{y \rightarrow 0^+} \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle \) exists. The continuity of \( F_\gamma[n] \) ensures that \( \lim_{y \rightarrow 0^+} \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle \in \mathcal{P}_\lambda(\lambda) \). The inequality, equation (36), contradicts the definition of \( \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle \). Thus, we conclude that \( D^- (\lambda) = \langle \Psi^-_\lambda | \hat{V}_{ee} | \Psi^-_\lambda \rangle \). Similarly, \( D_\lambda(\lambda) = \langle \Psi^+_\lambda | \hat{V}_{ee} | \Psi^+_\lambda \rangle \).

For a fixed \( n(\gamma) \), we now analyze the number of discontinuous points, where \( D(\lambda) \equiv D^-(\lambda) - D_\lambda(\lambda) > 0 \). Lemma 4 shows that when \( D(\lambda) > 0 \), \( \mathcal{P}_\lambda(\lambda) \) has multiple elements which are distinguished by difference in the expectation value of \( \hat{V}_{ee} \) and also in the expectation value of \( \hat{T} \). At this discontinuous point, we have a change in the minimizing state from \( \langle \Psi^+_\lambda | \rangle \) to \( \langle \Psi^-_\lambda | \rangle \) by reducing \( \lambda \). Therefore, we have the next definition.

**Definition 5.** A point where \( D(\lambda) > 0 \) is called a transition point in the model space.

We should note that a priori \( |\Psi^+_\lambda \rangle \) and \( |\Psi^-_\lambda \rangle \) are defined independently with each other. Lemma 4 implies that for a point with \( D(\lambda) = 0 \), we can identify \( |\Psi^+_\lambda \rangle \) with \( |\Psi^-_\lambda \rangle \) and replace one with the other. Thus the point with \( D(\lambda) = 0 \) is not a level crossing point.

**Theorem 6.** (i) In \( [0, 1] \), we have at most a finite number of transition points, where \( F_\gamma[n] \) has a finite discontinuity, which is greater than an arbitrary small number \( \epsilon \). (ii) At an accumulation point of the discontinuous points \( D(\lambda_i) \) \( i = 1, 2, \ldots, \infty \) with \( \lambda_i \in (0, 1) \), and \( \lambda_i < \lambda_{i+1} \), we have \( D(\lambda_i) \rightarrow 0 \) for \( i \rightarrow \infty \).

(i) For any finite number \( \epsilon > 0 \), we have a set \( \Lambda(\epsilon) \) of discontinuous points, at which \( D(\lambda) > \epsilon \). Assume that the number of elements of \( \Lambda(\epsilon) \) is more than the countable infinite. We can select a countable infinite subset of \( \Lambda(\epsilon) \) and name it \( \hat{\Lambda}(\epsilon) \). Points in \( \hat{\Lambda}(\epsilon) \) are in \( [0, 1] \) and are to be ordered as \( \lambda_i < \lambda_{i+1} \). This is due to the selection axiom. Let us number the points in \( \hat{\Lambda}(\epsilon) \) as \( \lambda_i \) \( i = 1, 2, \ldots \). We have

\[
D_\lambda(\lambda_i) < D^-(\lambda_i) \leq D_\lambda(\lambda_{j-1}) < D^-(\lambda_{j-1}),
\]

\[
D_\lambda(\lambda_j) < D^- (\lambda_j) - \epsilon < D^-(\lambda_{j-1}) - 2\epsilon < D^-(\lambda_1) - j\epsilon.
\]

Since the set \( \hat{\Lambda}(\epsilon) \) is infinite, we have an integer \( J > D^-(\lambda_1)/\epsilon \) for which the derivative \( D_\lambda(\lambda_j) \) becomes strictly negative. This result contradicts to the increasing property of \( F_\gamma[n] \). Thus, the set \( \Lambda(\epsilon) \) has to be a finite set.
We can show two conditions on the minimizing
Here, we used a notation for the charge density given by
10
\[ J. Phys. A: Math. Theor. \textbf{44} (2011) 135305 \]
K Kusakabe and I Maruyama

(ii) We consider \( \inf_i D(\lambda_i) \) for \( i = 1, 2, \ldots \). Owing to (i), a finite non-zero infimum is

denied. Now consider \( D = \lim_{N \to \infty} \sup_{\lambda_i N} D(\lambda_i) \). Assume that \( D > 0 \). Then, we can
find an integer \( l_1 \), for which \( D(\lambda_{l_1}) \geq D \). But we can also find another integer \( l_2 > l_1 \) for
which \( D(\lambda_{l_2}) \geq D \), because of the definition of \( D \). Then we have an infinite series of \( \lambda_i \)
(\( i = 1, 2, \ldots \)) with \( D(\lambda_i) \geq D > 0 \), which contradicts (i). Thus, \( D = 0 \).

\[ \square \]

Lemma 7. For \( n(\mathbf{r}) \in \mathcal{I}_N \), the function \( \frac{d}{d\lambda} F_\lambda[n] \) of \( \lambda \) is Lipschitz continuous in \([0, 1]\) and we have

\[ \int_0^1 d\lambda \frac{d}{d\lambda} F_\lambda[n_{\Psi}] = F_{\lambda_{01}}[n] - F_{\lambda_{00}}[n]. \]  

(37)

For \( \forall \Psi \in H^1 \), we have a finite \( R \) satisfying \( \langle \Psi|H_{\text{ext}}|\Psi \rangle \leq R \). Choose \( R \) such that \( D(0) \leq R \). Since \( F_\lambda[n] \) is continuous monotone increasing and concave, for

\[ 0 \leq \lambda_1 < \lambda_2 \leq 1 \], we have

\[ 0 \leq F_{\lambda_2}[n] - F_{\lambda_1}[n] \leq D(\lambda_2 - \lambda_1) \leq D(\lambda_2 - \lambda_1) \leq R(\lambda_2 - \lambda_1). \]  

(38)

Thus, we have equation (37).

\[ \square \]

6. The Kohn–Sham minimization scheme

To discuss the relevance of our theorems for the discussion of ground-state phase transitions, we introduce a Kohn–Sham minimization scheme [13, 17]. For an external potential \( v_{\text{ext}}(\mathbf{r}) \), we have a ground state of the Coulomb system, \(|\Psi_{\text{GS}}\rangle\), which gives a ground-state density, \( n_{\text{GS}}(\mathbf{r}) \). First, we have a next equality

\[ E_0[v_{\text{ext}}] = \langle \Psi_{\text{GS}}|\hat{T} + \hat{V}_{\text{ex}}|\Psi_{\text{GS}} \rangle + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\text{GS}}(\mathbf{r}) \]

\[ = \min_n \left[ F[n] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right] \]

\[ = \min_n \left[ \min_{\Psi \rightarrow n} \left\{ \langle \Psi|\hat{T}|\Psi \rangle + \int d^3 r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\} + \int d^3 r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right] \]

\[ = \min_{\Psi} \left[ \langle \Psi|\hat{T}|\Psi \rangle + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right] \]

\[ \leq \min_{\Psi} G_{0,v_{\text{ext}}}[\Psi]. \]  

(39)

Here, we used a notation for the charge density given by \(|\Psi\rangle\) as

\[ n_{\Psi}(\mathbf{r}) \equiv \langle \Psi|\hat{n}(\mathbf{r})|\Psi \rangle. \]  

(40)

We can show two conditions on the minimizing \( \Psi \) of \( G_{0,v_{\text{ext}}}[\Psi] \). Note that

\[ G_{0,v_{\text{ext}}}[\Psi] = \langle \Psi|\hat{T}|\Psi \rangle + F_{\lambda_{01}}[n_{\Psi}] - F_{\lambda_{00}}[n_{\Psi}] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \].  

(41)

Then we have

\[ G_{0,v_{\text{ext}}}[\Psi] \geq \min_{\Psi \rightarrow n_{\Psi}} \left\{ \langle \Psi|\hat{T}|\Psi \rangle + F_{\lambda_{01}}[n_{\Psi}] - F_{\lambda_{00}}[n_{\Psi}] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right\} \]

\[ = F_{\lambda_{01}}[n_{\Psi}] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \]

\[ \geq F_{\lambda_{01}}[n_{\text{GS}}] + \int d^3 r v_{\text{ext}}(\mathbf{r}) n_{\text{GS}}(\mathbf{r}). \]  

(42)
We see that equalities in equation (42) are satisfied:

(i) if \( \Psi \) is identical to a state \( \Psi' \), which minimizes \( \langle \Psi' | \hat{T} | \Psi' \rangle \), with the constraint that \( \Psi' \rightarrow n_\Psi \), and

(ii) if \( n_\Psi \) is identical to the true ground-state charge density \( n_{\text{GS}}(r) \).

Thus, the minimizing process of \( G_{0,\text{ext}}[\Psi] \) gives us a state that reproduces \( n_{\text{GS}}(r) \) and minimizes \( \langle \Psi | \hat{T} | \Psi \rangle \). Two fundamental statements are addressed here.

(i) A minimizing state \( \Psi \) of \( G_{0,\text{ext}}[\Psi] \) is the state which is searched in the constrained minimization of \( F_{\lambda,\text{ext}}[n_{\text{GS}}] \). Thus, \( \Psi \) is the state motivated to be searched in the Kohn–Sham scheme.

(ii) We do not need to have a secular equation to define the minimization process of \( G_{0,\text{ext}}[\Psi] \) for our discussion.

The definition of \( G_{0,\text{ext}}[\Psi] \) suggests to us that we have plenty of models for electron systems. Actually, we have another equality:

\[
E_0[\text{ext}] = \min_\Psi G_{\lambda,\text{ext}}[\Psi].
\]  

(43)

\[ 
G_{\lambda,\text{ext}}[\Psi] = \langle \Psi | \hat{T} + \lambda V_{\text{ext}} | \Psi \rangle + \int \frac{d \lambda'}{d \lambda} F_{\lambda}[n_\Psi] + \int d^3 r v_{\text{ext}}(r)n_\Psi(r).
\]  

(44)

The wavefunction functional, \( G_{\lambda,\text{ext}}[\Psi] \), determines \( |\Psi_\lambda\rangle \), which may appear as a minimizing state in the definition of \( F_{\lambda}[n_{\text{GS}}] \). Therefore, when we fix \( v_{\text{ext}}(r) \), minimization of \( G_{\lambda,\text{ext}}[\Psi] \) with \( \lambda \in [0, 1] \) produces a set of states \( \{|\Psi_\lambda\rangle\} \) and thus the function \( F_{\lambda}[n_{\text{GS}}] \) of \( \lambda \) as

\[
F_{\lambda}[n_{\text{GS}}] = \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{\text{ext}} | \Psi_\lambda \rangle.
\]  

(45)

We may introduce the Hartree term to formulate a much familiar form in DFT:

\[
G_{0,\text{ext}}[\Psi] = \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} n_\Psi(r)n_\Psi(r') + \int d^3 r v_{\text{ext}}(r)n_\Psi(r)
\]

\[
+ \int_0^1 d \lambda' \left\{ \frac{d}{d \lambda} \min_{n_\Psi} \langle \Psi | \hat{T} + \lambda V_{\text{ext}} | \Psi \rangle - \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} n_\Psi(r)n_\Psi(r') \right\}
\]

\[
= \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} n_\Psi(r)n_\Psi(r') + \int d^3 r v_{\text{ext}}(r)n_\Psi(r)
\]

\[
+ \int_0^1 d \lambda' \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} \left\{ \langle \Psi_\lambda | : \hat{n}(r) \hat{n}(r') : | \Psi_\lambda \rangle - n_\Psi(r)n_\Psi(r') \right\}
\]

\[
= \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} n_\Psi(r)n_\Psi(r')
\]

\[
+ E_{\text{ext}}[n_\Psi] + \int d^3 r v_{\text{ext}}(r)n_\Psi(r).
\]  

(46)

Similarly, we have

\[
G_{\lambda,\text{ext}}[\Psi] = \langle \Psi | \hat{T} + \lambda \hat{V}_{\text{ext}} | \Psi \rangle + \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} n_\Psi(r)n_\Psi(r')
\]

\[
+ \int_0^1 d \lambda' \frac{1}{2} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} \left\{ \langle \Psi_\lambda | : \hat{n}(r) \hat{n}(r') : | \Psi_\lambda \rangle - n_\Psi(r)n_\Psi(r') \right\}
\]

\[
+ \int d^3 r v_{\text{ext}}(r)n_\Psi(r)
\]
\[ = \langle \psi | \hat{T} + \lambda \hat{V}_{\text{ee}} | \psi \rangle + \frac{1 - \lambda}{2} \int d^3r \ d^3r' \frac{e^2}{|r - r'|} n_{\psi}(r)n_{\psi}(r') \]
\[ + E_{\text{xc},\lambda}[n_{\psi}] + \int d^3r v_{\text{ee}}(r)n_{\psi}(r). \]  

We call \( G_{\lambda,\nu_{\text{ee}}}[\psi] \) the \( \lambda \)-parametrized model energy functional. All of these models can determine \( E_\lambda[v_{\text{ee}}] \) as shown in equation (43) via a determination of \( |\psi_\lambda\rangle \). The charge density of \( |\psi_\lambda\rangle \) satisfies \( n_{\psi}(r) = n_{\text{GS}}(r) \). When \( 0 < \lambda < 1 \), since a reduced-interaction \( \lambda \hat{V}_{\text{ee}} \) appears in the definition of \( G_{\lambda,\nu_{\text{ee}}}[\psi] \), its minimizing state, \( |\psi_\lambda\rangle \), is represented by a summation of Slater determinants.

7. Existence of \( \varepsilon \) vicinity

From now on, we consider possible level crossings in \( F_\lambda[n_{\text{GS}}] \) given in equation (45). A level crossing occurs, when two or more states appear as minimizing states \( |\psi_\lambda\rangle \) of \( \hat{T} + \lambda \hat{V}_{\text{ee}} \) and when a jump in Dini’s derivatives, \( D(\lambda) > 0 \), occurs.

Existence of the crossing points is exemplified by a phase transition from the normal state to a ferromagnetic state recognized in the uniform electron gas system [11, 14]. At the phase boundary, we have two uniform electron gas ground states, i.e. a paramagnetic state without spin polarization and a partially ferromagnetic state with a finite total spin. In general, we need to assume that crossing points appear at some of \( \lambda \in [0, 1] \). Once there appears a crossing point, we can count the number of crossing points on the \( \lambda \) axis.

First, we note that the level crossings happen at discretized points on the \( \lambda \) axis. Two statements of theorem 6 deny the possibility of having crossing points with \( D(\lambda) > 0 \) continuously or densely on the \( \lambda \) axis. Next we need to consider a case with countable infinite numbers of crossing points in a finite region of \( \lambda \). This case causes appearance of accumulation points of the crossing points on the \( \lambda \) axis.

Thus, we can choose a finite interval of \( \lambda \) satisfying one of two possible conditions for \( D(\lambda) \): (i) \( \forall \lambda \in (\lambda_a, \lambda_b) \), \( D(\lambda) = 0 \) or (ii) one of the boundaries \( \lambda_l \) \( (l = a \text{ or } b) \) is an accumulation point of \( D(\lambda_l) > 0 \) and \( \lim_{\lambda \to \infty} D(\lambda_l) = 0 \). Our concern is whether or not case (ii) occurs at \( \lambda_0 = 1 \) for a \( v \)-representable ground state density.

Consider a unique ground state \( |\psi_{\text{GS}}\rangle \) of an electron system in the external potential \( v_{\text{ee}}(r) \), which has an electron charge density \( n_{\text{GS}}(r) \). Symbolically, we write the \( v \)-representability of \( n_{\text{GS}}(r) \) as \( n_{\text{GS}}(r) \in A_N \) [7]. Here \( A_N \) represents a set of density, which is given by a ground state of an electron system in an external potential. The ground state is supposed to be stable against small perturbation. Let us assume that the point of \( \lambda = 1 \) is an accumulation point of the level crossings along the \( \lambda \) axis, and that we have case (ii).

Crossing points are labeled as \( \lambda_i \) \( (i = 1, 2, \ldots, \infty) \) and \( \lambda_i < \lambda_{i+1} \) for the present discussion. At any level crossing point \( \lambda_i \), owing to lemma 4 there are at least two minimizing states \( |\psi_{\lambda_i}^+\rangle \) and \( |\psi_{\lambda_i}^-\rangle \). The expectation values \( \langle \hat{T} + \lambda_i \hat{V}_{\text{ee}} \rangle \) by these states are the same at the crossing point. However, \( |\psi_{\lambda_i}^+\rangle \) and \( |\psi_{\lambda_i}^-\rangle \) are distinguished by \( \langle \hat{V}_{\text{ee}} \rangle \) and \( \langle \hat{T} \rangle \). Thus, they are linearly independent as state vectors. We can also show that \( \langle \psi_{\lambda_i}^+ | \hat{V}_{\text{ee}} | \psi_{\lambda_i}^- \rangle \) decreases, when \( i \) increases, as exemplified in the proof of theorem 6.

In between two neighboring crossing points, we have a continuous change in \( |\psi_{\lambda}\rangle \) and \( D(\lambda) = 0 \). The state \( |\psi_{\lambda_i}^+\rangle \) is connected to \( |\psi_{\lambda_i}^-\rangle \). We may select \( |\psi_{\lambda_i}^+\rangle \) as a representative state for this finite range \([\lambda_i, \lambda_{i+1}]\).

The existence of a big number of level crossing points at a close vicinity of this accumulation point requires the existence of plenty of nearly degenerate states \( |\psi_{\lambda_i}^\pm \rangle \) with \( i = 1, 2, \ldots, \infty \). Here, the state \( |\psi_{\lambda_i}^+\rangle \) might not be an eigenstate of any potential problem,
but minimizes just the expectation value of $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$ keeping the density. They are not distinguished by the primary order parameter, $n(r)$, nor by difference in any external symmetry breaking observed by the external potential $v_{\text{ext}}(r)$. Only internal degrees of freedom distinguish these infinite numbers of $|\Psi^\lambda_c\rangle$.

We should note that only to have these states does not directly mean existence of infinite numbers of degenerate eigenstates at $\lambda = 1$. This is because we have the possibility that all $|\Psi^\lambda_c\rangle$ except for $|\Psi_{\text{GS}}\rangle$ become non-eigenstates of $\hat{H}$, but are just variational states. Furthermore, if continuous change in $|\Psi^\lambda_c\rangle$ is allowed in a finite range of $\lambda$, only one minimizing state appears as a unique minimum for $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$ in the range.

However, the state $|\Psi^\lambda_c\rangle$ exists and may be used as variational states at any $\lambda \in [0, 1]$. By a simple inspection, we can see that at $\lambda = 1$, the variational energies of $\langle \Psi^\lambda_c | \hat{T} + \hat{V}_{ee} | \Psi^\lambda_c \rangle$ are separated by a finite gap with each other. However, when $\lambda = 1$ is an accumulation point, we have $|\langle \Psi^\lambda_c | \hat{T} + \hat{V}_{ee} | \Psi^\lambda_c \rangle - |\langle \Psi_{\text{GS}} | \hat{T} + \hat{V}_{ee} | \Psi_{\text{GS}} \rangle| \to 0$ for $i \to \infty$. Thus the gap for $i \gg N$ should be much smaller than any energy separation in the energy spectrum of the finite size system.

To discuss the accumulation points further, we now analyze existence or non-existence of a potential $v_\lambda(r)$ which gives a secular equation determining a state vector $|\Phi_\lambda\rangle$. Namely, for $\lambda = 1 - \delta \lambda$ with $0 < \delta \lambda \ll 1$, we formulate a quantum mechanical problem, whose solution $|\Phi_\lambda\rangle$ satisfies $||\langle \Phi_\lambda | \hat{H}(r) | \Phi_\lambda \rangle - n_{\text{GS}}(r)||_{\text{loc}} = 0$, and $|\Phi_\lambda\rangle \to |\Psi_{\text{GS}}\rangle$ for $\lambda \to 1$. Symbolically, we write this statement on another $v$-representability of $n_{\text{GS}}(r)$ as $n_{\text{GS}}(r) \in A_{\lambda,N}$. Here $A_{\lambda,N}$ represents a set of density, which is given by a ground state of a Fermion system with the reduced Coulomb interaction, $\lambda V_{ee}$, in an external potential.

For simplicity, we consider a compact space by introducing a cube with volume $L^3$ under the periodic boundary condition. Then, we can introduce a Fourier series expansion for the potential $v_\lambda(r)$, which is used as the Lagrange multiplier to fix the charge density of $|\Phi\rangle$, as

$$v_\lambda(r) = \sum_{G} v_{\lambda,G} \exp(iG \cdot r).$$

Consider an $N$ electron state $|\Phi\rangle$. We introduce a functional

$$Q[|\Phi\rangle, v_{\lambda,G}, E : \delta \lambda] = \langle \Phi | \hat{T} + (1 - \delta \lambda) \hat{V}_{ee} + \int d^3 r v_{\lambda,G}(r) \hat{n}(r) | \Phi \rangle$$

$$+ \int d^3 r v_{\lambda,G}(r) \left[ |\langle \Phi | \hat{n}(r) | \Phi \rangle - n_{\text{GS}}(r) | - E \left[ |\langle \Phi | \Phi \rangle - 1 \right] \right]$$

$$= \langle \Phi | \hat{T} + \hat{V}_{ee} + \int d^3 r v_{\lambda,G}(r) \hat{n}(r) | \Phi \rangle$$

$$+ \langle \Phi | \sum_{G \neq 0} \sum_{\sigma} v_{\lambda,G} c_{\lambda,G,\sigma}^\dagger c_{\lambda,G,\sigma} - \delta \lambda \hat{V}_{ee} \rangle$$

$$- \sum_{G \neq 0} v_{\lambda,G} n_{\text{GS}}(-G) - E \left[ |\langle \Phi | \Phi \rangle - 1 \right].$$

(49)

Here, $n_{\text{GS}}(G)$ is the Fourier component of $n_{\text{GS}}(r)$, $c_{G,\sigma}$ are electron annihilation operators with the spin $\sigma$, and $E = E - Nv_{\lambda,0}$. By making derivatives of $Q$ with respect to variables except for a parameter $\delta \lambda$, we have next secular equations. The variation of $Q$ with respect to $|\Phi\rangle$ gives us

$$\left\{ \hat{H} + \hat{H}_{\delta \lambda} \right\} |\Phi\rangle = E |\Phi\rangle,$$

(50)

$$\hat{H}_{\delta \lambda} = \sum_{G \neq 0} \sum_{\sigma} v_{\lambda,G} c_{\lambda,G,\sigma}^\dagger c_{\lambda,G,\sigma} - \delta \lambda \hat{V}_{ee}.$$
We also have constraints from the variations of $Q$ with respect to $E$ and $v_{λ,G}$ as

$$\langle Φ|Φ\rangle = 1,$$  

$$\sum_{G} \sum_{σ} ⟨Φ|c^d_{G,σ}c_{G,σ}|Φ⟩ = n_{GS}(G).$$  

At $λ = 1, δ\lambda = 0$, the solution of equations (50), (52) and (53) is given by the normalized state $|Ψ_{GS}\rangle$ with $v_{λ,G} = 0$ for all $G$. For any $v_0(r) ∈ L^{3/2} + L^∞$ or equivalently for any set of $v_{λ,G}$ with $δ\lambda > 0$, we have a normalized eigenstate $|Φ⟩$ of equations (50) and (52). So the construction of $v_{λ,G}$ to meet equation (53) is the problem. If $v_{λ,G}$ exists, $n_{GS}(r) ∈ A_{λ,N}$.

**Lemma 8.** When a unique ground state of $\hat{H}$ gives the charge density $n_{GS}(r)$, and if there happens accumulation of points $λ_i (i = 1, 2, \ldots, ∞)$ satisfying $0 < λ_i < λ_{i+1} < 1$ and $D(λ_i) > 0$, $n_{GS}(r)$ is not in $A_{λ,N}$. We have a series of potentials $v_{λ_i}(r)$, which gives a set of pure states $|Ψ_{λ_i}\rangle$, and $||⟨Ψ_{λ_i}|\hat{H}(r)|Ψ_{λ_i}⟩ − n_{GS}(r)||_∞ → 0$ as $i → ∞$.

To show this lemma, we classify possible conditions and deny possibilities except for a case that $n_{GS}(r)$ is not in $A_{λ,N}$, which is case 4 below.

**Case 1.** There exists $v_{λ}(r)$, and $|Ψ^+_λ⟩$ and $|Ψ^-_λ⟩$ are eigenstates of $\hat{H} + \hat{H}_λ = \hat{T} + λ\hat{V}_{ee} + \int d^3rv_λ(r)\hat{h}(r)$.

**Case 2.** There exist $v^+_λ(r)$ and $v^-_λ(r)$, which are different from each other more than a constant. Two states, $|Ψ^+_λ⟩$, are eigenstates of $\hat{T} + λ\hat{V}_{ee} + \int d^3rv^+_λ(r)\hat{h}(r)$, respectively.

**Case 3.** One of $|Ψ^+_λ⟩$ and $|Ψ^-_λ⟩$ is an eigenstate of $\hat{T} + λ\hat{V}_{ee} + \int d^3rv_λ(r)\hat{h}(r)$, and the other is not.

**Case 4.** Both of minimizing states, $|Ψ^+_λ⟩$ and $|Ψ^-_λ⟩$, are not eigenstates of any potential problem given as $\hat{T} + λ\hat{V}_{ee} + \int d^3rv_λ(r)\hat{h}(r)$.

We first deny case 1. Let us assume that the solution $v_{λ,G}$ exists for $n_{GS}(r)$. It means that we have a minimum of $Q$, which is given by an eigenstate $|Φ⟩$ of equation (50). If we insert $|Ψ_{λ_i}\rangle$ in the functional $Q$, we have

$$Q[|Ψ_{λ_i}\rangle, v_{λ,G}, E : δ\lambda] = \langle Ψ_{λ_i}|\hat{T} + λ\hat{V}_{ee}|Ψ_{λ_i}\rangle + \int d^3rv_{ext}(r)n_{GS}(r)$$

$$\leq ⟨Φ|\hat{T} + λ\hat{V}_{ee}|Φ⟩ + \int d^3rv_{ext}(r)n_{GS}(r)$$

$$= Q[|Φ⟩, v_{λ,G}, E : δ\lambda].$$

Thus, by the variational principle of the quantum mechanics, we see that $|Ψ_{λ_i}\rangle$ is also an eigenstate of equation (50). If we choose $λ = λ_i$, we have two degenerate eigenstates, $|Ψ^+_λ⟩$ and $|Ψ^-_λ⟩$. They are orthogonal with each other. By taking the limit $i → ∞$, we have two limiting states, $|Ψ^+_∞⟩$ and $|Ψ^-_∞⟩$, since these state vectors are in a Banach space and existence of the weak limit is ensured by $⟨Ψ^+_i|\hat{V}_{ee}|Ψ^+_i⟩ → ⟨Ψ_{GS}|\hat{V}_{ee}|Ψ_{GS}\rangle$ owing to theorem 6. Orthogonality between $|Ψ^+_∞⟩$ and $|Ψ^-_∞⟩$ holds. Of course $λ_∞ = 1$. These states minimize $Q[|Ψ⟩, v_{λ,G}, E : δ\lambda = 0]$. This means that the ground state has to be degenerate, which contradicts to the uniqueness of the ground state providing $n_{GS}(r)$.

In case 2, we have two independent potentials $v^+_λ(r)$ and $v^-_λ(r)$, both of which give the same density $n_{GS}(r)$. This case contradicts the Hohenberg–Kohn theorem [1] and thus it is denied at any $i$.

In case 3, we again have a difficulty. Both of $|Ψ^+_λ⟩$ and $|Ψ^-_λ⟩$ give the same variational energy for $\hat{T} + λ\hat{V}_{ee} + \int d^3rv_λ(r)\hat{h}(r)$. The variational principle shows that a state having the
variational energy of the lowest eigenstate gives a degenerate eigenstate. This fact contradicts an assumption that one of these two states is not an eigenstate of any potential problem.

So we conclude with case 4, which says that $v_{\lambda_i, G}$ does not exist, when $\lambda = 1$ is an accumulation point. Since $n_{GS}(r) \in \mathcal{I}_N$, we know the existence of an $N$-particle density matrix $\Gamma$, which gives the infimum of the Lieb functional [7]. For a mixed state $\Gamma$ has to be

$$\Gamma = \sum \Gamma_i |\Psi_{\lambda_i}^i\rangle \langle \Psi_{\lambda_i}^i|.$$  \hspace{1cm} (55)

$|\Psi_{\lambda_i}^i\rangle$ is given as an eigenstate of a potential problem and these states are orthogonal with each other. Since the limit of $\lambda_i \to 1$ is given as a pure state, when $i \to \infty$, coefficients $\Gamma_i$ and state vectors satisfy

$$\Gamma_i \to \delta_{i,0},$$  \hspace{1cm} (56)

$$|\Psi_{\lambda_i}^i\rangle \to |\Psi_{1 GS}\rangle.$$  \hspace{1cm} (57)

Thus, the second statement of the lemma holds.

The meaning of this lemma is somewhat redundant. When we have an accumulation point at $\lambda = 1$, we have no potential series, $v_{\lambda_i}(r)$, whose pure ground state reproduces exactly $n_{GS}(r)$. Thus, case 4, if it is found, gives an example of an $N$-representable density which is in $\mathcal{A}_N$ but not in $\mathcal{A}_{\lambda,N}$ for $\lambda < 1$. This density is apparently not pure-state $v$-representable in any Kohn–Sham scheme. The accumulation of crossing points for a ground state density contradicts a picture of the ordinal Kohn–Sham scheme, which assumes that a unique ground state of the Coulomb problem is reproduced by a non-interacting system with an optimized potential.

In this case, we should follow the present lemma to know of the existence of a converging series of quantum mechanical models. Actually, the potential series of $v_{\lambda_i}(r)$, whose ground state density is slightly different from the final solution, can be used to find a Cauchy sequence of $n_{\lambda_i}(r)$ converging to $n_{GS}(r)$. This converging series is found in the model space of the multi-reference generalization of the Kohn–Sham scheme. We may call the region of the model space an $\varepsilon$-vicinity, in which a convergence of a simulation is guaranteed.

Conversely, if a density $n_{GS}(r)$ is pure-state $v$-representable in a Kohn–Sham scheme including a multi-reference generalization, there is no accumulation of crossing points at $\lambda = 1$. In this case, we have a well-defined $\varepsilon$-vicinity around the true ground state in the model space, in which no level crossing is found. More precisely, we have a next statement. If the density $n_{GS}(r)$ is $v$-representable also for $\lambda < 1$, the accumulation of phase transition points is forbidden when $\lambda \to 1$. Finding a convergence in the density searched in an optimization process of model quantum systems may allow us to conclude no remaining level-crossing point along a line approaching in the true Coulomb system given by $\hat{H}$. Therefore, we conclude the existence of an $\varepsilon$ vicinity around the Coulomb system in the model space, where no essential phase transition occurs in the direction to reduce the interaction strength by introducing $\lambda < 1$, and keeping the charge density $n(r)$ unchanged.

Now we re-analyze the potential, $v_{\lambda, G}$, in a perturbative argument. Although this problem was treated more elegantly by Kohn [18], we want to show a subtle problem on the existence of $v_{\lambda, G}$. We have the limiting solution of $|\Psi_{GS}\rangle$ with $v_{\lambda, G} = 0$, which is an eigensolution of equation (50) at least as a stationary state. The construction of $Q$ is based on the quantum mechanical variational principle, and the limit of $Q$ for $\lambda \to 1$ should behave regularly. In order to inspect on the $v$-representability of the normal solution $n_{GS}(r)$ for $\lambda < 1$, we argue a perturbative construction method of $v_{\lambda, G}$. When the spectrum of $\hat{H}$ is normal, and when the
excited states are written as $|\Psi_i\rangle$, the solution of equation (50) is represented by the ordinal perturbation theory as

$$|\Phi\rangle = \frac{1}{C} \left( |\Psi_{GS}\rangle + \sum_i \frac{1}{E_0 - E_i} |\Psi_i\rangle \langle \Psi_i |\hat{H}_{\lambda} |\Psi_{GS}\rangle + o(\delta\lambda) \right). \quad (58)$$

The expectation value in equation (53) gives

$$\sum_G \sum_\sigma \langle \Psi| \hat{V}_{\lambda}\rangle |\Psi_{GS}\rangle v_{\lambda, G} = \delta\lambda B_\sigma + c.c. + o(\delta\lambda). \quad (59)$$

Here, $C$ is a normalization constant. In general, we have a non-zero vector $B_\sigma$. Since the matrix $A_{G, P}$ is a Hermite matrix, we have a solution $v_{\lambda, P}$ of equation (53) in $o(\delta\lambda)$. Thus, we may utilize the determination method of $v_{\lambda, P}$ to analyze the Kohn–Sham method, in which the density $n_{GS}(r)$ is reproduced by another artificial model system.

However, we find a difficulty in equation (59). The required conditions amount to the same number as $v_{\lambda, P}$. So once we consider higher-order conditions for $\lambda$ as independent, the number of the conditions is over the number of $v_{\lambda, P}$. This suggests that the solution could be found in a non-local potential. Even if so, the number of conditions is too large. If we consider all the expansions in equation (59) as functions of $\lambda$ and $v_{\lambda, P}$, the determination equations form simultaneous equations of $v_{\lambda, P}$. The structure is not trivial for higher order terms. Since they are nonlinear determination equations, the solution is expected to exist only when all the expressions are derived exactly.

Before ending this section, we summarize conditions for lemma 4 and theorem 6. The proofs of these statements show that the expectation value of the relevant interaction term has to be positive and finite, i.e. $0 < \langle V_{ee} \rangle < \infty$. The convexity (or precisely the concavity nature of $F_\lambda[n]$) comes from the linear nature of the $\lambda$-modified $F_\lambda[n]$ with respect to the parameter $\lambda$. The constrained minimization allows us to conclude both the continuous nature of the functional and the existence of minimizing states, which give Dini’s derivative of the parametrized energy density functional.

8. Summary and conclusions

In section 5, we consider the $\lambda$ modification of $F[n]$, while the primary order parameter $n(r)$ does not change. We consider a space of models, $G_{\lambda,1_{\text{in}}}[\Psi]$, with $\lambda \in [0, 1]$ in section 6.

In the model space, at a discontinuous point of $F_\lambda[n]$ with fixed $n(r)$, the minimizing states, $|\Psi^+_\lambda\rangle$ and $|\Psi^-_\lambda\rangle$, exist. The existence of discontinuous points may be detected by $\frac{d}{dn} F_\lambda[n]$ or $\frac{d}{dn} F[n]$. The latter behaves as a delta function at the discontinuous points. We can use these functions as an indicator for discontinuous transition points in a set of states giving $\Psi \to n(r)$. 

16
Owing to the above discussion, we have a physical conclusion on the universal energy density functional. Consider a true density $n_{GS}(r)$, which is given by a ground state in an external potential $v_{\text{ext}}(r)$. If the state is nondegenerate (or at least finitely degenerated) and if it is stable, we have no accumulation point of the level crossing points for $F_\lambda[n_{GS}]$ at $\lambda = 1$ in the searching process utilizing a potential problem with the reduced interaction strength. Thus, when we move away from $\lambda = 1$ on the $\lambda$ axis, we have an $\epsilon$ vicinity, where no level crossing occurs in the model space, which is to be defined by a secular equation of the many-Fermion system with the reduced interaction.

From the pioneering discussion on a multi-reference generalization of DFT by Savine et al [19], there have been several formulations of the multi-reference density functional theory (MR-DFT) [13, 19, 20]. In a MR-DFT formulation, one of the authors considered general modification of the universal energy density functional [13, 21]. In addition to the Kohn–Sham description of the true density [2], we have plenty of effective descriptions using model Fermion systems. The models include partially correlated systems, whose ground state is obtained in multiple Slater determinants. We can introduce the distance between two models given by the norm of the charge density and then the set of models with the charge distance becomes a space of models. An advantage of this generalization of DFT is that we can search for an optimized model in a space of models including non-interacting Fermion models and interacting Fermion models guided by the density functional variational theory [22]. Our generalization may allow us to introduce limited low-energy quantum fluctuations, which are separated from high-energy contributions with respect to the energy scale, as well as a strategy to separate short- and long-range contributions of the Coulomb interaction in the short-range DFT [23].

In an optimization process in the model space, the density is searched in a $\nu$-representable subset. Thus, in a realization of MR-DFT, we never meet the accumulation of unreachable crossing points, when we see a convergence of the density in a searching step. The existence of an $\epsilon$-vicinity in the model space suggests that we have a physically converged model, which may continuously connect to the true electron system. Even when the original Kohn–Sham model is separated from the electron system by crossing points, the generalized Kohn–Sham model in MR-DFT can be settled in the $\epsilon$-vicinity.

Acknowledgments

This work was supported by the Global COE Program (Core Research and Engineering of Advanced Material-Interdisciplinary Education Center for Materials Science), MEXT, Japan, Grand Challenges in next-generation integrated nanoscience, Grant-in-Aid for Scientific Research in Priority Areas (nos 17064006, 19051016) and a Grants-in-Aid for Scientific Research (no 19310094).

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