A Mathematical Aspect of Hohenberg-Kohn Theorem*  

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Abstract

The Hohenberg-Kohn theorem plays a fundamental role in density functional theory, which has become a basic tool for the study of electronic structure of matter. In this article, we study the Hohenberg-Kohn theorem for a class of external potentials based on a unique continuation principle.

Keywords: density functional theory, electronic structure, unique continuation principle, Hohenberg-Kohn theorem.

AMS subject classifications: 81V70.

1 Introduction

Density functional theory (DFT) is the most widely used many-body approach for electronic structure calculations and has significantly impacted on modern science and engineering (see, e.g., [6, 19, 20, 21, 24, 29]), of which Hohenberg-Kohn theorem lies at the heart. We see that the development of materials science, quantum chemistry, molecular biology, and condensed-matter physics require to describe and understand the many-particle systems of thousands and hundreds of electrons and nuclei. We note that the basic mathematical model for electronic structure is the Schrödinger equation, which is set for the many-particle wavefunction of the system in high dimensions. However, it is intractable to solve the Schrödinger equation directly even using the modern advanced supercomputers except for few systems. Instead of using wavefunctions in high dimensions, DFT applies the particle density in three dimensions to model the system. Derived from DFT, the so-called Kohn-Sham model [9], which is equivalent to the Schrödinger equation, is tractable. We understand that the theoretical basis of DFT is the Hohenberg-Kohn theorem.

Due to its subtleties, however, DFT is not entirely elaborated yet (c.f., e.g., [10, 11, 12, 17, 18, 22, 25, 27, 28] and references cited therein). For instance, the existing proofs of Hohenberg-Kohn theorem usually assume directly or indirectly that the particle density functional is differentiable or the particle density is positive or the particle wavefunction does not vanish on a set of positive measure. We see that the particle density functional is not Gâteaux differentiable [13, 14, 18], whether the particle density is positive is still open [4, 23], and that the particle wavefunction does not vanish on a set of positive measure is unclear in a real system (c.f. [22, 23]). We refer to [2, 5, 6, 10, 12, 13, 17, 18, 22, 23, 27] and references cited therein for discussions on the Hohenberg-Kohn theorem.

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In this paper, we prove the Hohenberg-Kohn theorem for external potentials that the associated wavefunctions do not vanish in an open set. We understand from Theorem XIII.57 of [23] together with its comment just below that the wavefunction of electronic Schrödinger equation does not vanish on an open set, from which we obtain that Hohenberg-Kohn theorem holds true for Coulomb potentials [27], too. We note that the wavefunction does not vanish in an open set is relatively mild assumption [23, 26].

2 Ground state and density

The Hamiltonian of a system of interacting particles in an external potential $v$, including any problem of electrons and nuclei, is written as

$$
\mathcal{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_{x_i}^2 + \sum_{i=1}^{N} v(x_i) + \frac{1}{2} \sum_{i,j=1, i\neq j}^{N} \frac{e^2}{|x_i - x_j|},
$$

where $\hbar$ is Planck’s constant divided by $2\pi$, $m_e$ is the mass of the electron, $\{x_i : i = 1, \ldots, N\}$ are the variables that describe the electron positions, and $e$ is the electronic charge. Let $T = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_{x_i}^2$ be the kinetic energy operator, $V_{ee} = \frac{1}{2} \sum_{i,j=1, i\neq j}^{N} \frac{e^2}{|x_i - x_j|}$ be the electron-electron repulsion energy operator, and $\rho(x) \equiv \rho^\Psi(x) = N \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} \int_{\mathbb{R}^{3(N-1)}} |\Psi((x, \sigma_1), (x_2, \sigma_2), \ldots, (x_N, \sigma_N))|^2 dx_2 \cdots dx_N$ be the single-particle density. We have the energy of the system as follows

$$
E = (\Psi, \mathcal{H}\Psi) = (\Psi, (T + V_{ee})\Psi) + \int_{\mathbb{R}^3} v(x)\rho(x)dx.
$$

We understand that for an electronic Coulomb system, the external potential

$$
v(x) = -\sum_{j=1}^{M} \frac{Z_j e^2}{|x - r_j|},
$$

is determined by $\{Z_j : j = 1, 2, \ldots, M\}$, which are the valence charges of the nuclei, and $\{r_j : j = 1, 2, \ldots, M\}$, which are the positions of the nuclei.

Let $\mathcal{H}_0 = T + V_{ee}$ and $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. The total Hamiltonian is $\mathcal{H}_v = \mathcal{H}_0 + \mathcal{V}$, where

$$
\mathcal{V} = \sum_{i=1}^{N} v(x_i).
$$

The associated ground state energy $E(v)$ is

$$
E(v) \equiv E(v, N) = \inf \{ (\Psi, \mathcal{H}_v\Psi) : \Psi \in \mathcal{W}_N \},
$$

(2.1)
where
\[ W_N = \{ \Psi \in H^1(\mathbb{R}^{3N}) : \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} \int_{\mathbb{R}^{3N}} |\Psi|^2 \, dx_1 \cdots dx_N = 1 \} \]

Since there may or may not be a minimizer \( \psi \) in \( W_N \) and if there is one it may not be unique \[18\], we introduce a set of minimizers
\[ G_v \equiv G_{v,N} = \arg \inf \{ (\Psi, H_v \Psi) : \Psi \in W_N \} \]
\[ V_N = \{ v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) : G_v \neq \emptyset \} \]
Any \( \Psi \) in \( G_v \) is called a ground state of (2.1). If \( \Psi \in G_v \), then
\[ H_v \Psi = E(v) \Psi \quad (2.2) \]
in the distributional sense. We see from the Schrödinger equation (2.2) that the density \( \rho \) of ground state is determined by the external potential \( v \).

3 Proof of Hohenberg-Kohn theorem
The following property, whose proof can be found in [27] (c.f. also \[3, 16, 18, 22\]), is crucial and useful:

**Lemma 3.1.** Given \( v, v' \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \). Let \( \rho_v = \rho^{\Psi_v} \) and \( \rho_{v'} = \rho^{\Psi_{v'}} \) with \( \Psi_v \in G_v \) and \( \Psi_{v'} \in G_{v'} \). If \( \rho_v = \rho_{v'} \), then
\[ \left( \sum_{j=1}^N (v' - v)(x_j) - (E(v') - E(v)) \right) \Psi_v = 0 \quad a.e. (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}. \]

In our analysis, we need the following helpful conclusion, which is a modified version of Lemma 1 of [22].

**Lemma 3.2.** Let \((a, b) \subset \mathbb{R}\). If \( w \in L^1((a, b)^3) \) satisfies
\[ \sum_{j=1}^N w(x_j) = C \quad a.e. (x_1, x_2, \ldots, x_N) \in (a, b)^3N \quad (3.1) \]
for some constant \( C \), then \( w(x) = C/N \quad a.e. x \in (a, b)^3 \).

**Proof.** We use the similar argument as that in [22]. Let \( J_\epsilon(x) = \epsilon^{-3} J(x/\epsilon) \), where
\[ J(x) = \begin{cases} J \exp \left( -1/(1 - |x|^2) \right) & \text{if } |x| < 1, \\ 0 & \text{if } |x| \geq 1, \end{cases} \]
with
\[ J = 1/\int_{\mathbb{R}^3} \exp \left( -1/(1 - |x|^2) \right) \]
We see that \( J_\epsilon(x) \) is nonnegative, belongs to \( C_0^\infty(\mathbb{R}^3) \), satisfies
\[ \int_{\mathbb{R}^3} J_\epsilon(x) \, dx = 1, \]
and $J_x \ast \tilde{w} \in C^\infty(\mathbb{R}^3)$ (see e.g. page 36 of [1]), where

$$(J_x \ast \tilde{w})(x) = \int_{\mathbb{R}^3} J_x(x - y) \tilde{w}(y) dy$$

and

$$\tilde{w}(x) = \begin{cases} w & \text{if } x \in (a, b)^3, \\ 0 & \text{if } x \in \mathbb{R}^3 \setminus (a, b)^3. \end{cases}$$

Therefore, we obtain from (3.1) that

$$\sum_{j=1}^{N} (J_x \ast \tilde{w})(x_j) = C \forall (x_1, x_2, \ldots, x_N) \in (a, b)^{3N}. \tag{3.2}$$

Setting $x_j = x(j = 1, 2, \ldots, N)$ in (3.3), we get

$$(J_x \ast \tilde{w})(x) = C/N \forall x \in (a, b)^3.$$ 

Using the fact that $(J_x \ast \tilde{w})(x)$ converges to $\tilde{w}(x)$ a.e. (see e.g. Theorem 2.29 of [1]) and $\tilde{w} = w$ in $(a, b)^3$, we then arrive at the conclusion and complete the proof. \hfill \Box

To restate and prove the Hohenberg-Kohn theorem, we recall the unique continuation principle, which is significant in the context of partial differential equations (see, e.g., [7, 23, 26] and references cited therein).

**Definition 3.1.** Equation (2.2) has the unique continuation property if every solution that vanishes on an open set of $\mathbb{R}^3$ vanishes identically.

Let $V$ be the set of all the external potentials $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ such that the unique continuation principle holds true for (2.2). We observe that $V_C \subset V$ (see, e.g., [7] or Theorem XIII.57 the comment just below, page 226 of [23]), where

$$V_C = \left\{ - \sum_{j=1}^{M} Z_j e^2 : Z_j \in \mathbb{R}, r_j \in \mathbb{R}^3(j = 1, 2, \ldots, M); M = 1, 2, \ldots \right\}.$$

More precisely, if $v \in V_C$ and $\Psi \in \mathcal{G}_v$ satisfies (2.2) and vanishes on an open set of $\mathbb{R}^{3N}$, then $\Psi \equiv 0$ on $\mathbb{R}^{3N}$.

Now we are able to prove that the density $\rho$ of ground state is uniquely determined by the external potential $v$, apart from an additive constant in some open set.

**Theorem 3.1.** Let $\Psi_v \in \mathcal{G}_v$ and $\Psi_{v'} \in \mathcal{G}_{v'}$ with $v, v' \in V$. If $v$ and $v'$ differ by more than just a constant (in the sense of almost everywhere) in some open set, then $\rho^{\Psi_v} \neq \rho^{\Psi_{v'}}$.

**Proof.** Let $v$ and $v'$ differ by more than just a constant in $(a, b)^3$, where $a < b$. If $\rho^{\Psi_v} = \rho^{\Psi_{v'}}$, we see from Lemma 3.1 and the unique continuation principle that

$$\sum_{i=1}^{N} (v' - v)(x_i) = E(v') - E(v) \text{ a.e. } (x_1, x_2, \ldots, x_N) \in (a, b)^{3N},$$

We conjecture that (c.f. Remarks (ii) of [18])

$$V = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3).$$

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which together with Lemma 3.2 leads to

$$(v' - v)(x) = (E(v') - E(v))/N \text{ a.e. } x \in (a, b)^3.$$ 

This is a contradiction to that $v$ and $v'$ differ by more than just a constant in $(a, b)^3$. We complete the proof. □

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