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ORIGINAL PAPER

Hohenberg–Kohn theorem for Coulomb type systems and its generalization

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Abstract Density functional theory (DFT) has become a basic tool for the study of electronic structure of matter, in which the Hohenberg–Kohn theorem plays a fundamental role in the development of DFT. In this paper, we present a simple, selfcontained and mathematically rigorous proof using the Fundamental Theorem of Algebra. We also show the Hohenberg–Kohn theorem for systems with some more general external potentials.

Keywords Coulomb system · Density functional theory · Electronic structure · Fundamental Theorem of Algebra · Hohenberg–Kohn

Mathematics Subject Classification (2000) 81V70

1 Introduction

The modern formulation of density functional theory (DFT) originated in the work of Hohenberg and Kohn [11], on which based the other classic work in this field by Kohn and Sham [14], the Kohn–Sham equation, has become a basic mathematical model of much of present-day methods for treating electrons in atoms, molecules, condensed matter, and man-made structures [6,9,12,23,25].

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Although it is quite profound, DFT is not entirely elaborated yet (c.f., e.g., [5,17,18,22,26,28] and references cited therein). Since the relevant assumptions are incompatible with the Kato cusp condition, Kryachko has pointed out that the usual *reductio ad absurdum* proof of the original Hohenberg–Kohn theorem is unsatisfactory [15,16,21]. Note that Kato theorem [13] tells the electron-nucleus cusp conditions at nucleus positions only, we are not able to uniquely determine the electron density just from the cusp conditions without using any other information such as the analyticity of density shown in [7,8], though the electron density uniquely determines the external Coulombic potential. Consequently, there is a gap in the proof of the theorem by using the Kato theorem in [16], for instance. Eschrig provided a proof of the theorem based on a conjecture that is not easily proved mathematically [6]. We note that Lieb has tried to examine the theorem rigorously [22]. But Lieb's proof required that the N-particle wavefunction does not vanish in a set of positive measure that was unclear in a real system (c.f., e.g., [26]) until Mezey established the holographic theorem [24] and Fournais et al proved the analyticity of density away from the nuclei [7,8]. We see that one may use the Hohenberg–Kohn variational principle to show the Hohenberg–Kohn theorem, provided that the differentiability of the DFT variational is well set up [17,21]. We also understand that there are several fine approaches trying to solve mathematical problems associated with DFT, in which some sophisticated mathematics is directly or indirectly involved. We refer to [1–4,10,15,17,18,29,19,21,22,24,26,28,30] and references cited therein for discussions on the Hohenberg–Kohn theorem.

In this paper, we shall present a simple, selfcontained and mathematically rigorous proof by using the Fundamental Theorem of Algebra only (see Sect. 4). We also show the Hohenberg–Kohn theorem for systems with some more general external potentials (see Sect. 5).

2 Hohenberg–Kohn theorem

We see that the approach of Hohenberg and Kohn is to formulate DFT as an exact theory of many-body systems. The formulation applies to any system of interacting particles in an external potential v, including any problem of electrons and fixed nuclei, where the Hamiltonian can be written as

$$\mathcal{H} = T + \sum_{i=1}^{N} v(x_i) + V_{ee}. \tag{2.1}$$

Here

$$T = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_{x_i}^2$$

is the kinetic energy operator,

$$V_{ee} = \frac{1}{2} \sum_{i,j=1, i\neq j}^{N} \frac{e^2}{|x_i - x_j|}$$

is the electron-electron repulsion energy operator, with $\hbar$ is Planck's constant divided by 2π, 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. For an electronic Coulomb system,

$$v(x) \equiv v_{\{Z_j\},\{r_j\}}(x) = -\sum_{j=1}^{M} \frac{Z_j e^2}{|x - r_j|} \tag{2.2}$$

is determined by $\{Z_j : j = 1, 2, \ldots, M\}$, which are the charges of the nuclei, and $\{r_j : j = 1, 2, \ldots, M\}$, which are the positions of the nuclei. The energy of the system can be expressed by

$$E = (\Psi, \mathcal{H}\Psi) = (\Psi, (T + V_{ee})\Psi) + \int_{\mathbb{R}^3} v(x)\rho(x)dx, \tag{2.3}$$

where

$$\begin{aligned} \rho(x) &\equiv \rho^{\Psi}(x) \\ &= N \sum_{\sigma_1,\sigma_2,\ldots,\sigma_N} \int_{\mathbb{R}^{3(N-1)}} |\Psi((x,\sigma_1),(x_2,\sigma_2),\ldots,(x_N,\sigma_N))|^2 dx_2 \ldots dx_N \end{aligned} \tag{2.4}$$

is the single-particle density.

Consider Coulomb potential set

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

Let $\mathcal{H}_0 = T + V_{ee}$ and v be a single-particle potential in $\mathbb{V}_C$. 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 defined to be

$$E(v) \equiv E(v, N) = \inf\{(\Psi, \mathcal{H}_v\Psi) : \Psi \in \mathscr{W}_N\}, \tag{2.5}$$

where

$$\mathscr{W}_N = \{\Psi \in H^1(\mathbb{R}^{3N}) : \sum_{\sigma_1,\sigma_2,\ldots,\sigma_N} \int_{\mathbb{R}^{3N}} |\Psi|^2 dx_1 \ldots dx_N = 1\}.$$

Note that there may or may not be a minimizer ψ in $\mathscr{W}_N$, and if there is one it may not be unique [22]. Thus, we should introduce a set of minimizers

$$\mathscr{G}_v \equiv \mathscr{G}_{v,N} = \arg\inf\{(\Psi, \mathcal{H}_v\Psi) : \Psi \in \mathscr{W}_N\}.$$

Any Ψ in $\mathscr{G}_v$ is called a ground state of (2.5). If $\Psi \in \mathscr{G}_v$, then

$$\mathcal{H}_v\Psi = E(v)\Psi \tag{2.6}$$

in the distributional sense.

The original Hohnberg–Kohn theorem (see page B865 of [11]) states that the external potential v "is a unique functional of" the electronic density in the ground state,"apart from a trivial additive constant." In our notation, Lieb's statement of this theorem may be written as the following (see Theorem 3.2 of [22]):

Theorem 1 *Suppose $\Psi_v \in \mathscr{G}_v$ and $\Psi_{v'} \in \mathscr{G}_{v'}$. If $v \neq v' + constant$, then $\rho^{\Psi_v} \neq \rho^{\Psi_{v'}}$.*

For Coulomb type systems, indeed, we may state the Hohenberg-Kohn theorem as follows:

Theorem 2 *Suppose $\Psi_v \in \mathscr{G}_v$ and $\Psi_{v'} \in \mathscr{G}_{v'}$ with $v, v' \in \mathbb{V}_C$. If $v \neq v'$, then $\rho^{\Psi_v} \neq \rho^{\Psi_{v'}}$.*

3 Lemmas

To prove Theorem 2, we need some lemmas.

Lemma 1 *For any $n \geq 2$, there exist non-zero polynomials $\{H_{n,j}(s_1, s_2, \ldots, s_n) : j = 0, 1, 2, \ldots, 2^{n-1}\}$ with real coefficients satisfying*

(i) *$H_{n,j}(s_1, s_2, \ldots, s_n)(j = 1, 2, \ldots, 2^{n-1})$ are homogeneous:*

$$H_{n,j}(\lambda s_1, \lambda s_2, \ldots, \lambda s_n) = \lambda^j H_{n,j}(s_1, s_2, \ldots, s_n), \qquad \forall \lambda \in \mathbb{R}, \quad j = 1, 2, \ldots, 2^{n-1},$$
$$H_{n,0}(s_1, s_2, \ldots, s_n) = 1,$$

and $H_{n,2^{n-1}}(s_1, s_2, \ldots, s_n)$ is a monic polynomial of degree 2^{n-1}.

(ii) *If $t_j \in \mathbb{R}(j = 1, 2, \ldots, n)$ and*

$$\delta = \sum_{j=1}^{n} t_j,$$

then

$$\sum_{j=0}^{2^{n-1}} H_{n,j}\left(t_1^2, t_2^2, \ldots, t_n^2\right)\delta^{2\left(2^{n-1}-j\right)} = 0. \tag{3.1}$$

Proof We prove the conclusion by induction on n. First, for $n = 2$, $t_1 + t_2 = \delta$, a direct calculation implies

$$t_1^4 + t_2^4 - 2t_1^2t_2^2 - 2\delta^2\left(t_1^2 + t_2^2\right) + \delta^4 = 0.$$

Namely, Lemma 1 is true for $n = 2$.

For the induction step, suppose Lemma 1 is true for n. Let

$$\sum_{j=1}^{n+1} t_j = \delta.$$

By the induction hypothesis, we have from

$$\sum_{j=1}^{n} t_j = \delta - t_{n+1}$$

that there exist non-zero polynomials

$$\{H_{n,j}(s_1, s_2, \ldots, s_n) : j = 0, 1, 2, \ldots, 2^{n-1}\}$$

with real coefficients satisfying $H_{n,j}(s_1, s_2, \ldots, s_n)(j = 1, 2, \ldots, 2^{n-1})$ are homogeneous, $H_{n,2^{n-1}}(s_1, s_2, \ldots, s_n)$ is a monic polynomial of degree 2^{n-1}, and

$$\sum_{j=0}^{2^{n-1}} H_{n,j}(t_1^2, t_2^2, \ldots, t_n^2)(\delta - t_{n+1})^{2(2^{n-1}-j)} = 0. \tag{3.2}$$

Applying Newton binomial theory, we then get that

$$\begin{aligned}
&H_{n,2^{n-1}}\left(t_1^2, t_2^2, \ldots, t_n^2\right) + \delta^{2^n} + t_{n+1}^{2^n} \\
&\quad + \sum_{j=1}^{2^{n-1}-1} H_{n,j}\left(t_1^2, t_2^2, \ldots, t_n^2\right) \sum_{l=0}^{2^{n-1}-j} \binom{2^n - 2j}{2l} \delta^{2^n-2j-2l} t_{n+1}^{2l} \\
&\quad + \sum_{l=1}^{2^{n-1}-1} \binom{2^n}{2l} \delta^{2^n-2l} t_{n+1}^{2l} \\
&= \delta t_{n+1}\left(\sum_{j=1}^{2^{n-1}-1} H_{n,j}\left(t_1^2, t_2^2, \ldots, t_n^2\right) \sum_{l=1}^{2^{n-1}-j} \binom{2^n - 2j}{2l-1} \delta^{2^n-2j-2l} t_{n+1}^{2l-2}\right) \\
&\quad + \delta t_{n+1} \sum_{l=1}^{2^{n-1}} \binom{2^n}{2l-1} \delta^{2^n-2l} t_{n+1}^{2l-2}.
\end{aligned}$$

Taking squares of both sides of the above =, we arrive at the conclusion of Lemma 1 when n is replaced by $n+1$. This completes the proof.

The following conclusion results from page 78 of [6] (c.f. also [20,22,26]):

Lemma 2 *Given $v, v' \in \mathbb{V}_C$. Let $\rho_v = \rho^{\Psi_v}$ and $\rho_{v'} = \rho^{\Psi_{v'}}$ with $\Psi_v \in \mathscr{G}_v$ and $\Psi_{v'} \in \mathscr{G}_{v'}$. If $\rho_v = \rho_{v'}$, then*

$$\left(\sum_{i=1}^{N}(v'-v)(x_i) - (E(v')-E(v))\right)\Psi_v = 0 \quad \text{in } \mathbb{R}^{3N}. \tag{3.3}$$

Proof For completion, we present a proof here, which essentially comes from the proof of Theorem 1 of [26]. We see that

$$\begin{aligned} E(v) &= (\Psi_v, \mathcal{H}_v\Psi_v) \le (\Psi_{v'}, \mathcal{H}_v\Psi_{v'})dx \\ &= E(v') - \int_{\mathbb{R}^3} \rho_{v'}(v'-v)dx. \end{aligned}$$

Similarly,

$$E(v') \le E(v) - \int_{\mathbb{R}^3} \rho_v(v-v')dx.$$

Thus we obtain that if $\rho_v = \rho_{v'}$, then

$$E(v') = E(v) - \int_{\mathbb{R}^3} \rho_v(v-v')dx,$$

or

$$\int_{\mathbb{R}^3} \rho_v(v-v')dx = E(v) - E(v'),$$

which leads to $E(v) = (\Psi_{v'}, \mathcal{H}_v\Psi_{v'})$. Therefore $\Psi_{v'} \in \mathscr{G}_v$ and

$$\mathcal{H}_v\Psi_{v'} = E(v)\Psi_{v'}.$$

By a similar argument, we have

$$\mathcal{H}_{v'}\Psi_v = E(v')\Psi_v.$$

Since

$$\mathcal{H}_v\Psi_v = E(v)\Psi_v,$$

we arrive at (3.3). This completes the proof.

Due to the Fundamental Theorem of Algebra (c.f., e.g., [27]), every non-zero single-variable polynomial with real or complex coefficients has exactly as many real or complex zeroes as its degree, if each zero is counted up to its multiplicity. Hence we have a multivariate version of the Fundamental Theorem of Algebra as follows:

Lemma 3 *The Lebesgue's measure of the set of zeroes of any non-zero multivariate polynomial with real coefficients is zero.*

4 Proof of Theorem 2

In this section, we prove Theorem 2, the new statement of Hohenberg-Kohn theorem.

Proof Let $\rho_v = \rho^{\Psi_v}$ and $\rho_{v'} = \rho^{\Psi_{v'}}$. It is sufficient to prove that $v = v'$ if $\rho_v = \rho_{v'}$.

Note that there exist $m \geq 1, r_j \in \mathbb{R}^3$ and $\alpha_j \in \mathbb{R} (j = 1, 2, \ldots, m)$ such that

$$(v' - v)(x) = \sum_{j=1}^{m} \frac{\alpha_j}{|x - r_j|}.$$

Suppose $v' \neq v$, we have $\alpha_{j_0} \neq 0$ for some $j_0 \in \{1, 2, \ldots, m\}$.

Let $\{H_{n,j}(s_1, s_2, \ldots, s_n) : j = 0, 1, 2, \ldots, 2^{n-1}\}$ be the non-zero polynomials with real coefficients satisfying the conclusion of Lemma 1 with $n = mN$ and

$$\begin{aligned} \delta &= \frac{\alpha_{j_0}}{|x_1 - r_{j_0}|}, \\ t_1 &= E(v') - E(v), \\ \{t_l : l = 2, 3, \ldots, n\} &= \left\{ L \frac{-\alpha_j}{|x_i - r_j|} : i = 1, 2, \ldots, N; j = 1, 2, \ldots, m \right\} \setminus \{-\delta\}. \end{aligned}$$

We see that if equation

$$\sum_{i=1}^{N} (v' - v)(x_i) = E(v') - E(v) \tag{4.1}$$

holds, then there exists a non-zero multivariate polynomial $P(s_1, s_2, \ldots, s_n)$ with real coefficients such that

$$\begin{aligned} &P\left(|x_1 - r_1|^2, \ldots, |x_i - r_j|^2, \ldots, |x_N - r_m|^2\right) = 0, \\ &x_i \in \mathbb{R}^3 \setminus \{r_j : j = 1, 2, \ldots, m\}, \quad i = 1, 2, \ldots, N. \end{aligned} \tag{4.2}$$

As a result, if $(x_1, x_2, \ldots, x_N)$ is any zero of (4.1), then $(x_1, x_2, \ldots, x_N)$ is an zero of (4.2). Note that $P(|x_1 - r_1|^2, \ldots, |x_i - r_j|^2, \ldots, |x_N - r_m|^2)$ is a polynomial of

$(x_1, x_2, \ldots, x_N)$ with real coefficients. We obtain from Lemma 3 that the set of zeroes of (4.1) are of zero measure in $\mathbb{R}^{3N}$. Since

$$\sum_{i=1}^{N}(v' - v)(x_i) - (E(v') - E(v))$$

is continuous over domain

$$\{(x_1, x_2, \ldots, x_N) : x_i \in \mathbb{R}^3 \setminus \{r_j : j = 1, 2, \ldots, m\}, i = 1, 2, \ldots, N\}$$

as a function of $(x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$, we must have $\Psi_v = 0$ almost every where in $\mathbb{R}^{3N}$ from (3.3), which is a contradiction to

$$\sum_{\sigma_1,\sigma_2,\ldots,\sigma_N} \int_{\mathbb{R}^{3N}} |\Psi_v|^2 dx_1 \ldots dx_N = 1.$$

This completes the proof.

5 Generalization

We point out that our arguments can be applied to establishing Hohnberg-Kohn type theorem for other kinds of external potentials.

Let $x = (\xi_1, \xi_2, \xi_3) \in \mathbb{R}^3$, define $\mathbb{V} = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, S= the set of positive rational numbers, and

$$\mathbb{V}_G = \mathbb{V} \cap \text{span}\left\{ \frac{\xi_1^i \xi_2^j \xi_3^k}{|x - r|^s} : i, j, k = 0, 1, 2, \ldots; r \in \mathbb{R}^3; 2 > s \in S \right\}. \quad (5.1)$$

Note that Lemma 2 is valid when $\mathbb{V}_C$ is replaced by $\mathbb{V}$. Applying Lemma 3, we obtain from the proof of Theorem 2 that Theorem 2 is also true when $\mathbb{V}_C$ is replaced by $\mathbb{V}_G$. Namely, we have

Theorem 3 *Suppose $\Psi_v \in \mathscr{G}_v$ and $\Psi_{v'} \in \mathscr{G}_{v'}$ with $v, v' \in \mathbb{V}_G$. If $v \neq v'$, then $\rho^{\Psi_v} \neq \rho^{\Psi_{v'}}$.*

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