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. Unfortunately, the existing proofs are incomplete; besides, the statement of the Hohenberg-Kohn theorem for many-electron Coulomb systems is not perfect. In this paper, we shall restate the Hohenberg-Kohn theorem for Coulomb type systems and present a rigorous proof by using the Fundamental Theorem of Algebra. We also show the Hohenberg-Kohn theorem for systems with more general external potentials.

Keywords: Coulomb system, density functional theory, electronic structure, Fundamental Theorem of Algebra, Hohenberg-Kohn theorem.

AMS subject classifications: 81V70.

1 Introduction

The modern formulation of density functional theory (DFT) originated in the work of Hohenberg and Kohn [4], on which based the other classic work in this field by Kohn and Sham [7], 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 [1, 2, 5, 12, 13]. Although it is quite profound, DFT is not entirely elaborated yet (c.f., e.g., [11, 14, 16] 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 [8, 9]. Note that Kato theorem [6] 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, 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 [9]. We note that Lieb has tried to examine the theorem rigorously [11]. But Lieb's proof required that the N-particle wavefunction does not vanish in a set of positive measure that is unclear in a real system (c.f. [14]). We refer to [3, 8, 10, 11, 14, 16] and references cited therein for discussions on the Hohenberg-Kohn theorem. Indeed, the statement of the original Hohenberg-Kohn theorem for many-electron Coulomb systems is not perfect (see Section 2).

In this paper, we shall state the Hohenberg-Kohn theorem for Coulomb type systems precisely (see Theorem 2.2) and present a rigorous proof by using the Fundamental Theorem

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of Algebra (see Section 4). Finally, in Section 5, we show the Hohenberg-Kohn theorem for systems with more general external potentials.

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

$$\mathcal{H} \quad = \quad -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e}\nabla_{x_i}^2 + \sum_{i=1}^{N} v(x_i) + \frac{1}{2}\sum_{i,j=1,i\neq j}^{N} \frac{e^2}{|x_i - x_j|}, \tag{2.1}$$

where $\hbar$ is Planck's constant divided by $2\pi, m_e$ is the mass of the electron, $\{x_i : i = 1, \cdots, N\}$ 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 $\{Z_j : j = 1, 2, \cdots, M\}$, which are the valence charges of the nuclei, and $\{r_j : j = 1, 2, \cdots, M\}$, which are the positions of the nuclei. The energy of the system can be expressed by

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

where

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

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, and

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

is the single-particle density.

Let $\mathcal{H}_0 = T + V_{ee}$ and v be a single-particle potential in function space

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

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 defined to be

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

where

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

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 [11]. 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 [4]) 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 [11]):

Theorem 2.1. *Suppose $\Psi_v \in \mathscr{G}_v$ and $\Psi_{v'} \in \mathscr{G}_{v'}$. If $v \neq v' + constant$, then $\rho^{\Psi_v} \neq \rho^{\Psi_{v'}}$.*

Consider Coulomb potential set

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

Obviously, $\mathbb{V}_C \subsetneq \mathbb{V}$.

It will be shown by the Fundamental Theorem of Algebra that for any $v, v' \in \mathbb{V}_C$, $v \neq v' + constant$ for any constant if $v \neq v'$ (see Section 4 for details), which means that the requirement $v \neq v' + constant$ in the Hohnberg-Kohn theorem or Theorem 2.1 is superfluous for electronic Coulomb system. More precisely, $v \neq v' + constant$ in the Hohnberg-Kohn theorem should be replaced by $v \neq v'$. Therefore the Hohenberg-Kohn theorem or Theorem 2.1 for Coulomb type systems should be restated as follows:

Theorem 2.2. *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 2.2, we need some lemmas.

Lemma 3.1. *For any $n \geq 2$, there exist non-zero polynomials $\{H_{n,j}(s_1, s_2, \cdots, s_n) : j = 0, 1, 2, \cdots, 2^{n-1}\}$ with real coefficients satisfying*

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

$$\begin{aligned} H_{n,j}(\lambda s_1, \lambda s_2, \cdots, \lambda s_n) &= \lambda^j H_{n,j}(s_1, s_2, \cdots, s_n), \ \forall \lambda \in \mathbb{R}, j = 1, 2, \cdots, 2^{n-1}, \\ H_{n,0}(s_1, s_2, \cdots, s_n) &= 1, \end{aligned}$$

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

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

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

then

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

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

$$t_1^2 + 2t_1t_2 + t_2^2 = \delta^2$$

and hence

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

Namely, (3.1) is true for $n = 2$.

For the induction step, suppose (3.1) is true for n. If

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

then

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

By the induction hypothesis, we have that there exist non-zero polynomials $\{H_{n,j}(s_1, s_2, \cdots, s_n) : j = 0, 1, 2, \cdots, 2^{n-1}\}$ with real coefficients satisfying $H_{n,j}(s_1, s_2, \cdots, s_n)(j = 1, 2, \cdots, 2^{n-1})$ are homogeneous, $H_{n,2^{n-1}}(s_1, s_2, \cdots, s_n)$ is a monic polynomial of degree 2^{n-1}, and

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

Applying Newton binomial theory, we then get that

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

Taking squares of both sides of the above =, we arrive at the conclusion of Lemma 3.1 when n is replaced by $n + 1$. This completes the proof. □

The following conclusion results from the proof of Theorem 1 of [14] (c.f. also [11]):

Lemma 3.2. *Given $v, v' \in \mathbb{V}$. 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*

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

Proof. For completion, we present a proof here, which essentially comes from the proof of Theorem 1 of [14]. We see that

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

Similarly,

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

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

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

or

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

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., [15]), 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 3.3. *The Lebesgue's measure of the set of zeroes of any non-zero multivariate polynomial with real coefficients is zero.*

4 Proof of Theorem 2.2

In this section, we prove Theorem 2.2, the precise and 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 $\alpha_j \in \mathbb{R}(j = 1, 2, \cdots, m)$ 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 $j_0 \in \{1, 2, \cdots, m\}$.

Let $\{H_{n,j}(s_1, s_2, \cdots, s_n) : j = 0, 1, 2, \cdots, 2^{n-1}\}$ be the non-zero polynomials with real coefficients satisfying the conclusion of Lemma 3.1 with $n = mN$ and

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

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 $P(s_1, s_2, \cdots, s_n)$ with real coefficients such that

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

As a result, if $(x_1, x_2, \cdots, x_N)$ is any zero of (4.1), then $(x_1, x_2, \cdots, x_N)$ is an zero of (4.2). Note that $P(|x_1 - r_1|^2, \cdots, |x_i - r_j|^2, \cdots, |x_N - r_m|^2)$ is a polynomial of $(x_1, x_2, \cdots, x_N)$ with real coefficients. We obtain from Lemma 3.3 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

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

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

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

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. For instance, let $x = (\xi_1, \xi_2, \xi_3) \in \mathbb{R}^3$ and define

$$\mathbb{V}_G = \mathbb{V} \cap \operatorname{span}\left\{ \frac{\xi_1^i \xi_2^j \xi_3^k}{|x-r|^n} : i, j, k, n = 0, 1, 2, \cdots ; r \in \mathbb{R}^3 \right\}. \tag{5.1}$$

Applying Lemma 3.3, indeed, we obtain from the proof of Theorem 2.2 that Theorem 2.2 is also true when $\mathbb{V}_C$ is replaced by $\mathbb{V}_G$. Namely, we have

Theorem 5.1. *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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References

[1] H. Eschrig, *The Fundamentals of Density Functional Theory*, Teubner, Stuttgart, 1996.

[2] E. K. U. Gross and R. M. Dreizler (eds.), *Density Functional Theory*, Plenum Press, New York, 1995.

[3] N. Hadjisavvas and A. Theophilou, *Rigorous formulation of the Kohn-Sham theory*, Phy. Rev. A., **30** (1984), pp. 2183-2186.

[4] P. Hohenberg and W. Kohn, *Inhomogeneous gas*, Phys. Rev., **136** (1964), pp. B864-B871.

[5] F. Jensen, *Introduction to Computational Chemistry*, Wiley, New York, 1999.

[6] T. Kato, *On the eigenfunctions of many-particle systems in quantum mechanics*, Commun. Pure Appl. Math., **10** (1957), pp. 151-177.

[7] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. A, **140** (1965), pp. 4743-4754.

[8] E. S. Kryachko, *On the original proof by reductio ad absurdum of the Hohenberg-Kohn theorem for many-electron Coulomb systems*, Int. J. Quantum Chem., **103** (2005), pp. 818-823.

[9] E. S. Kryachko, *On the proof by reductio ad absurdum of the Hohenberg-Kohn theorem for ensembles of fractionally occupied states of Coulomb systems*, Int. J. Quantum Chem., **106** (2006), pp. 1795-1798.

[10] M. Levy, *University variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solutions of thev-representability problems*, Proc. Nat. Acad. Sci. USA, **76** (1979), pp. 6062-6065.

[11] E. H. Lieb, *Density functionals for Coulomb systems*, Int. J. Quantum Chem., **24** (1983), pp. 243-277.

[12] R. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press, London, 2004.

[13] R. G. Parr and W. T. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.

[14] R. Pino, O. Bokanowski, E. V. Ludeña, and R. L. Boada, *A re-statement of the Hohenberg-Kohn theorem and its extension to finite subspaces*, Theor. Chem. Account, **118** (2007), pp. 557-561.

[15] F. Smithies, *A forgotten paper on the fundamental theorem of algebra*, Notes Rec. R. Soc. Lond., **54** (2000), pp. 333-341.

[16] W. Szczepanik, M. Dulak, and T. A. Wesolowski, *Comment on "On the original proof by reductio ad absurdum of the Hohenberg-Kohn theorem for many-electron Coulomb systems"*, Int. J. Quantum Chem., **107** (2007), pp. 762-763.