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Citation: *J. Chem. Phys.* **149**, 204112 (2018); doi: 10.1063/1.5055814

View online: <https://doi.org/10.1063/1.5055814>

View Table of Contents: <http://aip.scitation.org/toc/jcp/149/20>

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Density functional theory from spherically symmetric densities

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(Received 11 September 2018; accepted 15 November 2018; published online 30 November 2018)

In a recent paper, Theophilou [J. Chem. Phys. **149**, 074104 (2018)] proved that in molecules and solids, a set of spherically symmetric densities determines uniquely the external potential. Here an alternative derivation of Theophilou's new theorem is presented. A somewhat more general version is also proved via constrained search. Euler equations and Kohn-Sham equations are derived for spherically symmetric densities. Published by AIP Publishing. <https://doi.org/10.1063/1.5055814>

I. INTRODUCTION

Density functional theory (DFT) provides one of the most powerful and efficient methods for studying electron structures. The main reason of this success is that in DFT the electron density is the basic variable. According to the Hohenberg-Kohn theorem,¹ the density determines uniquely the external potential. Consequently, the density is sufficient to determine all properties of the system.

In certain cases, only a part of the density is enough. Theophilou^{2,3} proved that the total electron density of an atom is determined by the l-shell part of the density. Examples can be found in Refs. 4 and 5.

Recently, Theophilou⁶ introduced a novel version of the density functional theory. He proved that in atoms, molecules, and solids, only a set of the spherical parts of the density around each nucleus determines uniquely the external potential.

Here we give an alternative proof to this theorem and extend the theory using constrained search.^{12,13} Then we derive Euler equations and generate Kohn-Sham (KS) equations via constrained search.

Although DFT is an exact theory, the exact form of the exchange-correlation functional is unknown and approximations should be applied in calculations. In this new formalism, the functionals depend on the set of spherically symmetric densities instead of the density. That is, here we have different functionals. It might happen that these functionals can be more easily and/or accurately approximated than the well-known standard functionals.

The paper is organized as follows: Section II treats Kato's theorem and provides an alternative proof of Theophilou's theorem 1. Section III presents the Hohenberg-Kohn theorems to the set of spherically symmetric densities via constrained search. In Sec. IV, the Kohn-Sham equations for the set of spherically symmetric densities are derived. Section V is dedicated to discussion.

II. KATO'S THEOREM

If we consider atoms, molecules, or solids, the Hamiltonian is

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$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}, \quad (1)$$

where \hat{T} and \hat{V}_{ee} are the kinetic energy and the electron-electron energy operators and

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i), \quad (2)$$

$$v(\mathbf{r}) = - \sum_{\beta=1}^M \frac{Z_{\beta}}{|\mathbf{r} - \mathbf{R}_{\beta}|}. \quad (3)$$

\mathbf{R}_{β} and Z_{β} are the position vectors and atomic numbers of the nuclei, while N and M stand for the number of electrons and nuclei. Denote $\varrho(\mathbf{r})$ as the electron density and define the spherical average of $\varrho(\mathbf{r})$ with respect to the nucleus β as

$$\bar{\varrho}_{\beta}(r_{\beta}) = \frac{1}{4\pi} \int_{\Omega_{\beta}} \varrho(\mathbf{r}) d\Omega_{\beta}, \quad (4)$$

where $r_{\beta} = |\mathbf{r} - \mathbf{R}_{\beta}|$ and Ω_{β} stands for the angles.

Consider the following theorem:

Theophilou's theorem 1. The set of densities $\bar{\varrho}_{\beta}(r_{\beta})$ ($\beta = 1, \dots, M$) determines uniquely the external potential.

The proof in Ref. 6 proceeds by *reductio ad absurdum*. Here an alternative proof is provided using Kato's theorem.

It was Bright Wilson⁷ who first utilized Kato's theorem to prove that the electron density is sufficient in principle to determine all molecular properties of a Coulomb system.

Kato's theorem⁸ formulated for the density^{9,10} can be written as

$$Z_{\beta} = - \frac{1}{2\varrho(\mathbf{r} = \mathbf{R}_{\beta})} \left. \frac{\partial \bar{\varrho}_{\beta}(r_{\beta})}{\partial r_{\beta}} \right|_{r_{\beta}=0}. \quad (5)$$

The partial derivatives are taken at the nuclei β . So the cusps of the density reveal the position of the nuclei and the atomic numbers Z_{β} . The number of electrons can be easily obtained by integrating the density

$$N = \int \varrho(\mathbf{r}) d\mathbf{r}. \quad (6)$$

We can now use Kato's theorem for the following proof:

Alternative proof of Theophilou's theorem 1. Equation (5) can be rewritten as

$$\left. \frac{\partial \bar{\varrho}_{\beta}(r_{\beta})}{\partial r_{\beta}} \right|_{r_{\beta}=0} = -2Z_{\beta} \bar{\varrho}_{\beta}(r_{\beta} = 0). \quad (7)$$

Here we utilized the result that $\varrho(\mathbf{r} = \mathbf{R}_\beta) = \bar{\varrho}_\beta(r_\beta = 0)$, that is, the density and the spherical average of the density takes the same value at the nucleus; see Eq. (8) in Ref. 11. The consequence of Eq. (7) is that the set of densities $\bar{\varrho}_\beta(r_\beta)$ ($\beta = 1, \dots, M$) yields Z_β , \mathbf{R}_β , M , and N as

$$N = 4\pi \int \bar{\varrho}_\beta(r_\beta) r_\beta^2 dr_\beta. \quad (8)$$

Note that the integral in Eq. (8) should produce the same N for any β . Hence, we are aware of the external potential $v(\mathbf{r})$ in (3).

III. HOHENBERG-KOHN THEOREMS OF THE SET OF SPHERICALLY SYMMETRIC DENSITIES VIA CONSTRAINED SEARCHES

First of all, we can observe that Theophilou's theorem holds for external potentials more general than (3). It is true for

$$v(\mathbf{r}) = \sum_{\beta=1}^M v_\beta(r_\beta), \quad (9)$$

that is, for a potential that is given by a sum of terms and each term v_β depends only on the distance from the nucleus β .

Now, of course, Kato's theorem is not valid as the potential (9) can be different from (3). Still, Theophilou's theorem holds.

Theorem 1. The set of spherically symmetric densities $\{\bar{\varrho}\}$ determines the external potential.

Proof of Theorem 1. The set of spherically symmetric densities $\bar{\varrho}_1, \bar{\varrho}_2, \dots, \bar{\varrho}_M$ is shortly denoted by $\{\bar{\varrho}\}$.

Constrained search^{12,13} is applied to avoid the v -representability problem. The functionals are defined for the sets of spherically symmetric densities. The constrained-search specifies the functional Q as

$$Q[\{\bar{\varrho}\}] = \min_{\Psi \rightarrow \{\bar{\varrho}\}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \quad (10)$$

The minimum is searched with the constraint that each wave function generates the set $\{\bar{\varrho}\}$. Denoting by Ψ_{min} the wave function for which the minimum is attained, we observe that the set $\{\bar{\varrho}\}$ determines Ψ_{min} . Using this wave function, all properties of the system may be computed including the external potential and the density. So we arrived at the following corollary:

Corollary. There exists a one-to-one map between the density and the set of spherically symmetric densities $\{\bar{\varrho}\}$.

Theorem 2. For an N -electron system with external potential v , the energy of a trial set of N -electron spherically symmetric densities $\{\bar{\varrho}\}$ is always greater than or equal to the true ground-state energy of the system.

Proof of Theorem 2. The energy functional of the system takes the form

$$E[\{\bar{\varrho}\}] = Q[\{\bar{\varrho}\}] + 4\pi \sum_{\beta=1}^M \int \bar{\varrho}_\beta(r_\beta) v_\beta(r_\beta) r_\beta^2 dr_\beta, \quad (11)$$

where in the last term the form (9) of the external potential was utilized. The energy can be obtained by minimization

$$E = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle \quad (12)$$

that can be rewritten by nested minimization

$$E = \min_{\{\bar{\varrho}\}} \left\{ \min_{\Psi \rightarrow \{\bar{\varrho}\}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + 4\pi \sum_{\beta=1}^M \int \bar{\varrho}_\beta(r_\beta) v_\beta(r_\beta) r_\beta^2 dr_\beta \right\}. \quad (13)$$

If the outer minimization is not complete, the energy is very large. Thus,

$$\begin{aligned} E_0 = E[\{\bar{\varrho}_0\}] &= Q[\{\bar{\varrho}_0\}] + 4\pi \sum_{\beta=1}^M \int \bar{\varrho}_{\beta,0}(r_\beta) v_{\beta,0}(r_\beta) r_\beta^2 dr_\beta \\ &\leq Q[\{\bar{\varrho}\}] + 4\pi \sum_{\beta=1}^M \int \bar{\varrho}_\beta(r_\beta) v_{\beta,0}(r_\beta) r_\beta^2 dr_\beta = E[\{\bar{\varrho}\}]. \end{aligned} \quad (14)$$

The subscript 0 refers to the minimization set.

Supposing that the functional (10) is functionally differentiable, we are led to the Euler equations

$$v_\beta(r_\beta) = -\frac{\delta Q}{\delta \bar{\varrho}_\beta}, \quad \beta = 1, \dots, M, \quad (15)$$

up to a constant. Observe that we have several Euler equations. The number of equations is equal to the number of the nuclei. In the original theory, there is only one Euler equation.

IV. KOHN-SHAM EQUATIONS FOR SET OF SPHERICALLY SYMMETRIC DENSITIES

Kohn-Sham equations¹⁴ are extremely useful for calculations. Therefore, it is worthwhile to generate a non-interacting system. Construct the Hamiltonian as

$$\hat{H}^0 = \hat{T} + \sum_{i=1}^N w(\mathbf{r}_i), \quad (16)$$

$$w(\mathbf{r}) = \sum_{\beta=1}^M w_\beta(r_\beta). \quad (17)$$

The non-interacting Hamiltonian \hat{H}^0 is defined so that the set of spherically symmetric densities coming from the non-interacting wave function Φ is the same as the given set of the true interacting system. Moreover, the non-interacting (Kohn-Sham) potential w (17) is similarly partitioned as the external potential (3). For a nondegenerate state, the non-interacting wave function Φ can be simply expressed with one-particle functions and the Kohn-Sham equations can be readily gained from the non-interacting Schrödinger equation as

$$\left[-\frac{1}{2} \nabla^2 + w(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i, \quad (18)$$

where density ϱ is given by

$$\varrho = \sum_{i=1}^N |\phi_i|^2. \quad (19)$$

To derive the Kohn-Sham potential w , we define the non-interacting kinetic energy functional for the sets

$$K[\{\bar{\varrho}\}] = \min_{\Phi \rightarrow \{\bar{\varrho}\}} \langle \Phi | \hat{T} | \Phi \rangle. \quad (20)$$

The minimization is done over all non-interacting wave functions Φ generating the same set of spherically symmetric densities as the true interacting system possesses. Then, the total energy of the KS system takes the form

$$E_s[\{\bar{\varrho}\}] = K[\{\bar{\varrho}\}] + 4\pi \sum_{\beta=1}^M \int \bar{\varrho}_{\beta}(r_{\beta}) w_{\beta}(r_{\beta}) r_{\beta}^2 dr_{\beta}. \quad (21)$$

Supposing that the functional (20) is functionally differentiable, we are led to the non-interacting Euler equations

$$w_{\beta}(r_{\beta}) = -\frac{\delta K}{\delta \bar{\varrho}_{\beta}}, \quad \beta = 1, \dots, M, \quad (22)$$

up to a constant. Define now the Hartree and exchange-correlation functional $E_{Hxc}[\{\bar{\varrho}\}]$ as the difference of the true kinetic plus electron-electron functional $Q[\{\bar{\varrho}\}]$ and the non-interacting kinetic energy functional $K[\{\bar{\varrho}\}]$

$$E_{Hxc}[\{\bar{\varrho}\}] = Q[\{\bar{\varrho}\}] - K[\{\bar{\varrho}\}]. \quad (23)$$

Then from the Euler equations (15) and (22), we are led to

$$w_{\beta}(r_{\beta}) = v_{\beta}(r_{\beta}) + v_{Hxc,\beta}(r_{\beta}), \quad \beta = 1, \dots, M, \quad (24)$$

where the Hartree plus exchange-correlation part is defined as

$$v_{Hxc,\beta}(r_{\beta}) = \frac{\delta E_{Hxc}}{\delta \bar{\varrho}_{\beta}}, \quad \beta = 1, \dots, M. \quad (25)$$

Substituting the terms $w_{\beta}(r_{\beta})$ in (24) into Eq. (17), we arrive at the Kohn-Sham potential w .

V. DISCUSSION

It is enlightening to compare the functionals Q and K with the corresponding constrained-search functionals of the original DFT. The functional $F[\varrho]$ is defined as

$$F[\varrho] = \min_{\Psi \rightarrow \varrho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \quad (26)$$

The minimum is searched over all over wave functions Ψ leading to the given density ϱ . The non-interacting kinetic energy of the original DFT is defined as

$$T_s[\varrho] = \min_{\Phi \rightarrow \varrho} \langle \Phi | \hat{T} | \Phi \rangle. \quad (27)$$

The minimization is over all wave functions providing the given density ϱ .

Observe that the functionals Q (K) and F (T_s) are different. While F and T_s are functionals of the density $\varrho(\mathbf{r})$, Q and K are functionals of the set of spherically symmetric densities $\{\bar{\varrho}\}$. However, because of the corollary to Theorem 1, Q and F should take the same value at the ground state of the system. In addition, K and T_s are also equal at the ground state.

It is worth mentioning that the present formalism can also be used in case of degenerate states. As Kato's theorem is

true for degenerate states as well, the proof of Theophilou's theorem is also valid. The constrained search technique is also well-founded for degenerate states. However, it is more appropriate to follow Theophilou's proposal.⁶ His subspace theory has several favourable properties. For example, the subspace density has the symmetry of the external potential. Kato's theorem has been derived for the subspace densities.¹⁵ The functionals Q and K can be defined via constrained search as functionals of the subspace density.

As the exchange-correlation functional is not exactly known, approximations should be used in computations. Functionals depend on the set of spherically symmetric densities instead of the density in this formalism. Since we have here different functionals, the approximations should also be different. Maybe, one can find approximations that are more accurate than the well-known standard ones.

Numerical methods based on the special form of the external potential (9) have been applied for a long time. The fact that the density close to a nucleus is roughly spherically symmetric is utilized in the so-called muffin-tin approximation proposed by Slater.¹⁶ For a detailed discussion of the subject, see the book by Vitos.¹⁷ These methods are used to compute electron structures of solids. It is worth considering similar methods in molecular applications in the light of the theory based on spherically symmetric densities.

In summary, an alternative derivation of Theophilou's theorem is provided. A somewhat more general version is also proved utilizing constrained search. Euler equations and Kohn-Sham equations are derived for spherically symmetric densities.

ACKNOWLEDGMENTS

This research was supported by the National Research, Development and Innovation Fund of Hungary, financed under 123988 funding scheme and by the EU-funded Hungarian Grant (EFOP-3.6.2-16-2017-00005).

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