Abstract

Recently, Theophilou (J. Chem. Phys. 149 074104 (2018)) showed that a set of spherically symmetric densities determines uniquely the external potential in molecules and solids. Here, spherically symmetric Kohn-Sham-like equations are derived. The spherical densities can be expressed with radial wave functions. Expression for the total energy is also presented.
I. INTRODUCTION

Recently, Theophilou [1] proposed a novel form of the density functional theory. He showed that a set of the spherical averages of the density around the nuclei determines uniquely the external potential in case of atoms, molecules or solids. Afterwards [2], an alternative proof to this theorem was put forward and the theory was generalized via constrained search. Euler equations have also been derived. There are as many Euler equations as the number of nuclei. It has also been shown [3] that any of the spherically symmetric densities obeys a Schrödinger-like differential equation which is equivalent to the Euler equation of this density. The exact effective potential is presented explicitly in terms of wave-function expectation values.

The Kohn-Sham equations have been obtained via constrained search [2]. The Kohn-Sham potential is proved to be a functional of the set of spherically symmetric densities. While the Euler equations are spherically symmetric, the Kohn-Sham equations do not have spherical symmetry.

It is natural to ask the question whether it is possible to derive spherically symmetric Kohn-Sham equations that generate the spherically symmetric densities. Here we show that the answer is affirmative. We argue that the reduction to spherically symmetric equations leads to an enormous simplification provided that an accurate enough approximation to the unknown functional is available.

The following arrangement is adapted. The main results of the papers [1] and [2] are summarized in the following section. The spherical Kohn-Sham-like equations are derived in Section 3. The last section is dedicated to discussion. The classical electron-electron potential and energy are compared with the usual ones in the appendix.

II. DFT WITH SPHERICALLY AVERAGED DENSITIES

The Hamiltonian has the form

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V},
\]

(1)

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

\[
\hat{V} = \sum_{i=1}^{N} v(r_i)
\]

(2)
\( v(r) = -\sum_{\beta=1}^{M} \frac{Z_{\beta}}{|r - R_{\beta}|} \)  

(3)

is the external potential. \( N, M, Z_{\beta} \) and \( R_{\beta} \) denote the number of electrons, the number of nuclei, the atomic number and the position vector of the nuclei, respectively.

Theophilou constructed [1] the spherical average of the electron density \( \varrho(r) \) with respect to the nucleus \( \beta \)

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

(4)

where \( \Omega_{\beta} \) denotes the angles. Let the symbol \( \{ \bar{\varrho} \} \) stand for the set of spherically symmetric densities \( \bar{\varrho}_{1}, \bar{\varrho}_{2}, ..., \bar{\varrho}_{M} \). It has been proved that this set determines the external potential. A functional \( Q \) of the set has been defined [2] using the constrained search of Levy [4] and Lieb [5] as

\[ Q[\{ \bar{\varrho} \}] = \min_{\Psi \rightarrow \{ \bar{\varrho} \}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \]

(5)

where the minimum is searched with the constraint that each wave function generates the set \( \{ \bar{\varrho} \} \). It has also been proved that there exists a one-to-one map between the density and the set of spherically symmetric densities \( \{ \bar{\varrho} \} \). If \( Q[\{ \bar{\varrho} \}] \) is functionally differentiable we can arrive at the Euler equations

\[ v_{\beta}(r_{\beta}) = -\frac{\delta Q}{\delta \bar{\varrho}_{\beta}}; \quad \beta = 1, ..., M \]

(6)

up to a constant. There are as many Euler equations as the number of the nuclei.

The non-interacting Hamiltonian \( \hat{H}^{0} \) has the form

\[ \hat{H}^{0} = \hat{T} + \sum_{i=1}^{N} w(r_{i}), \]

(7)

where

\[ w(r) = \sum_{\beta=1}^{M} w_{\beta}(r_{\beta}). \]

(8)

The potential \( w \) is determined by the condition that the set \( \{ \bar{\varrho} \} \) calculated with the non-interacting wave function \( \Phi \) be the same as the original set [2].

In the absence of degeneracy \( \Phi \) can be given by one-particle functions and the Kohn-Sham equations takes the form

\[ \left[ -\frac{1}{2} \nabla^2 + w(r) \right] \phi_{i} = \varepsilon_{i} \phi_{i}, \]

(9)
where the density \( \varrho \) is

\[
\varrho = \sum_{i=1}^{N} |\phi_i|^2. \tag{10}
\]

The non-interacting kinetic energy functional has been defined as

\[
K[\{\varrho\}] = \min_{\Phi \to \{\varrho\}} \langle \Phi | \hat{T} | \Phi \rangle. \tag{11}
\]

The minimization is done over all wave functions \( \Phi \) that yield the same set of spherically symmetric densities as the true interacting system. Writing the total energy of the non-interacting system in the form

\[
E_a[\{\varrho\}] = K[\{\varrho\}] + 4\pi \sum_{\beta=1}^{M} \int \varrho_\beta(r_\beta) w_\beta(r_\beta) r_\beta^2 dr_\beta \tag{12}
\]

the non-interacting Euler equations can be gained

\[
w_\beta(r_\beta) = -\frac{\delta K}{\delta \varrho_\beta}; \quad \beta = 1, \ldots, M \tag{13}
\]

up to a constant.

The difference of \( Q[\{\varrho\}] \) and \( K[\{\varrho\}] \) has been defined as the Hartree and exchange-correlation functional \( E_{Hxc}[\{\varrho\}] \)

\[
E_{Hxc}[\{\varrho\}] = Q[\{\varrho\}] - K[\{\varrho\}]. \tag{14}
\]

Comparison of the Euler equations (10) and (13) yields

\[
w_\beta(r_\beta) = v_\beta(r_\beta) + v_{Hxc,\beta}(r_\beta); \quad \beta = 1, \ldots, M. \tag{15}
\]

The last term in Eq. (15)

\[
v_{Hxc,\beta}(r_\beta) = \frac{\delta E_{Hxc}}{\delta \varrho_\beta}; \quad \beta = 1, \ldots, M \tag{16}
\]

stands for the Hartree and exchange-correlation potential. Now, we can compute the Kohn-Sham potential \( w \) in Eq. (8) using \( w_\beta(r_\beta) \) in (15).

### III. SPHERICAL KOHN-SHAM-LIKE EQUATIONS

Define the functional

\[
K_\alpha[\{\varrho\}] = \min_{\Phi \to \{\varrho\}} \langle \Phi | \hat{T} | \Phi \rangle. \tag{17}
\]
The minimization is done over all wave functions \( \Phi \) that yield the spherically averaged density \( \bar{\rho}_\alpha \). That is, we minimize the functional

\[
\langle \Phi | \hat{T} + \hat{U}_\alpha | \Phi \rangle,
\]

where

\[
U_\alpha(r_1, \ldots, r_N) = \sum_{i=1}^{N} u_\alpha(r^i_\alpha)
\]

and

\[
r^i_\alpha = |r_i - R_\alpha|.
\]

Expression (18) can be rewritten as

\[
\langle \Phi | \hat{T} | \Phi \rangle + 4\pi \int \bar{\rho}_\alpha(r_\alpha) u_\alpha(r_\alpha) r^2_\alpha dr_\alpha.
\]

The minimization leads to the Kohn-Sham equations

\[
\left[ -\frac{1}{2} \nabla^2 + u_\alpha(r_\alpha) \right] \psi^\alpha_i = \epsilon^\alpha_i \psi^\alpha_i.
\]

The Kohn-Sham potential \( u_\alpha \) depends only on the radial distance from the center \( \alpha \). That is, we have “atomic” Kohn-Sham equations. Introducing radial wave functions \( P^\alpha_i \), the kinetic energy \( K_\alpha \) can be rewritten as

\[
K_\alpha = -\frac{1}{2} \sum_i \int P^\alpha_i \left( \frac{d^2 P^\alpha_i}{dr^2_\alpha} - \frac{l_i(l_i + 1)}{r^2_\alpha} P^\alpha_i \right) dr_\alpha.
\]

The variation leads to the radial equations

\[
-\frac{1}{2} \frac{d^2 P^\alpha_i}{dr^2_\alpha} + \frac{l_i(l_i + 1)}{2r^2_\alpha} P^\alpha_i + u_\alpha(r_\alpha) P^\alpha_i = \epsilon^\alpha_i P^\alpha_i.
\]

The spherically averaged density \( \bar{\rho}_\alpha \) can be expressed with the radial wave functions \( P^\alpha_i \)

\[
4\pi r^2_\alpha \bar{\rho}_\alpha(r_\alpha) = \sum_i \lambda_i [P^\alpha_i(r_\alpha)]^2.
\]

\( \lambda_i \) are the occupation numbers and the sum goes for the orbitals. (For convenience only one subscript is applied.)

The radial equations (24) can be derived in another way. First, we have to write the total energy of the original interacting system with the spherically averaged densities:

\[
E = \tilde{K} + \tilde{E}_{Hxc} - 4\pi \sum_{\alpha=1}^{M} \int \bar{\rho}_\alpha(r_\alpha) \frac{Z_\alpha}{r_\alpha} r^2_\alpha dr_\alpha.
\]
Define $Z$ as the sum of the atomic numbers
\[ Z = \sum_{\alpha=1}^{M} Z_{\alpha}. \]  
(27)

For a neutral system $Z = N$. It is convenient to define the non-interacting kinetic energy $\tilde{K}$ as a sum of spherical terms $K_{\alpha}$ (Eq. (23)). However, as all these terms are constructed for all the $N$ electrons, we have to multiply them with the factor $Z_{\alpha}/Z$.
\[ \tilde{K} = \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{Z} K_{\alpha}. \]  
(28)

Consider the partition of $\tilde{E}_{Hxc}$
\[ \tilde{E}_{Hxc} = \tilde{J} + \tilde{E}_{xc}. \]  
(29)

Define the “spherical” classical Coulomb energy \[ \tilde{J} = 2\pi \sum_{\alpha} \frac{Z_{\alpha}}{Z} \int_{0}^{\infty} \tilde{\rho}(r_{\alpha}) \tilde{u}_{J}^{\alpha}(r_{\alpha}) r_{\alpha}^{2} dr_{\alpha}, \]  
(30)

where
\[ \tilde{u}_{J}^{\alpha}(r_{1}) = 4\pi \left( \frac{1}{r_{1}} \int_{0}^{r_{1}} \tilde{\rho}(r_{2}) r_{2}^{2} dr_{2} + \int_{r_{1}}^{\infty} \tilde{\rho}(r_{2}) r_{2} dr_{2} \right). \]  
(31)

We emphasize that $\tilde{J}$ differs from the usual classical Coulomb energy. Their relationship is presented in the appendix. The exchange-correlation term $\tilde{E}_{xc}$ is defined by Eqs. (26) and (29). Naturally, $\tilde{E}_{xc}$ is also different from the standard exchange-correlation energy. It can be rewritten as
\[ \tilde{E}_{xc} = \sum_{\alpha} \frac{Z_{\alpha}}{Z} \tilde{E}_{xc}. \]  
(32)

We emphasize that $\tilde{E}_{xc}$ is a functional of all spherically averaged densities. It cannot be written as a sum of terms that depend on only one of the spherically averaged densities.

The variation of the total energy with respect to the radial wave function $P_{i}^{\alpha}$ leads to the radial equations
\[ \frac{Z_{\alpha}}{Z} \left[ -\frac{1}{2} \frac{d^{2} P_{i}^{\alpha}}{dr_{i}^{2}} + \frac{l_{i}(l_{i} + 1)}{2r_{i}^{2}} P_{i}^{\alpha} + (\tilde{u}_{J}^{\alpha} + \tilde{u}_{xc}^{\alpha}) P_{i}^{\alpha} \right] - \frac{Z_{\alpha}}{r_{i}} P_{i}^{\alpha} = \tilde{\epsilon}_{i}^{\alpha} P_{i}^{\alpha}, \]  
(33)

where
\[ \tilde{u}_{xc}^{\alpha} = \frac{\delta \tilde{E}_{xc}}{\delta \tilde{\rho}_{\alpha}}. \]  
(34)
Eq. (33) can be rewritten as

$$-\frac{1}{2} \frac{d^2 P_\alpha}{dr_\alpha^2} + \frac{l_i(l_i + 1)}{2 r_\alpha^2} P_\alpha + (\bar{u}_j^\alpha + \bar{u}_{xc}^\alpha) P_\alpha - \frac{Z}{r_\alpha} P_\alpha = \epsilon_i^\alpha P_\alpha, \quad (35)$$

where

$$\epsilon_i^\alpha = \frac{Z}{Z_\alpha} \epsilon_i^\alpha. \quad (36)$$

Comparing Eqs. (24) and (35) we obtain

$$u_\alpha(r_\alpha) = \bar{u}_j^\alpha(r_\alpha) + \bar{u}_{xc}^\alpha(r_\alpha) - \frac{Z}{r_\alpha}. \quad (37)$$

IV. DISCUSSION

As we use the set of spherically averaged densities as basic variable we write the total energy of the original interacting system with the spherically averaged densities. This form (Eq. (26)) is different from the usual partition of the total energy

$$E = T_s + J + E_{xc} - 4\pi \sum_{\alpha=1}^{M} \int \bar{\sigma}_\alpha(r_\alpha) \frac{Z_\alpha}{r_\alpha^2} \frac{r_\alpha^2}{dr_\alpha}, \quad (38)$$

where $T_s$, $J$ and $E_{xc}$ are the standard non-interacting kinetic, the classical Coulomb repulsion and the exchange-correlation energies, respectively. The last (external) term is the same in Eqs. (26) and (38), the others are different. Only their sum is the same:

$$\tilde{K} + \tilde{J} + \tilde{E}_{xc} = T_s + J + E_{xc} \quad (39)$$

Our main result is Eq. (35). Note that in all these radial equations the “external” term is the same. We first might think that a term with $Z_\alpha$ instead of $Z$ would be more appropriate. However, in that case we would have an “atom” with $N$ electrons and atomic number $Z_\alpha$. As $N$ is generally much larger than $Z_\alpha$, we will not have a bound system. So, our equation with $Z$ is correct. Certainly, we have an “atom” with atomic number $Z$ only in the asymptotic limit $r_\alpha \rightarrow \infty$, that is, very far from any nucleus. All other value of $r_\alpha$ the “effect” of the nuclei is different from $-Z/r_\alpha$. This difference is included in the exchange-correlation potential $\bar{u}_{xc}$. That means that in our case exchange-correlation is not universal, it depends on all atomic numbers. Of course, it is not surprising as we do not have independent atoms, the atomic-like equations cannot be independent, they are related via exchange-correlation.
Appendix

Consider the classical Coulomb interaction potential

\[ v_J(r_1) = \int dr_2 \frac{\varrho(r_2)}{r_{12}}. \]  

(40)

The density can be expanded around a center \( \alpha \)

\[ \varrho(r) = \bar{\varrho}(r) + \sum_{l>0,m} \varrho_{lm}(r) Y_{lm}(\hat{r}). \]  

(41)

Substitution of the expansion

\[ \frac{1}{r_{12}} = \sum_{lm} \frac{4\pi}{2l+1} r_l^l Y^*_{lm}(\hat{r}_1) Y_{lm}(\hat{r}_2) \]  

(42)

into \( v_J \) we obtain

\[ v_J(r_\alpha) = u_\alpha J(r_\alpha) + \sum_{l>0,m} v_{lm}^J(r_\alpha) Y_{lm}(\hat{r}_\alpha), \]  

(43)

where \( u_\alpha^J(r_\alpha) \) is given by Eq. (31) and

\[ v_{lm}^J(r_\alpha) = \frac{4\pi}{2l+1} \left( \frac{1}{r_{1l+1}} \int_0^{r_1} \varrho_{lm}(r_2) r_{2l}^{l+2} dr_2 + \int_{r_1}^{\infty} \varrho_{lm}(r_2) \frac{r_l^l}{r_{2l-1}^l} dr_2 \right). \]  

(44)

Using Eq. (27) we can rewrite Eq. (43) as

\[ v_J(r) = \frac{1}{Z} \sum_\alpha Z_\alpha v_J(r_\alpha) = \frac{1}{Z} \sum_\alpha Z_\alpha \bar{v}_J^\alpha(r_\alpha) + \frac{1}{Z} \sum_\alpha Z_\alpha \sum_{l>0,m} v_{lm}^J(r_\alpha) Y_{lm}(\hat{r}_\alpha). \]  

(45)

The first term in Eq. (45) is the spherical Hartree potential proposed by Theophilou

\[ v_J^{\text{Theo}}(r) = \sum_\alpha v_J^{\text{Theo}}(r_\alpha) \]  

(46)

\[ v_J^{\text{Theo}}(r_\alpha) = \frac{Z_\alpha}{Z} \bar{u}_J^\alpha((r_\alpha). \]  

(47)

That is, the usual Hartree potential can be written as

\[ v_J(r) = v_J^{\text{Theo}}(r) + \tilde{v}_J(r) \]  

(48)

with

\[ \tilde{v}_J(r) = \frac{1}{Z} \sum_\alpha Z_\alpha \sum_{l>0,m} v_{lm}^J(r) Y_{lm}(\hat{r}_\alpha). \]  

(49)
The classical Coulomb interaction energy is given by
\[ J = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varrho(r_1) \varrho(r_2)}{r_{12}} = \frac{1}{2} \int d\mathbf{r}_1 \varrho(r_1) v_J(r_1). \]  
(50)

Substituting \( v_J \) into \( E_J \) we obtain
\[ J = \tilde{J} + \sum_{l>0,m} E_{Jlm} \],  
(51)

where \( \tilde{J} \) (Eq. (30)) is the spherical Hartree energy defined by Theophilou [1] and
\[ E_{Jlm} = 2\pi \int_0^\infty \varrho_{lm}(r) v_{Jlm}^*(r) r^2 dr. \]  
(52)

\( E_J \) can also be written as
\[ J = \tilde{J} + \tilde{E}_J, \]  
(53)

where
\[ \tilde{E}_J = \sum_{l>0,m} E_{Jlm}^* . \]  
(54)

That is, both the usual hartree potential and the energy are different from the spherical forms defined by Theophilou [1] and applied here.

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