Orbital-free spherical density functional theory

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Abstract

Recently, it has been proved that a set of spherically symmetric densities uniquely
determines the Coulomb external potential. Utilizing this theorem, a previous method
is extended to construct an orbital-free density functional theory. Auxilary spheri-
cal non-interacting systems and Kohn–Sham-like equations are constructed. A set of
spherical generating functions are defined. These functions have two extra variables
and are reduced to the set of spherically symmetric densities if the extra variables
are equal to zero. Euler equations are rewritten as Schrödinger-like equations for
the square root of the spherically symmetric generating functions. Generalized Pauli
potentials are defined, and it is shown that these potentials can be calculated in the
knowledge of the generating functions. The Euler equations can be solved with these
Pauli potentials.

1 Introduction

In density functional theory (DFT), the key variable is the density [1, 2]. The ground-
state density alone in principle determines all properties of the system. There are
cases when even a part of the density has this remarkable property [3–7]. Recently,
Theophilou [8] proved an even more fascinating statement: the spherical averages
of the ground-state density around the nuclei determine uniquely the external poten-

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tial of molecules and solids. Later, the present author provided an alternative proof to Theophilou's theorem, extended the theory [9, 10] and formalized the spherical potential functional theory [11]. Spherically symmetric Euler equations have been derived [9, 10]. It has been shown that each spherically averaged density satisfies a Schrödinger-like differential equation [12].

In this paper, an orbital-free scheme is derived taking advantage of the spherical symmetry. In standard DFT, the Euler equation is often written as

$$\frac{\delta T_s}{\delta \varrho} + v_{KS} = \mu, \tag{1}$$

where T_s, v_{KS} and μ are the non-interacting kinetic energy, the Kohn–Sham (KS) potential and the chemical potential, respectively. The Kohn–Sham (KS) potential is generally written as a sum of the external v, the classical Coulomb v_J and the exchange-correlation v_{xc} potentials:

$$v_{KS} = v + v_J + v_{xc} \tag{2}$$

Partitioning T_s as

$$T_s = T_w + T_p \tag{3}$$

Equation (1) takes the form

$$\frac{\delta T_w}{\delta \varrho} + v_p + v_{KS} = \mu. \tag{4}$$

T_w is the full Weizsäcker kinetic energy [13]

$$T_w = \frac{1}{8} \int \frac{|\nabla \varrho|^2}{\varrho} d\mathbf{r} \tag{5}$$

and T_p is the Pauli energy [14–16] resulting from the Pauli principle. Using the functional derivatives

$$\frac{\delta T_w}{\delta \varrho} = \frac{1}{8} \left| \frac{\nabla \varrho}{\varrho} \right|^2 - \frac{1}{4} \frac{\nabla^2 \varrho}{\varrho} = \varrho^{-1/2} \left(-\frac{1}{2} \nabla^2 \right) \varrho^{1/2} \tag{6}$$

and

$$v_p = \frac{\delta T_p}{\delta \varrho}, \tag{7}$$

where v_p is the Pauli potential and Eq. (1) can be rewritten as a Schrödinger-like equation for the square root of the density

$$\left[-\frac{1}{2} \nabla^2 + v_p + v_{KS} \right] \varrho^{1/2} = \mu \varrho^{1/2}. \tag{8}$$

The density can be determined solving the Euler equation (1) [or Eq. (8)]. As this equation does not contain the KS orbitals, this way of obtaining the solution is referred to as the orbital-free scheme. This approach has a considerable advantage as only the single Euler equation has to be solved contrary to the KS method. The orbital-free approach implies enormous simplification in the calculations, because there might be many KS equations if a large system with a lot of electrons is considered.

However, the orbital-free procedure is hindered by the fact that the kinetic energy functional is unknown. Therefore, the Pauli energy and potential are also unknown. But, as the knowledge of the kinetic energy functional would lead to an important progress in DFT calculations, great efforts have been taken in this direction (see e. g. [17–21]).

Not all orbital-free methods utilize the non-interacting KS system. In the true interacting system the kinetic energy is different from the non-interacting one. In studying the kinetic energy, information-theoretical concepts have turned to be extremely useful. There is a relationship between the quantum mechanical kinetic energy and Fisher information [22]:

$$E^{\text{kin}} = \frac{1}{8} \int \frac{|\nabla \varrho(\mathbf{r})|^2}{\varrho(\mathbf{r})} d\mathbf{r} + \frac{1}{8} \int \varrho(\mathbf{r}) I_F^f(\mathbf{r}) d\mathbf{r}. \tag{9}$$

The first term—the Weizsäcker kinetic energy T_w—is proportional to the Fisher information I

$$T_w = \frac{1}{8} I. \tag{10}$$

$$I_F^f(\mathbf{r}) = \int \frac{[\nabla_\mathbf{r} f(\mathbf{r}_2, \ldots, \mathbf{r}_N)|\mathbf{r})]^2}{f(\mathbf{r}_2, \ldots, \mathbf{r}_N)|\mathbf{r})} d\mathbf{r}_2 ... d\mathbf{r}_N \tag{11}$$

is a Fisher information density associated with the conditional density

$$f(\mathbf{r}_2, \ldots, \mathbf{r}_N)|\mathbf{r}) = \frac{|\Psi|^2}{\varrho(\mathbf{r})}. \tag{12}$$

Ψ is the wave function.

An efficient method is formalized in the true interacting system connecting the Levy–Lieb constrained search and the Quantum Monte Carlo method [23–28]. The ground-state energy is given by

$$E_0 = \min_\varrho \left(\min_f (\Gamma[\varrho, f]) + T_W + \int v(\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r} \right), \tag{13}$$

where

$$\begin{aligned} \Gamma[\varrho, f] = \frac{1}{8} \int \varrho(\mathbf{r}) I_F^f(\mathbf{r}) d\mathbf{r} \\ + \frac{N-1}{2} \int \varrho(\mathbf{r}) \left[\int \frac{f(\mathbf{r}_2, \ldots, \mathbf{r}_N)|\mathbf{r})]}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 ... d\mathbf{r}_N \right] d\mathbf{r} \end{aligned} \tag{14}$$

The central question of the method is how to determine f in an efficient way. In a physically motivated explicit guess form were adapted to f with one free parameter, while in a further step Quantum Monte Carlo method were applied to determine f numerically. These versions have the advantage that a single functional Γ has to be approximated, while in the orbital-free methods formalized within the non-interacting KS system both the non-interacting kinetic energy and the exchange-correlation energy functionals.

In this paper, the problem is treated in a different way. For spherically symmetric systems, the present author has already presented a method [29–33] in which there is no need for the kinetic energy functional. Now, this approach is extended to any Coulomb system utilizing the fact that in the recent version of DFT spherically symmetric densities are the key quantities. A set of spherically symmetric generating functions $\{\xi\}$ is defined. These functions have two extra variables and $\{\xi\}$ reduces to the set of spherically symmetric densities if these variables are equal to zero. Schrödinger-like equations are derived for the square root of the spherically symmetric generating functions. Generalized Pauli potentials are defined and is shown that these potentials can be calculated in the knowledge of the generating functions. The Euler equations can be solved with these Pauli potentials.

The paper is organized as follows: In Sects. 2 and 3, the theory with a set of spherically averaged densities and the corresponding non-interacting scheme are summarized. In Sect. 4, differential equations for the spherically symmetric densities are derived. The generating functions and the generalized Pauli potentials are introduced, and differential equations are derived in Sect. 5. The last section is devoted to discussion.

2 Theory with a set of spherically averaged densities

Let the external potential be

$$v(\mathbf{r}) = \sum_{\alpha=1}^{M} v_\alpha(r_\alpha) \tag{15}$$

in the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}. \tag{16}$$

$\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and the electron–electron energy operators and

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i). \tag{17}$$

A term in Eq. (15) depends only on the distance from a center α: $r_\alpha = |\mathbf{r} - \mathbf{R}_\alpha|$. A well-known example is the Coulomb potential:

$$v(\mathbf{r}) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_\alpha}. \tag{18}$$

N, M, Z_α and $\mathbf{R}_\alpha$ stand for the number of electrons, the number of nuclei, the atomic number and the position vector of the nuclei, respectively.

To define spherically symmetric averages $\bar{\varrho}_\alpha(r_\alpha)$, we shift the origin of the coordinate system to the center α, use spherical coordinates and average ϱ for the angles Ω_α

$$\bar{\varrho}_\alpha(r_\alpha) = \frac{1}{4\pi} \int_{\Omega_\alpha} \varrho(\mathbf{r}_\alpha) d\Omega_\alpha. \tag{19}$$

Now, let $\{\bar{\varrho}\}$ denote the set of spherically symmetric densities $\bar{\varrho}_\alpha(r_\alpha)$ ($\alpha = 1, \ldots, M$). According to Theophilou's theorem [8] the set $\{\bar{\varrho}\}$ determines uniquely the external potential. Originally, the theorem was formalized for $v(\mathbf{r})$ with the form of Eq. (18). Later it was extended to the general case of Eq. (15) [9]. It was also shown that if $v(\mathbf{r})$ has the form of Eq. (18) the theorem follows from Kato's theorem [9]. If $v(\mathbf{r})$ is given by Eq. (15) the theorem can be proved [9] using constrained search [34].

A universal functional Q was defined as [9]

$$Q[\{\bar{\varrho}\}] = \min_{\Psi \to \{\bar{\varrho}\}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \tag{20}$$

The search is over all antisymmetric wave functions Ψ that yield the given set $\{\bar{\varrho}\}$.

Then the energy minimum

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \tag{21}$$

can be rewritten as

$$E = \min_{\{\bar{\varrho}\}} \left\{ Q[\{\bar{\varrho}\}] + 4\pi \sum_{\alpha=1}^{M} \int \bar{\varrho}_\alpha(r_\alpha) v_\alpha(r_\alpha) r_\alpha^2 dr_\alpha \right\}, \tag{22}$$

where Eq. (15) was utilized.

It was proved that the external potential is uniquely determined by the set $\{\bar{\varrho}\}$, and consequently, there exists a one-to-one map between ϱ and the set $\{\bar{\varrho}\}$ if v has the form of Eq. (15). Furthermore, the energy of a trial set of spherically symmetric densities is always greater than or equal to the true ground-state energy of the system.

The functional derivative of the energy functional $E[\{\bar{\varrho}\}]$ leads to the Euler equations

$$v_\alpha(r_\alpha) = -\frac{\delta Q}{\delta \bar{\varrho}_\alpha}; \quad \alpha = 1, \ldots, M \tag{23}$$

up to a constant, provided that Q [Eq. (20)] is functionally differentiable. It is worth mentioning that generally there are several Euler equations, as many as the number of centers in Eq. (15). (In standard DFT, there is only one Euler equation.)

3 The non-interacting scheme

DFT calculations generally utilize the Kohn–Sham (KS) scheme, in which the particles move independently in a local (Kohn–Sham) potential.

The non-interacting kinetic energy functional for a set $\{\bar{\varrho}\}$ is defined as

$$K[\{\bar{\varrho}\}] = \min_{\Phi \to \{\bar{\varrho}\}} \langle \Phi | \hat{T} | \Phi \rangle, \tag{24}$$

that is, the search is over all non-interacting wave functions Φ yielding the set $\{\bar{\varrho}\}$. In standard KS theory, the KS density is the same as the true density. Correspondingly, here the KS set $\{\bar{\varrho}\}$ should also be equal to the true set. This constraint can be assured by a set of Lagrange multipliers $w_\alpha(r_\alpha)$:

$$\min_{\Phi \to \{\bar{\varrho}\}} \langle \Phi | \hat{T} | \Phi \rangle + 4\pi \sum_{\alpha=1}^{M} \int \bar{\varrho}_\alpha(r_\alpha) w_\alpha(r_\alpha) r_\alpha^2 \mathrm{d}r_\alpha. \tag{25}$$

The minimization leads to the non-interacting Euler equations

$$w_\alpha(r_\alpha) = -\frac{\delta K}{\delta \bar{\varrho}_\alpha}; \quad \alpha = 1, \ldots, M \tag{26}$$

up to a constant.

Observe that Eq. (25) provides the total energy $E_{\mathrm{s}}[\{\bar{\varrho}\}]$ of a non-interacting system in a local KS potential

$$w(\mathbf{r}) = \sum_{\alpha=1}^{M} w_\alpha(r_\alpha). \tag{27}$$

The non-interacting wave function Φ and kinetic energy K can be expressed with one-particle functions. Then the variation with respect to the orbitals leads to the Kohn–Sham equations

$$\left[-\frac{1}{2}\nabla^2 + w(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i, \tag{28}$$

with

$$\varrho = \sum_{i=1}^{N} |\phi_i|^2. \tag{29}$$

In order to derive a relationship between $w_\alpha(r_\alpha)$ and $v_\alpha(r_\alpha)$, the Hartree and exchange-correlation functional $E_{\text{Hxc}}[\{\bar\varrho\}]$ was defined as [9]

$$E_{\text{Hxc}}[\{\bar\varrho\}] = Q[\{\bar\varrho\}] - K[\{\bar\varrho\}]. \tag{30}$$

Then the Euler equation (23) and (26) lead to

$$w_\alpha(r_\alpha) = v_\alpha(r_\alpha) + v_{\text{Hxc},\alpha}(r_\alpha); \quad \alpha = 1, \ldots, M, \tag{31}$$

with

$$v_{\text{Hxc},\alpha}(r_\alpha) = \frac{\delta E_{\text{Hxc}}}{\delta \bar\varrho_\alpha}; \quad \alpha = 1, \ldots, M. \tag{32}$$

Substituting $w_\alpha(r_\alpha)$ in (31) into Eq. (27), we arrive at the Kohn–Sham potential w.

4 Differential equations for the spherically symmetric densities

It is worth utilizing the fact that the members of the set $\{\bar\varrho\}$ are spherically symmetric. First a set of radial densities $\{\sigma\}$ are defined as $\sigma_\alpha(r_\alpha)$ ($\alpha = 1, \ldots, M$), where

$$\sigma_\alpha(r_\alpha) = 4\pi r_\alpha^2 \bar\varrho_\alpha(r_\alpha). \tag{33}$$

It has recently been shown [12] that $\sigma_\alpha(r_\alpha)$ satisfies the radial equation

$$\hat{h}_{\text{eff}}^\alpha(r_\alpha)\sigma_\alpha^{1/2}(r_\alpha) = \mu\sigma_\alpha^{1/2}(r_\alpha); \quad \alpha = 1, \ldots, M, \tag{34}$$

where

$$\hat{h}_{\text{eff}}^\alpha(r_\alpha) = -\frac{1}{2}\frac{d^2}{dr_\alpha^2} + v_\alpha(r_\alpha) + v_{\text{eff}}^\alpha(r_\alpha). \tag{35}$$

μ is the chemical potential, the negative of the ionization energy I:

$$\mu = E - E_{N-1}^0. \tag{36}$$

The ground-state energies of the N and the $N-1$ electron systems with the same v are denoted by E and E_{N-1}^0, respectively. The derivation and the form of the effective potential $v_{\text{eff}}^\alpha(r_\alpha)$ can be found in [12].

Observe that $v_\alpha(r_\alpha)$ can be expressed from Eqs. (34) and (35)

$$v_\alpha(r_\alpha) = \mu + \frac{1}{2\sigma_\alpha^{1/2}}\frac{d^2\sigma_\alpha^{1/2}}{dr_\alpha^2} + v_{\text{eff}}^\alpha(r_\alpha). \tag{37}$$

A comparison of Eqs. (23) and (37) reveals that Eq. (34) are equivalent to the Euler equation (23).

Consider now Coulomb systems with external potential (18). To solve the Euler equation (23), first radial wave functions P_i^α yielding the given spherical set $\{\sigma\}$ are introduced.

First, another non-interacting kinetic energy is defined:

$$\tilde{K} = \sum_{\alpha=1}^{M} \frac{Z_\alpha}{Z} K_\alpha, \tag{38}$$

where

$$K_\alpha = -\frac{1}{2} \sum_i \lambda_i^\alpha \int P_i^\alpha(r_\alpha) \left(\frac{\mathrm{d}^2 P_i^\alpha(r_\alpha)}{\mathrm{d}r_\alpha^2} - \frac{l_i(l_i+1)}{r_\alpha^2} P_i^\alpha(r_\alpha) \right) \mathrm{d}r_\alpha. \tag{39}$$

Observe that $\tilde{K}$ is different from K. The sum of Z_α is denoted by

$$Z = \sum_{\alpha=1}^{M} Z_\alpha. \tag{40}$$

For a neutral system $Z = N$. $\sigma_\alpha(r_\alpha)$ can be expressed with P_i^α as

$$\sigma_\alpha(r_\alpha) = \sum_i \lambda_i^\alpha [P_i^\alpha(r_\alpha)]^2. \tag{41}$$

λ_i^α are the occupation numbers and the sum goes for the occupied orbitals.

The "spherical" classical Coulomb energy $\tilde{J}$ was defined in Ref. [8] as

$$\tilde{J} = \frac{1}{2} \sum_\alpha \frac{Z_\alpha}{Z} \int_0^\infty \sigma_\alpha(r_\alpha) \tilde{u}_J^\alpha(r_\alpha) dr_\alpha, \tag{42}$$

where

$$\tilde{u}_J^\alpha(r_1) = \left(\frac{1}{r_1} \int_0^{r_1} \sigma_\alpha(r_2) dr_2 + \int_{r_1}^\infty \frac{\sigma_\alpha(r_2)}{r_2} dr_2 \right). \tag{43}$$

We emphasize that $\tilde{J}$ differs from the usual classical Coulomb energy.

Now, the true total energy is rewritten as

$$E = \tilde{K} + \tilde{J} + \tilde{E}_{\mathrm{xc}} - \sum_{\alpha=1}^{M} \int \sigma_\alpha(r_\alpha) \frac{Z_\alpha}{r_\alpha} dr_\alpha. \tag{44}$$

Observe that the last term in Eq. (44) follows from the Coulomb external potential. The exchange-correlation term $\tilde{E}_{\mathrm{xc}}$ is defined by Eq. (44). Because of Eq. (40) Eq.

$\tilde{E}_{xc}$ can be recast as

$$\tilde{E}_{xc} = \sum_{\alpha} \frac{Z_{\alpha}}{Z} \tilde{E}_{xc}. \tag{45}$$

The radial equations can be derived by the variation of E with respect to the P_i^{α}:

$$\frac{Z_{\alpha}}{Z} \left[-\frac{1}{2} \frac{d^2 P_i^{\alpha}(r_{\alpha})}{dr_{\alpha}^2} + \frac{l_i(l_i+1)}{2r_{\alpha}^2} P_i^{\alpha}(r_{\alpha}) + \left(\tilde{u}_J^{\alpha}(r_{\alpha}) + \tilde{u}_{xc}^{\alpha}(r_{\alpha}) \right) P_i^{\alpha}(r_{\alpha}) \right]$$
$$-\frac{Z_{\alpha}}{r_{\alpha}} P_i^{\alpha}(r_{\alpha}) = \tilde{\epsilon}_i^{\alpha} P_i^{\alpha}(r_{\alpha}), \tag{46}$$

where

$$\tilde{u}_{xc}^{\alpha} = \frac{\delta \tilde{E}_{xc}}{\delta \bar{\varrho}_{\alpha}}. \tag{47}$$

Equation (46) can be rewritten as

$$-\frac{1}{2} \frac{d^2 P_i^{\alpha}(r_{\alpha})}{dr_{\alpha}^2} + \frac{l_i(l_i+1)}{2r_{\alpha}^2} P_i^{\alpha}(r_{\alpha}) + \left(\tilde{u}_J^{\alpha}(r_{\alpha}) + \tilde{u}_{xc}^{\alpha}(r_{\alpha}) \right) P_i^{\alpha}(r_{\alpha})$$
$$-\frac{Z}{r_{\alpha}} P_i^{\alpha}(r_{\alpha}) = \epsilon_i^{\alpha} P_i^{\alpha}(r_{\alpha}), \tag{48}$$

where

$$\epsilon_i^{\alpha} = \frac{Z}{Z_{\alpha}} \tilde{\epsilon}_i^{\alpha}. \tag{49}$$

Introducing the notation

$$u_{\alpha}(r_{\alpha}) = \tilde{u}_J^{\alpha}(r_{\alpha}) + \tilde{u}_{xc}^{\alpha}(r_{\alpha}) - \frac{Z}{r_{\alpha}}. \tag{50}$$

Equation (48) takes the form

$$-\frac{1}{2} \frac{d^2 P_i^{\alpha}(r_{\alpha})}{dr_{\alpha}^2} + \frac{l_i(l_i+1)}{2r_{\alpha}^2} P_i^{\alpha}(r_{\alpha}) + u_{\alpha}(r_{\alpha}) P_i^{\alpha}(r_{\alpha}) = \epsilon_i^{\alpha} P_i^{\alpha}(r_{\alpha}). \tag{51}$$

Equation (51) can be solved if appropriate approximation for the potential $\tilde{u}_{xc}^{\alpha}$ is available. Then σ_{α} can be calculated using Eq. (41). In this paper, however, an orbital-free approach is proposed and Eq. (51) is applied only in the derivation.

5 Generating functions

Define now generating functions

$$\xi_\alpha(r_\alpha) = \sum_i f_i^\alpha \lambda_i^\alpha \sigma_i^\alpha(r_\alpha), \tag{52}$$

where

$$\sigma_i^\alpha(r_\alpha) = [P_i^\alpha(r_\alpha)]^2. \tag{53}$$

The factors f_i^α are selected as

$$f_i^\alpha = e^{-\beta\epsilon_i^\alpha - \gamma l_i(l_i+1)} \tag{54}$$

with any real β and γ. Observe that the generating function ξ_α gives σ_α if $\beta = \gamma = 0$. ξ_α can be considered as an extension of the radial densities σ_α. Note that ξ_α depends not only on r_α but also on the parameters β and γ. This broadening makes it possible to derive an orbital-free scheme.

First of all a differential equation is derived for ξ_α.

Dividing Eq. (51) by $P_i^\alpha(r_\alpha)$, differentiating with respect to r_α (denoted by $'$), then multiplying by $\sigma_i^\alpha(r_\alpha)$ we are led to

$$-\frac{1}{2} P_i^\alpha(r_\alpha)(P_i^\alpha(r_\alpha))''' + \frac{1}{2} (P_i^\alpha(r_\alpha))'(P_i^\alpha(r_\alpha))'' - \frac{l_i(l_i+1)}{r_\alpha^3} \sigma_i^\alpha(r_\alpha)$$
$$+(u_\alpha(r_\alpha))' \sigma_i^\alpha(r_\alpha) = 0. \tag{55}$$

Multiplying Eq. (51) by $(P_i^\alpha(r_\alpha))'$ and combining it with Eq. (55) we obtain

$$P_i^\alpha(r_\alpha)(P_i^\alpha(r_\alpha))''' + 3(P_i^\alpha(r_\alpha))'(P_i^\alpha(r_\alpha))'' = 2\frac{l_i(l_i+1)}{r_\alpha^2}(\sigma_i^\alpha(r_\alpha))'$$
$$+4u_\alpha(r_\alpha)(\sigma_i^\alpha(r_\alpha))' - 4\epsilon_i^\alpha(\sigma_i^\alpha(r_\alpha))' - 2\frac{l_i(l_i+1)}{r_\alpha^3}\sigma_i^\alpha(r_\alpha) + 2(u_\alpha(r_\alpha))'\sigma_i^\alpha(r_\alpha). \tag{56}$$

We can notice that

$$\frac{\partial\xi_\alpha(r_\alpha)}{\partial\beta} = -\sum_i f_i^\alpha \lambda_i^\alpha \epsilon_i^\alpha \sigma_i^\alpha(r_\alpha) \tag{57}$$

and

$$\frac{\partial\xi_\alpha(r_\alpha)}{\partial\gamma} = -\sum_i f_i^\alpha \lambda_i^\alpha l_i(l_i+1)\sigma_i^\alpha(r_\alpha). \tag{58}$$

Combining Eqs. (55)–(58), we arrive at the following differential equation for ξ_α

$$(\xi_\alpha(r_\alpha))''' = 8u_\alpha(r_\alpha)(\xi_\alpha(r_\alpha))' + 4(u_\alpha(r_\alpha))'\xi_\alpha(r_\alpha)$$
$$+ 8\frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\beta} - \frac{4}{r_\alpha^2}\frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\gamma} + \frac{4}{r_\alpha^3}\frac{\partial\xi_\alpha(r_\alpha)}{\partial\gamma}. \tag{59}$$

Equation (59) can be rewritten as

$$\frac{1}{2}\xi_\alpha(r_\alpha)(u_\alpha(r_\alpha))' + u_\alpha(r_\alpha)(\xi_\alpha(r_\alpha))' = -\tilde{F}_\alpha(r_\alpha), \tag{60}$$

where

$$\tilde{F}_\alpha(r_\alpha) = -\frac{1}{8}(\xi_\alpha(r_\alpha))''' - \frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\beta} + \frac{1}{2r_\alpha^2}\frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\gamma} - \frac{1}{2r_\alpha^3}\frac{\partial\xi_\alpha(r_\alpha)}{\partial\gamma}. \tag{61}$$

It is enlightening to express Eq. (60) in the form

$$-\frac{1}{2}[(\xi_\alpha(r_\alpha))^{1/2}]'' + [u_\alpha(r_\alpha) + v_\alpha^P(r_\alpha)](\xi_\alpha(r_\alpha))^{1/2} = \mu(\xi_\alpha(r_\alpha))^{1/2}. \tag{62}$$

Equation (62) is a generalized Euler equation for ξ_α with the generalized Pauli potential v_α^P satisfying the equation

$$\frac{1}{2}\xi_\alpha(r_\alpha)(v_\alpha^P(r_\alpha))' + v_\alpha^P(r_\alpha)(\xi_\alpha(r_\alpha))' = F_\alpha(r_\alpha), \tag{63}$$

where

$$F_\alpha(r_\alpha) = \mu(\xi_\alpha(r_\alpha))' - \frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\beta} + \frac{1}{2r_\alpha^2}\frac{\partial(\xi_\alpha(r_\alpha))'}{\partial\gamma} - \frac{1}{2r_\alpha^3}\frac{\partial\xi_\alpha(r_\alpha)}{\partial\gamma}. \tag{64}$$

If $\beta = \gamma = 0$ Eq. (62) reduces to the Euler equation for σ_α

$$-\frac{1}{2}[(\sigma_\alpha(r_\alpha))^{1/2}]'' + [u_\alpha(r_\alpha) + v_\alpha^P(r_\alpha)](\sigma_\alpha(r_\alpha))^{1/2} = \mu(\sigma_\alpha(r_\alpha))^{1/2}, \tag{65}$$

that is, to Eq. (34) with

$$u_\alpha(r_\alpha) + v_\alpha^P(r_\alpha) = v_\alpha(r_\alpha) + v_{\text{eff}}^\alpha(r_\alpha). \tag{66}$$

Equation (63) can be solved for the generalized Pauli potential

$$v_\alpha^P(r_\alpha) = \frac{2}{(\xi_\alpha(r_\alpha))^2}\int_0^{r_\alpha}\xi_\alpha(r_1)F_\alpha(r_1)dr_1. \tag{67}$$

v_α^P is an extension of the Pauli potential in Eq. (8). Its presence is due to the Pauli principle. This potential insures the appearance of the shell structure. ξ_α has also shell structure.

From ξ_α, one can immediately recover σ_α and can calculate the total energy from Eq. (44). $\tilde{K}$ can also be obtained from ξ_α. We define the quantity

$$\kappa_\alpha = -\frac{1}{2} \sum_i f_i^\alpha \lambda_i^\alpha \int P_i^\alpha(r_\alpha) \left(\frac{d^2 P_i^\alpha(r_\alpha)}{dr_\alpha^2} - \frac{l_i(l_i+1)}{r_\alpha^2} P_i^\alpha(r_\alpha) \right) dr_\alpha. \quad (68)$$

If $\beta = \gamma = 0$, κ_α is equal to K_α. Using Eqs. (51) and (68) takes the form

$$\kappa_\alpha = \sum_i f_i^\alpha \lambda_i^\alpha \epsilon_i^\alpha \int_0^\infty (P_i^\alpha(r_\alpha))^2 dr_\alpha - \int_0^\infty u_\alpha(r_\alpha)\xi_\alpha(r_\alpha)dr_\alpha. \quad (69)$$

Taking into account Eq. (57), we are led to

$$K_\alpha = \left[-\int_0^\infty \frac{\partial \xi_\alpha(r_\alpha)}{\partial \beta} dr_\alpha - \int_0^\infty \xi_\alpha(r_\alpha)u_\alpha(r_\alpha)dr_\alpha \right]\Bigg|_{\beta=\gamma=0}. \quad (70)$$

Then $\tilde{K}$ can be gained from Eqs. (38) and (44) provides the total energy.

6 Discussion

In Sect. 4, auxiliary spherical non-interacting systems and Kohn–Sham-like equations are constructed. These equations do not have to be solved, and they are only used in the derivation of the equations for the generating functions.

We can look upon the generating function as a generalization of the density. ξ_α depends not only on the variable r_α but it has two extra parameters: β and γ. Introducing the generating function makes it possible to derive a single differential equation for ξ_α. Therefore, instead of solving the Kohn–Sham equations, it is enough to solve the generalized Euler equation (62). It gives an advantage over Kohn–Sham procedure. On the other hand, it is unfavorable that we have two extra variables. But, as our final goal is to determine the density σ_α, we only need ξ_α and its derivatives at $\beta = \gamma = 0$. Therefore, it is enough to calculate ξ_α in the neigborhood of $\beta = \gamma = 0$.

Observe that not only the generating function has a physical meaning at $\beta = \gamma = 0$, but its derivatives, too.

$$\frac{\partial \xi_\alpha(r_\alpha)}{\partial \beta}|_{\beta=\gamma=0} = -\sum_i \lambda_i^\alpha \epsilon_i^\alpha \sigma_i^\alpha(r_\alpha) \quad (71)$$

is the negative of the non-interacting kinetic energy density of the center α and

$$\frac{\partial \xi_\alpha(r_\alpha)}{\partial \gamma}|_{\beta=\gamma=0} = -\sum_i \lambda_i^\alpha l_i(l_i+1)\sigma_i^\alpha(r_\alpha) \quad (72)$$

is the negative of the angular momentum density with respect to the center α. The importance of the kinetic energy in orbital-free approach is well known. The significance of taking into account the angular momentum has already been emphasized [19, 20]. It is an appealing feature of the present approach that the generating function contains this information in a simple way.

The Euler (34) contain the same chemical potential μ, because each member of the set has the same asymptotic behavior, and each of them decays as the density of the molecule [15, 35–37]:

$$\lim_{r_\alpha \to \infty} \frac{\partial \bar{\varrho}_\alpha(r_\alpha)}{\partial r_\alpha} = - \sqrt{-8\mu} \; . \tag{73}$$

As it can be seen from the definition (52), the asymptotic behavior of ξ_α is also governed by μ.

Equations (62)–(67) provide an orbital-free solution for ξ_α. One can follow the steps:

(i) An initial guess for ξ_α is needed, then F_α is calculated from Eq. (64).
(ii) v_α^P can be computed from Eq. (67).
(iii) The solution of Eq. (62) provides ξ_α. Observe that an approximation for the potential $\tilde{u}_{xc}^\alpha$ is needed. Obviously, the accuracy of the results will depend on the approximation of $\tilde{u}_{xc}^\alpha$.
(iv) Steps (i)–(iii) should be repeated until convergence.

Spherical functions have been applied in band structure calculations for a long time. In the vicinity of a nucleus, the density is almost spherically symmetric. Therefore, in the so-called muffin-tin approximation proposed by Slater [38], the nuclei are surrounded by spheres in which spherical potentials are applied, while in the region between the atomic spheres the potential is taken constant. Nowadays exact muffin-tin orbitals [39] are extensively used in materials science and engineering. Though the approach presented in this paper is different, there is some resemblance to the muffin-tin approximation. Therefore expertise in the latter method might be invaluable and productive in constructing adequate approximations for the potential $\tilde{u}_{xc}^\alpha$. It is expected that the present approach will be especially suitable for materials science.

In summary, our orbital-free approach is extended to Coulomb systems taking advantage of the recent version of DFT based on spherically symmetric densities. A set of spherically symmetric generating functions $\{\xi\}$ is defined. These functions having two extra variables are extensions of the spherically symmetric densities. $\{\xi\}$ reduces to the set of spherically symmetric densities if the extra variables are equal to zero. Euler equations are rewritten as Schrödinger-like equations for the square root of the spherically symmetric generating functions. Generalized Pauli potentials are defined and are shown that these potentials can be calculated in the knowledge of the generating functions. The Euler equations can be solved with these Pauli potentials.

Data availability Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Declarations

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