Decomposition Rule of Energy Functional in the Density-Functional Theory: Applications to Affinity and Hyperfine Structure of Helium-Like Atoms

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Energy functionals in the density-functional theory (DFT) do not have the linearity when the density is decomposed into separated parts in an arbitrary way. We find a decomposition rule for these functionals by a separation according to spin-up and spin-down densities. The electron-spin dipole-dipole (DD) and hyperfine interactions (HI) are used to treat helium-like atoms. Contrary to the expectation of electrons with one spin-up and one spin-down from the Pauli principle, our results indicate slight deviations therefrom, unavoidable though small. From the nature of interactions, we conclude that there must be Fermi-Coulomb and nuclear spin-holes in the electron distributions. Investigations with the DD are a kind of symmetry-breaking to the decomposition rule. This interaction also breaks the particle exchange symmetry. The largest (16%) of these discrepancies for helium-like atoms is $\text{H}^{-}$. It is suggested that magnetic effects between two electrons here are still too small. After the HI is added and replaced by a presumed smooth function, we obtained partial solutions in separated spatial regions for various magnitudes of interaction strength. Finally, a general fitting formula is given for this smoothed interaction. A pattern of nucleus is thus proposed to be detectable. The physics of counting electron numbers by density of states is discussed. Current theory of one electron occupying one low energy state is further reviewed, reported, and related to previous works in addition to the present mathematical intuition.

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1. Introduction

In the theory of density-functional of a many electron system, it is physical to have an additivity of electron numbers,

$$n_{\text{tot}} = n_1 + n_2.$$  \hspace{1cm} (1)

In current formalisms as seen in (6), (22), (24) etc. below, the energy-functional is formulated unphysically as
Nevertheless these formalisms are able to result many mathematical and computational correctness in interpretation of physical data. For these formalisms, we have reported a review of them in Appendix A. Although the DFT includes a consistent theory about electron behaviours, their distributions, even their dynamical tendencies, etc. but it is itself not consistent theoretically with the linearity consideration, say with (2). That means, although the density of electrons may be divided into a number of individual parts e.g., according to (1), but the total energy functional is not able to divide into these parts correspondingly, as (2). In this paper, we choose a particular way of separation in (8). Finally we obtain a combination law which has the linearity, to replace the simple linear combination (1) so that (2) becomes an equality. It is the decomposition rule (8) derived below.

In DFT for electrons in a Fermi sea, the density is our independent variable. The kinetic energy (KE) in the spin-independent (SI) and the spin-dependent (SD) formalisms are distinct. For the density \( n = n_+ + n_- \) and spin-density \( m = m_+ - m_- \) with the spin-up(down) density \( n_+ \)\( (n_-) \), we apply the above concept to the Thomas-Fermi kinetic energy densities per electron. Together with the Fermi momenta, they are given commonly as

\[
\epsilon_k = c_k n^\frac{3}{2}, \quad \epsilon_k^\pm = c_k (2n_\pm)^\frac{3}{2}, \quad c_k^\pm = \frac{1}{\sqrt{6\pi} (3\pi^2)^{\frac{3}{2}}} \text{ per electron; for } n_\pm = \frac{1}{2} (n \pm m); \quad k_F(n) = (3\pi^2 n)^{\frac{1}{3}}, \quad k_F^\pm(n_\pm) = (6\pi^2 n_\pm)^{\frac{1}{3}}
\]

for spin-up and spin-down totally and separately \([1,2]\) in atomic units. The derivation of (3) can be conferred with Appendix B. Total KE for SI and for SD are thus

\[
K_{SI}[n] = \int \epsilon_k n dr = c_k \int n^\frac{3}{2} dr;
\]

\[
K_{SD}[n,m] = \int \epsilon_k^+ n_+ dr + \int \epsilon_k^- n_- dr
\]

\[
= \int c_k (2n_+)^\frac{3}{2} n_+ dr + \int c_k (2n_-)^\frac{3}{2} n_- dr
\]

\[
= \frac{1}{2} c_k \left[ k_F(2n_+) \int (2n_+)^\frac{3}{2} dr + k_F(2n_-) \int (2n_-)^\frac{3}{2} dr \right]
\]

\[
= \frac{1}{2} c_k \int (n + m)^\frac{3}{2} dr + \frac{1}{2} c_k \int (n - m)^\frac{3}{2} dr;
\]

They are equal only for \( m = 0 \). As a comment, when we consider \( n_+ dr \) in (5) exactly equal to the density of states, and when the magnetic field \( H \neq 0 \), troublesome enters explained
in Appendix C. We are still not able to derive a decomposition rule such as (7) below if \( H \neq 0 \). To confirm with the nonlinearity statement above, here we have in the apparent forms

\[
K^{S1}[n_1 + n_2] \neq K^{S1}[n_1] + K^{S1}[n_2];
\]

\[
K^{SD}[n = n_+ + n_-, m = n_+ - n_-] = \frac{1}{2} \left( K^{S1}[2n_-] + K^{S1}[2n_+] \right),
\]

It is noted that

\[
K^{SD}[n = n_\pm, m = \pm n_\pm] = \frac{1}{2} K^{S1}[2n_\pm].
\]

Still we have

\[
K^{SD}[n = n_+ + n_-, m = n_+ - n_-] = K^{SD}[n_-, -n_-] + K^{SD}[n_+, n_+].
\] (6)

This shows that KE is not what we think classically, but spin-dependent for its decomposition. The details of how to formulate these terms are given in Appendix B. Consequently, when we consider the additivity of the density, \( n = n_+ + n_- \), we are then able to get generally the total KE functional \( K[n] \) as a given linear combination of functionals of \( n_\pm \) in the SD formalism. The exactly same manipulations applied to the exchange energy, we quote from (55) in Appendix B

\[
E_x^{S1}[n] = -c_e \int n^\frac{3}{2} \, dx, \quad c_e = \frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{2}},
\]

\[
E_x^{SD}[n,m] = \frac{c_e}{2} \int (n + m)^\frac{3}{2} \, dx - c_e \int (n - m)^\frac{3}{2} \, dx
\]

\[
= \frac{1}{2} \left( E_x^{S1}(2n_+) + E_x^{S1}(2n_-) \right).
\]

Because the theory is formulated in certain fixed particular formulas as shown in this paper, we assign them in functional forms with particular notations. Together with total energies for cases of SI and of SD without correlation energy, we denote generally as follows.

Variables \( z \) and \( u \) correspond \( z \rightarrow n \) and \( u \rightarrow m \)

\[
K[z] \equiv c_e \int z^\frac{3}{2} \, dx, \quad E_x[z] \equiv -c_e \int z^\frac{3}{2} \, dx,
\]

\[
E_x^{S1}[z] = K[z] + E_x[z],
\]

\[
E_x^{SD}[z,u] = \frac{1}{2} \left( K[z+u] + E_x[z+u] + K[z-u] + E_x[z-u] \right)
\] (7)

for total energies \( E_x^{S1}[n] \) and \( E_x^{SD}[n,m] \). As a comment, in the regime of applicability of the correlation energy, such as the Wigner correlation as a function of the total density \( n \), nothing is related to \( m \). About this point, we have a claimant in Ref. [2]. It can be
considered as only a constant perturbation. For a physical meaningful correlation in the view of this paper, it should be also obey the decomposition rule in some ways. As far as (21) below is concerned, what gives us troublesome is the magnetic field $H \neq 0$. This has been claimed above and in Appendix C.

Physics derived in Appendix B gives that in the field theory, we have the total energy equal to the sum of the KE and the exchange energy entirely without any other energies. This leads us to have that the general energy expression

$$E^{SD}[n, m] = \frac{1}{2} \{ E^{SI}[n + m] + E^{SI}[n - m] \}.$$  \hspace{1cm} (8)

Together with the definitions of $n$ and $m$, this equation gives the decomposition rule for energy functionals, in place of the linearity reduction. When we consider a small variation $m = \delta m$, we obtain from (8)

$$E^{SD}[n, 0] + \int dr \frac{\delta E^{SD}}{\delta m} \delta m = E^{SI}[n] + O[(\delta m)^2],$$  \hspace{1cm} (9)

$$\frac{\delta E^{SD}}{\delta m} = 0.$$  

Here we see that we do not know anything about the second variation $\delta^2 E$. This will provide a non-conservation of energy in a process, as been discussed in Refs. [3-5]. This is also quoted briefly in Appendix A. Therefore $E^{SD}[n, m]$ are stationary about $m$ at $m = 0$. It is obvious that we have also

$$\frac{\delta K^{SD}}{\delta m} = 0; \text{ and } \frac{\delta E^{SD}}{\delta m} = 0$$  \hspace{1cm} (10)

because of (5) and (55) which are in form of (8) or (7). The separation of this kind into SD formalism is familiar and used often currently, but the stationary principles in (9) and (10) appear for the first time here in this paper.

To investigate the above theory, the helium-like atom is chosen for its own clearness and the reason below. The energy is evaluated by means of the variationally determined wave function [6]

$$\Psi(r_1, r_2) = f(Z_{eff}, \tau_1) f(Z_{eff}, \tau_2),$$  \hspace{1cm} (11)

$$f(Z_{eff}, \tau) \equiv \left( \frac{qZ_{eff}}{\tau} \right)^{\frac{1}{2}} e^{-Z_{eff} \tau}, \quad Z_{eff} = Z - \frac{5}{16}.$$  

as the first approximation. Our illustration takes the kinetic part of the total energy in Ref. [7]. This KE is given in two different ways: The first one is by the expectation value of Hermitian conjugate scalar product in DFT [7]

$$K = \frac{1}{2} \int |\nabla \psi|^2 dr = \frac{1}{2} \int \frac{1}{\psi} \nabla \psi \nabla \psi^* dr.$$  \hspace{1cm} (12)
The second way is found by the straightforward operator calculation according to quantum mechanics (QM),

$$K \equiv K^{(H_{\text{form})}} = -\frac{1}{2} \int \psi^* \nabla^2 \psi d\tau.$$  \hspace{1cm} (13)

A great difference between (12) and (13) have been investigated on wave functions $\exp{k \cdot r}$ and $\exp{-k \cdot r}$ in a previous paper by the same author [8] for an investigation on the classical limit of hydrogen atom ground state. For example in case of $\exp{-k \cdot r}$, (12) gives $+k^2/2$ while (13) gives $-k^2/2$. It is a problem of Green theorem. Here we introduce a further mathematical physics sense which is frequently used in computational physics. We use the same identification of the dynamical observable as did in the Hartree-Fock equation, i.e.

$$A^\alpha \psi = \left( \frac{A^\alpha \psi}{\psi} \right) \psi,$$  \hspace{1cm} (14)

$$A^\alpha \equiv \left( \frac{A^\alpha \psi}{\psi} \right) = \text{a dynamical observable.}$$  \hspace{1cm} (15)

The sense of this kind is found to be used by Gibbs in the 19th century and by Schrodinger in his first paper on wave mechanics. Because in exact QM, we can not solve two electron atoms such as He-like atoms exactly, we have made efforts to formulate in many attempts and approaches. Here we make an estimation about the KE (as a dynamical observable) locally for single one electron in these atoms. From the result we decide how to choose and judge an alternative method to investigate the physics. Intuitively, our understanding came from the variational method with result given in (11). Explicitly this atom is more or less like with two identical electrons in the effectively screening coulombic field without other interactions. By this sense, in mathematical formulation, we have to write the Schrodinger and the equivalent Schrodinger equation with $f(r)$ from (11) as

$$-\frac{1}{2} \frac{1}{\psi(Z,1,2)} \left[ \nabla^2 + \nabla^2_f \right] \psi(Z,1,2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = E \Rightarrow$$

$$-\frac{1}{2} \frac{1}{f(Z_{eff}, r_1)} \nabla^2_f f(Z_{eff}, r_1) + \frac{1}{f(Z_{eff}, r_2)} \nabla^2_f f(Z_{eff}, r_2) \right) + V_{\text{coul}}(Z_{eff}, r_1)$$

$$+ V_{\text{coul}}(Z_{eff}, r_2) \Rightarrow E = 2E^H(Z_{eff}) \equiv -Z_{eff}^2,$$

$$V_{\text{coul}}(Z_{eff}, r) \equiv -\frac{Z_{eff}}{r} \frac{Z_{eff}}{Z} V_{\text{coul}}(Z, r)$$

where $V_{\text{coul}}(Z_{eff}, r_1)$ is supposed to be obtained from the virial theorem. The identity of the first electron and the second electron gives the same differential equation as an equivalent replacement

$$-\frac{1}{2} \frac{1}{f(Z_{eff}, r)} \nabla^2 f(Z_{eff}, r) + V_{\text{coul}}(Z_{eff}, r) = -\frac{Z_{eff}^2}{2}.$$

$$\hspace{1cm} (16)$$
From this equation, we study in parallel to DFT, viz., to consider the KE part of the total energy, but with a view from the conventional QM conceptions. We investigate with a calculation for the second electron KE in a process by which we plan to find the affinity of an electron. We call it the KE-in-affinity calculation. Electron affinity may be defined as the energy output of an electron injected into an atom from a free state. Here we consider the KE of the second electron moving or injecting into a He-like ion (one negative electronic charge) to form a neutral He-like atom. Different from usual consideration of the affinity, we consider instead by a process in which this injected electron is started at a position with zero KE. This position is considered as the zero energy reference level of KE where the potential energy is equal to \(-Z_{eff}^2/2\) from (17) by energy conservation and the identity of the two electrons inside the neutral He-like atom. As this electron moves inside this ion, KE increases from the zero value. At the same time, it starts to interact with the nucleus and the first electron. Therefore the KE is

\[
\left< K^{\text{KE}} \right> = -\frac{1}{2f(Z_{eff})} \nabla^2 f(Z_{eff}, \mathbf{r}) = -\frac{1}{2} \left[ Z_{eff}^2 + 2 \left< V_{eff} \right> \right]
\]

for a proposed effective potential energy \(V_{eff}\) met by the second electron, which is uncertain due to the complicated exact situation involved in the screening. For a consideration in the beginning for the second electron is at the zero KE position, we have two separated systems: one of them is the He-like ion and the other separated one is the second electron. After moving in the ion, it may still be kept as two separated systems but with mutual interaction with the effective potential \(V_{eff}\). This effective potential is due to the net nuclear charge \(Z\) without screening and the other electron cloud with total charge \(-Ze\). In the KE calculation, at every space point, KE is kept its value \((=\frac{1}{2}Z_{eff}^2 - 2V_{eff})\). In the meanwhile, the effective potential \(V_{eff}\) has the average as

\[
\left< V_{eff} \right> = \left( \frac{Z}{Z_{eff}} \right) < V_{\text{coul}} \left( Z_{eff}, \mathbf{r} \right) > + < V_{e-e} \left( r_{12} \right) > = -Z_{eff}^2 + \frac{5Z_{eff}}{8}
\]

for the second electron as a separated system. The same effective \(Z_{eff}\) is used for a reason given below. This way is closer to spirit of usual QM than the complete screening theories since in exact QM, we must write the system Hamiltonian in the beginning. In the theory of finding system Hamiltonian, bare nucleus and bare electrons without screening are the entities, i.e. particles, in classical situation. In comparison with the exact variational method, the nuclear charge is used as \(Z_{eff}\), but the electron is kept bare without screening. Incidentally, under the complete screening consideration, we must consider the screening effect of the nucleus when the nucleus is located in between the two electrons. This nearly QM way gives the KE

\[
\left< K^{\text{KE}} \right> = -\frac{1}{2} \left[ Z_{eff}^2 + 2 \left< V_{eff} \right> \right]
\]

\[
\equiv E_{k}^{\text{eff}}(Z_{eff}) \equiv Z_{eff}^2 - \frac{5}{8}Z_{eff} = \frac{Z_{eff}^2}{2} - 0.3125Z_{eff}
\]

\[
\neq \left< V_{\text{He\text{erm}}} \right> = \int f \left( -\frac{1}{2} \nabla^2 \right) \mathbf{r} d\mathbf{r} = -\frac{1}{2}Z_{eff}^2.
\]

(18)
This value is certainly different from the average of KE for the neutral He-like atom in usual QM without screening effects. It is also different from the value of the variational method by which we must have a factor $1/2$ for the electron-electron interaction. But it reveals a (theoretical) result for He-like atom for KE in KE-in-affinity evaluation.

After the second electron moves inside the He-like ion steadily, the whole system forms a neutral He-like atom. The second electron becomes then a member of the neutral He-like atom. The system becomes now a whole system, one system. From a many-body consideration, we have to put the potential energy $V_{e-e}(r)$ inside $< V_{e-e} >$ by $V_{e-e}/2$, such as in the variational method. However, we are still not clear about how and what are changed in this process by which we change from two separated systems into one single system. This is to be attacked in this paper.

Moreover, the second electron, though in the zero KE level in the beginning, spatially it exists inside the He-like ion (for $f(Z_{eff},r_2)$ in (11), $r_2 = 0 \rightarrow \infty$) entirely. There are no differences from physical configuration viewpoint between the moving second electron process and the naturally existed neutral He-like atom. From (11), we can see that this consideration is even not violating the exclusion principle. The two electrons expressed in (11) can be interpreted as two separated systems with weak interactions, or one two-electrons system interacted each other inside one system. When the energy conservation is kept rigorously, (18) gives us a puzzle for the change of this kind of consideration from two systems to one system. One of purposes of this paper is to attack this problem. Explicitly for brevity, the nowadays QM provides the exact $< f_{OP} > \approx Z_{eff}^2/2$. In KE-in-affinity calculation, it should be the value given by the equality in (18).

As a comment, the 'effective charge' $Z_{eff} = 2 - l/16$ comes from the variational method, actually from a many-body consideration. Here we have put this $Z_{eff}$ throughout, even for the KE-in-affinity consideration. This is because we have the same physical configuration for (i) neutral He-like atom and for (ii) the second electron started from a position of zero KE. Consequently, for an investigation, what considerations can be put here as alternative approaches, are that (a) one system or two systems consideration or (b) how to consider the electron-electron interaction. They are calculated and demonstrated above.

Moreover, in previous global results (cf. Appendix D) including the ferromagnetic effect \cite{1,2}, most $m$ are small except for H- ion for which has $m \approx 16\%$ of the total two electrons for only the electron dipole-dipole interaction (DD). This result has been taken serious considerations in polarized electron and proton productions. From this result, we need (5). The calculated KE from (5) for one of the two identical electrons of this helium-like atom in the state given in (11) for $m = 0$ is

$$K^{SD}_{He} = 3.85 \cdot 2^{-1} \cdot 1.5^{-1} \cdot 2^2 = 0.289 Z_{eff}^2 < \frac{1}{2} Z_{eff}^2.$$

This result confirms our conclusion derived from (18) above. Since in variational calculation, we use $< V_{e-e} > f/2$ instead of $< V_{e-e} >$ in (18), we can obtain only $K = Z_{eff}^2/2$ exactly. The process given here shows its validity for investigation of helium-like atoms by using DFT instead of using exact QM after we compare (19) with estimation in (18).

Now we need to propose another variational principle from statistical thermodynamics \cite{9} as an extension of (9) which implies the same one as in our previous paper \cite{2}. For a
uniform magnetic field \( H \), the first law in thermodynamics leads to
\[
\delta Q = dE - H \delta M_1 \tag{20}
\]
for the magnetization \( M_1 = \mu_B m \). For an adiabatic process (no heat flow) we find the variational result
\[
\frac{\delta E}{\delta M_1} = H, \tag{21}
\]
which becomes a stationary principle as \( H \) is reduced to zero in ferromagnetism. This also implies an origin of ferromagnetism as claimed in Appendix D. From statistical thermodynamics, (20) is applied to the canonical ensemble which is a subsystem of the microcanonical ensemble, the whole system. Thus (21) is used for a canonical ensemble inside a given microcanonical ensemble. Hence the law given in (20) is of course derived from the separability of a canonical ensemble from a microcanonical ensemble. The separability in this way is used in (28) and (29) below, but betrayed with (30). There is a symmetry broken.

To give a pictorial description within this framework, we are seeking a "spin-hole" subsystem for spin density in which we have the two spins of the two electrons are in parallel. Before any modification is made and obeys strictly the Pauli exclusion principle in a two-electron system which has one electron spin-up and one spin-down. From the density point of view we decompose the total density into \( n = n_+ + n_- \) and \( m = n_+ - n_- \). Inside this spin-hole we have \( m = n \) incorporated with the Pauli electron's ea's of spin-anti-parallel (with \( m = 0 \)). The existence of finite \( m \) leads the \( \delta \) hole compartment. The concept of the hole of this kind is originated in the Fermi holes derived from the Pauli exclusion principle. One of statements for this principle is that two electrons of parallel spin cannot occupy the same space point [10]. In terms of the pair correlation function
\[
\rho(r_1, r_2) = \frac{1}{2}
\]
at \( r_1 = r_2 \). When the possibility of one electron meeting another electron (with spin parallel) is \( 1/2 \), there is a void \( 1/2 \) of this electron at this point which is a kind of hole excluded out by the Pauli principle. This void exists over the whole space in the system here. Therefore in this paper we interpret the void (not \( 1/2 \) here) to contribute to the (density) holes totally. This void is expressed as a fraction of the total density. The spin-holes, as being given by the spin-density, are described also as a fraction of the total density \( n(r) \). In subsequent sections, we emphasize the peculiarity of our decomposition. Two interactions, the electron-spin DD and hyperfine interactions (HI) are introduced. The DD is a symmetry-breaking because its form gives no decomposition rule although we defined the rule in (8) above, and exhibits some properties rather physical but not mathematical. All of these two interactions are in contact forms so that we may have a theory to be able to detect the nuclear structure or pattern from such magnetic effects [11].

In Sec. II, we describe the DFT for the usage in the subsequent sections and state the complete global solutions. Together with the Appendix D, we calculate and tabulate the portions of discrepancies in heliumlike atoms. In Sec. III we discuss the role of the nuclear cusp condition and discuss how to smoothen the interaction function (IF) in HI. We obtain some results that we consider to be partial solutions.
II. Global solutions

In our previous investigations, particularly in Ref. [2], we have introduced $DD(Ed-d)$ for heliumlike atoms, and found the ferromagnetic effects, and used the density $n$ and spin-density $m$ as variables for our canonical ensemble. No complete results were included. Therefore we state here main results with an added HI ($E_F$). The energy functionals for these two interactions are

$$E_{d-d}[m] = -\frac{8\pi}{3}\mu_B^2 \int dr m^2(r),$$ \hspace{1cm} (22)

$$E_F[m] \equiv \sum_{\text{electrons}} \frac{8\pi}{3}\mu_B \int \frac{1}{2} \sigma_H[m(r)] m(r) |m(r)| dr,$$ \hspace{1cm} (23)

$$\sigma_H[m(r)] \equiv \frac{m(r)}{|m(r)|}$$

for the point nuclear magnetic moment $\mu$. The Pauli matrix along the magnetic field $\sigma_H[x]$ is further defined as a functional of density $x$ above so that

$$\sigma_H[m(r)]m(r)|m(r)| = +n_+\mu - n_-\mu.$$  

The above interactions are all $m$-dependent only. For HI, we have

$$E_F[m] \equiv E^{SD}_F[n,m = n_+ - n_-] = E_F[n_+] + E_F[n_-]$$

which obeys the decomposition rule (8) according to a separation of $n$ into $n_\pm$ with $\sigma_H[m]$. Notice the sign in the second term. It is linear and obeys (8) only after insert the functional $\sigma_H[m(r)]$. We see that for DD, $m^2$ is not able to decompose. It forms breaking-symmetry to our decomposition rule above. We employ the variational principle (21) to He-like atoms. The total energy functional is thus formulated for a uniform external magnetic field $H$ for the two-electron system from (7) as

$$E^{SD}[n,m] = \int \nu_{ext}(r)n(r)dr + \mu_B H \int m(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} drdr' \times G[n,m],$$ \hspace{1cm} (24)

$$G[n,m] = \frac{1}{2} [K(2n_+ + K(2n_-)] + E_x(2n_+) + E_x(2n_-)]$$

$$+ E_{d-d}[m] + E_F[n_+] + E_F[n_-]$$

$$= \frac{\zeta}{2} \int \left[(n + m)^\frac{3}{2} + (n - m)^\frac{3}{2}\right] dr - \frac{\zeta}{2} \int \left[(n + m)^\frac{3}{2} + (n - m)^\frac{3}{2}\right] dr$$

$$+ \frac{1}{2} \frac{8\pi}{3}\mu_B \int m^2 dr + \frac{16\pi}{3}\mu_B m(0)$$ \hspace{1cm} (25)

to define and formulate the canonical ensemble inside the two-electron system. According to the separability and showing the symmetry-breakings we write

$$E^{SD}[n,m] = E_+\pm[n_+] + E_-\pm[n_-] + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} drdr' \times E_{d-d}[m],$$

$$E_\pm[n_\pm] = \int \nu_{ext}(r)n_\pm(r)dr \pm \mu_B H \int n_\pm(r)dr + \frac{1}{2} [K(2n_\pm) + E_x(2n_\pm)]$$
As a comment, the separability of the $n_{\pm}$ here excluding the non-separable, symmetry-breaking electron-electron electrostatic potential term, i.e. the third term above in $E^{SD}[n, m]$ provides that the total energy consists two separable parts depending on $n_{\pm}$ respectively. Actually this electrostatic term is not included in the field theoretical total energy discussed in Appendix B. But it is important in the so-called $v$-representation in the DFT. The $n_{\pm}$ two parts are entirely independent on each other, such as (28) below. We are varying the total involved number of electron $n = n_+ + n_-$ if any variation for $n_{\pm}$ in general. Different from the usual DFT in which the whole system is put into consideration as indicated in the restricted condition for fixed

$$\int n(r) dr = N$$

the total number of electron considered. This implies that we must use the Lagrange multiplier method which is an added mathematical theory to the variational principle. We may meet other problems about its correctness.

In order to apply the variational principle (21) to (24), our first attempt is to evaluate the energy functional given in (24) for heliumlike atoms in a global way, with the nucleus point-like or structureless. The electron distribution is based on the wave function (11) as the first approximation. The total electron density is thus

$$n_{\pm}(r) = f(r)^2(\alpha^\pm \alpha + \beta^\pm \beta) = (2Z_{eff}^3/\pi) \exp(-2Z_{eff}r)$$

for spin-up(down) wave functions $\alpha(\beta)$. Now we propose our subsystem as "holes" incorporated within this two-electron system, viz.

$$n_{\pm}(r) = N n_{\pm}(r) = (2Z_{eff}^3/\pi) \exp(-2Z_{eff}r)$$

in which the portion factor $N$ indicates the fraction of the subsystem inside the two-electron system that is involved in our process. The separability in this way was given in our discussion on the canonical ensemble above in Introduction. The value of $N$ should lie between zero and unity, determined according to the theory. When $N$ is zero there is no "hole" subsystem at all whereas if $N$ is unity the whole system is a "hole". The spin-density is similarly proposed as "spin-hole" incorporated within this two-electron system with

$$m_{\pm}(r) = M n_{\pm}(r) = (2M Z_{eff}^3/\pi) \exp(-2Z_{eff}r)$$

in which $M$ varies from -1 to 1 determined according to the theory. When $M$ is -1, $m = -n_{\pm}$ all the electrons inside the system spin-down while $M$ is 1, $m = n_{\pm}$ all spin-up. Therefore the "spin-hole" means the portion of parallel spin in the distribution of a system of one spin-up and one spin-down electrons originally.

As comments here, the chemical system of a helium atom provides $M = 0$ and $N = 2$. After our calculations, we find that $|m|$ can be as large as 16%. To find the inconsistency, first we may think that the Pauli exclusion principle is violated. This point is investigated in Ref. [2]. The density-functional attack of the anti-parallel expectation of two electron is given in this section. With the contact DD and HI, we have $C$ and $F$ below as coupling constants. This is prepared for a nuclear pattern detection as explained below.
When C, F → 0, we have a pure electron system with kinetic and exchange energies. As also claimed in this paper, the DD contact interaction gives a symmetry breaking for the decomposition rule. If we add the correlation energy, the breaking of the symmetry must be larger. Even for the particle exchange symmetry, i.e., the violation of the Pauli principle, the effect of the breaking must be larger.

With the density \( n(r) \) and spin-density \( m(r) \) above, we are able to evaluate energy functionals given in (24). A complete description with algebraic solutions is given in Appendix D. All results given in Appendix D are derived from the variational principle (21). The numerical results of quantities defined in Appendix D are given in Table I in the Appendix D.

From Table I, we can see that the largest value of \( \mathcal{N} = -\mathcal{M}(\mathcal{H}^-) \approx 0.157 \) in (26) and (27) for \( \mathcal{H}^- \) ion. As also stated by Ref. [2], what we have here is that the total two-electron system has been magnetized as

\[
m(2e^-) = m(m.c.) + \delta m = 0 + m(r)
\]

where \( m(m.c.) \) denotes the spin-density in the microcanonical ensemble, \( m(m.c.) = 0 \) according to exclusion principle, and \( \delta m = m(r) = -0.157n_t \) given above for the canonical ensemble. It is for long time being for \( \mathcal{H}^- \) to have an incorrect affinity from (11) in sign of Ref. [6]. To state briefly the problem, the ground state energy for the \( \mathcal{H}^- \) is \( -2 \times 2^2/2 = -(11/16)^2 = -0.473 \) Hartree from the Ritz variation principle. The affinity of the second electron \( E_{affinity} = -1/2 - (-0.473) = -0.0273 \) Hartree, is negative. Experiments show that the ionization energy of the second electron is \( \approx 0.75 \) eV \( = 0.0275 \) Hartree. We have the correct value but opposite sign. The so-called exact solution of the \( \mathcal{H}^- \) ion, say 24-parameter result [12], gives \( E_{affinity} = 0.02773 \) Hartree an exact result but emphasizes heavily on influences of \( r_{12} \). The dependency of \( r_{12} \) makes the system unable to factorize into the product \( \psi(r_1)\psi(r_2) \) of two electrons. It is totally incompatible with the DFT. To the definition of affinity of the second electron, this solution is hardly to apply.

From a recent review for the \( \{1s,1d\}\)-state of helium atom [13], two individual electrons give correct results up to 5 or 6 figures for the unperturbed energies. Only beyond this accuracy, influences of \( \Theta \) enter. Now we investigate \( \mathcal{H}^- \) ion by our method here within the framework of DFT about this point. To specify our physical configuration, first for the part of spin-hole subsystem induced by the spin-density, we have actually a total of \( 2 \times 0.157 = 0.314 \) electron involved and all of them are spin-down. The total energy of this subsystem is

\[
E^{SD}[n, m] = \int v_{ext}(r)(2n_-(r))dr + \frac{c_2}{2} \int (2n_-(r))^2 dr - \frac{c_2}{2} \int (2n_-^2(r))^2 dr + \frac{1}{2} \int \frac{n_-(r)n_-(r')}{|r - r'|} drdr' - \frac{1}{3} \frac{8\pi}{3} \mu_B \int n_-(r)dr
\]

\[(28)\]

for \( n_- = (n - m)/2 \). Second part of this configuration has \( m(m.c.) = 0 \). The energy must be SI and obey the Pauli principle rigorously, and becomes
In order to get the total energy, we need to add another term, viz., the interaction energy \( E_{\text{int}} \) which is put as

\[
E_{\text{int}} = \int \frac{n_S(r) n_S(r')}{|r - r'|} \, dr \, dr',
\]

(30)

a symmetry-breaking term. The existence of this term is due to that the electrostatic effect exists throughout the whole electron density including the interaction between the SI and the SD parts. This term has been ignored in many literatures. First we use the spin-density \( M_s = -0.157 \) from Table I

\[
E_{S,D}[0.157n_t, -0.157n_t] = -Z \psi_f(2 \times 0.157) + \frac{3}{52} \psi_f(2 \times 0.157)^3
\]

\[
- \frac{3}{4} B \psi_f(2 \times 0.157)^3 + \frac{5}{16} \psi_f(2 \times 0.157)^2
\]

\[
- \frac{1}{2} 0.157^2 C = 0.157 \psi_B
\]

\[
= -0.1947 - 5.340 \times 10^{-3} \psi_B = 0.2721 \psi_B
\]

with quantities in (59)

\[
A = \frac{3 \times 2^{3/2}}{500} \psi_f, \quad B = \frac{3^{3/2}}{128} \psi_f, \quad C = \frac{4}{3} \psi_f^2 \psi_B, \quad F = \frac{16}{3} \psi_f \psi_B \psi_f
\]

The SI and the interaction parts are then

\[
E_{S,D}[0.843n_t] = -0.5484; \quad E_{\text{int}} = 0.2275.
\]

Consequently, the total energy of the two-electron system is

\[
E(H^-) = E_{S,D} + E_{S,I} + E_{\text{int}} = -0.5156 - 5.340 \times 10^{-3} \psi_B = 0.2721 \psi_B
\]

(31)

which implies the affinity of the second electron in atomic units

\[
E_{\text{affinity}} = -1/2 \cdot (-0.5156 - 5.340 \times 10^{-3} \psi_B - 0.2721 \psi_B)
\]

\[
= 0.0156 + 5.340 \times 10^{-3} \psi_B + 0.2721 \psi_B
\]

(32)

We see that we have obtained a result with correct sign smaller than the experimental value in comparison with the discussion above. As an examination, we use the double precision
in minisupercomputer for the calculations from the exact formulas

\[ M = \left( \frac{B}{A} \right)^3 = 0.1569210 \]

\[ E^{SD} = -0.209078 - 5.340 \times 10^{-3} \mu_B^2 - 0.2721 \mu_B \]

\[ E^{SI} = -0.590931, \quad E'_{\text{int}} = 0.227385. \]

The affinity energy is obtained as

\[ E'_{\text{affinity}} = -1/2 (-0.572624 - 5.340 \times 10^{-3} \mu_B^2 - 0.2721 \mu_B) \]

\[ = 0.072624 \times 10^{-3} \mu_B^2 + 0.2721 \mu_B. \]

We can see that this solution is larger than the experimental value. Therefore we conclude that we have a correct theoretical result apart from a calculational uncertainty. In turn, we have a right theory. Particularly we are treating this ion in its ground state and with a separable two-electron system, greatly different from solutions we have nowadays.

Here we have obtained an entirely new physical knowledge. From the results of \( E'_{\text{affinity}} \) and \( E''_{\text{affinity}} \), we see that the direct effect of the magnetic moments, as in (32), has only negligible influences in energy values due to the smallness of \( \mu_B \) and \( \mu \). Nevertheless if there are no magnetic effects, the physical treating will be spin-independent, i.e. for \( \delta m = m(r) = 0 \). In our thermodynamical speaking here, the whole system is a microcanonical ensemble. However the addition with the magnetic effect makes the physical process to separate the whole system into canonical ensemble and the reservoir (due to existence of these magnetic moments). This process influences and contributes the indicated change of the affinity from the unacceptable \(-0.0273 \text{ Hartrees}\) to the experimental verified value \( E'_{\text{affinity}} \) above. Conclusively, the indirect effects of magnetic moments do have dominated to influence the energy values. Notice that this is not a direct effect! But the involvement of these small \( \mu_B \) and \( \mu \) changes the entire physical process, thus changes the resulting energy values. The decomposition and the canonical ensemble idea together with DFT do provide the correct result for the affinity of H\(^-\) problem.

Furthermore from the description in the Appendix D, we make some comments on the quantity \( R_F \) in Table I

\[ R_F \equiv FA^3/(C B^3) = 78.3 Z^2 \mu_B/\mu_B. \]

which is the ratio of the portion due to HI and the portion due to DD in \( z^{(2)} \) and \( z^{(3)} \) given in the Appendix D. Here unexpectantly, starting from Li\(^+\) the magnitude of \( R_F > 1 \); thus the influence of HI is larger than that of DD. From Table I, for \( Z \) larger than 3, the effects of HI are actually dominant. According to considerations of energy, the spin-down case in the magnetic field \( H \) corresponds to the state of lower energy. The QM calculation of DD makes the expectation of DD positive [6]. Here hyperfine interaction dominates to make the expectation of HI negative [2] i.e. to have more spins parallel in spin-down direction. For examples, \( ^{209} \text{Bi}^{81+} \) has \( R_F \approx 9.9098 \times 10^4 \), a significant magnitude. We may have the conclusion that we need only to consider the HI part and neglect the DD part. From Ref. [2], we have (i) for only DD case, the solution of the \( m \) at saturation
\[ m = M_s^{DD} = -\left\{ \frac{B}{A} \left( 1 - \frac{BC}{A^2} \right) + O(\mu_B) \right\}^3 \]  

(34)

and (ii) for both DD and HI, we obtain

\[ m = M_s = -\left\{ \frac{B}{A} \left( 1 - \frac{BC}{A^2} [1 - R_F] \right) + O(\mu_B) \right\}^3. \]  

(35)

For \(^{209}\text{Bi}^{81+}\), \(M_s^{DD} \propto (B/A)^3 = 1.468 \times 10^{-12}\) but \(M_s^{HI} \propto (B/A)^3 = -8.172 \times 10^{-8}\). Theoretically, the spin-down part is increased greatly after introducing HI and the energy is lowered. A recent report on the hyperfine structure of \(^{209}\text{Bi}^{82+}\) as a reference to GSI (Darmstadt) can be found from Ref. [14]. For cluster studies, the configuration here may have some usages. The Bi result above may have an analysis for \(^{209}\text{Bi}^{81+}\), \(M_s^{HI} = (B/A)^3 = 3.748 \times 10^3\) and for \(^{81}\text{Br}^{33+}\), \(R_F = 4.040 \times 10^3\), they can be useful for \((\text{HBr}^+)^\text{Br}\) clusters [15].

For \(^{85}\text{Rb}^{35+}\), \(RF = 2.848 \times 10^3\) which is possible to be studied in a collision process [17] applying to surface collision and atomic delocalization cases [18]. Therefore for most elements \((Z \gg 3)\) the nuclear spin-hole due to HI is larger than the Fermi-Coulomb hole due to DD. Actually we may neglect the DD and consider the HI only in many cases. The total energy functional is then to obey the decomposition rule (8) totally since no more DD.

### III. Variational principle and local solutions

The influences of HI between the nucleus and the electron may be large relative to DD, as obtained in the preceding section. We need to explore HI further. In computational physics [2, 10], we believe the electron density \(\rho(r)\) near the nucleus at \(r = 0\) to obey the nuclear cusp condition

\[ \frac{d\rho}{dr} \Big|_{r=0} = -2Z\rho(0) \]  

(36)

after interaction processes of HI are smoothed [19]. An exponentially decreasing function (11) obviously fulfills this requirement. Nevertheless, there are still many puzzles about the global variations (variation of constants) treated in the preceding section. First, solutions \(x(1), x(2), x(3)\) in (64) to (66) etc. in Appendix D include a constant term of dependency of the coupling constant \(F\). Hence results of these solutions indicate that the influence (or correction) due to \(F\) applies over the whole space constantly. In the form of the HI (23) we have the contact S-function dependency of HI. The effect above appears too strong. At most, what we are able to understand are local or near-local influences. We introduce a local \(\delta\) variational ansatz,

\[ \frac{\delta F^{SD}[n,m]}{\delta m} = \mu_B H \]

\[ = \mu_B H + \frac{5}{6} \epsilon_0 \left[ (n + m)^{3/2} - (n - m)^{3/2} \right] \]

\[ - \frac{4}{6} \epsilon_0 \left[ (n + m)^{3/2} - (n - m)^{3/2} \right] - \frac{8\pi}{3} \mu_B m + \frac{16\pi}{3} \mu_B \rho(r) \]  

(37)
from (21). This manipulation rigorously follows from the variational principle instead of variation of constants used in global solutions. As a comment, in the previous treatment [1,2] for global solutions, the trial wave functions used for the variational method is typically a kind of \( f(Z_{\text{eff}}(r)) \) in (11). Any variations on the parameter \( Z_{\text{eff}} \) cause a change of the wave function or the physical configuration of the state globally over the whole space (\( r \in 0 \to \infty \)), even the normalization constant. This is by definition a global solution. In (37), we have a variation \( b(r) \) locally at \( r_0 \). The determination of the energy values, such as the \( S^{(2D)} \), above, is determined point by point in space. This is classical, such as we derive the Lagrange equation in classical dynamics. Therefore it is truly the so-called \( \delta \)-variation principle. The results of the deduction of this kind is defined as the local solution in this paper. They appear to have reliable results below in this paper.

We obtain a resultant algebraic equation from this equation (37) for \( y \) in DFT for the ground state configuration, i.e. the saturated magnetization

\[
y \equiv (-m)^{\frac{1}{2}} = (-m_\alpha)^{\frac{1}{2}} = n_{\alpha}^{-}\frac{3}{2},
\]

\[
A_1 y^2 + B_1 y + C_1 y^3 - F_1 \delta(r) = 0,
\]

\[
A_1 = \frac{5}{3} 2^{-\frac{5}{2}} c_4 = 3.7982, \quad B_1 = \frac{4}{3} 2^{-3} c_4 = 1.3307,
\]

\[
C_1 = \frac{8 \pi}{3} \mu_B^2 = 3.5520 \times 10^{-5},
\]

\[
F_1 = \frac{16 \pi}{3} \mu_B \mu = 3.8692 \times 10^{-8} \text{sgn}(\mu) \lambda,
\]

\[
\lambda \equiv |1836 \mu_0 / \mu_B| \sim O(\text{unity}).
\]

This cubic algebraic equation yields the solution

\[
m_\alpha = \left[ \frac{0.8 c_4}{2^{1/3} c_k} + \frac{32 \pi c_2 2^{-3/2} \mu_B^2}{5} + O(\mu_B^4) \right]^{1/3} + \frac{2 \mu_B}{\mu_B} \delta(r).
\]

A nuclear spin-hole arises naturally at the center \( r = 0 \), but the constant saturated magnetization of \( m_\alpha \) in the first term in the last equation applies non-physically over the whole space. We may claim that the solution from (37) for the local solution in the last equation is not reliable.

To correct this defect we propose a smooth interaction as an extension of (23) according to

\[
E_F^{(S)}[m] = \frac{16 \pi}{3} \mu_B \mu \int m(r) S(r) dr
\]

\[
= \frac{16 \pi}{3} \int dr \mu_B m(r) \int dr' \mu S(r') \delta(r - r').
\]

(39)

A contact interaction of the local electron magnetic moment \( -\mu_B \mu(r) \) and the local nuclear magnetic moment \( \mu S(r') \) arises here [14]. The localized \( b \)-function in (23) is now replaced by
the interaction function (IF) \( S(r) \). Similarly to the process to obtain (38) above, we perform a local variation with (21) including modification (39) to obtain an algebraic equation

\[
A_1 y_1^2 - B_1 y_1 + C_1 y_1 - s|F_1 S(r)| = 0, \quad s \equiv sgn(\mu S(r)).
\]  

(40)

It seems improper to solve this equation by algebra also after a consideration of non-physical constant term above for (38). Instead, to solve (40) by comparing the order of magnitude of each term and avoid constant solutions of \( y \) over the whole space, we list 1 partial solutions" according to the order of magnitude for non-zero nuclear magnetic moments as follows,

\[ |
\begin{align*}
\text{(I)} & |S(r)| \gg \frac{A_1^2}{C_1^2|F_1|} \sim \frac{1.1244 \times 10^{14}}{\lambda} \\
y^2 \text{ and } y^3 \text{-terms negligible} \\
y^{(I)} &= -\{s|F_1 S(r)|/C_1\}^{\frac{1}{2}} \\
m_4^{(I)} &= s|F_1 S(r)|/C_1 = s \cdot 1.0890 \times 10^{-3}|\mu S(r)|. \\
\text{(II)} & \frac{A_1^2}{C_1^2|F_1|} \gg |S(r)| \gg \frac{B_1 A_1}{|F_1|} \sim \frac{1.7382 \times 10^{8}}{\lambda} \\
y^2 \text{ and } y^3 \text{-terms negligible} \\
y^{(II)} &= \pm \{s|F_1 S(r)|/A_1\}^{\frac{1}{2}} \\
m_4^{(II)} &= \mp \{s|F_1 S(r)|/A_1\}^{\frac{1}{2}} \\
&= \mp 1.0282 \times 10^{-12}\lambda^{\frac{1}{2}}|S(r)|^{\frac{1}{2}}, \text{ for } s = +1. \\
\text{(III)} & \frac{A_1^2}{|F_1|} \sim \frac{1.706 \times 10^{7}}{\lambda} \gg |S(r)| \\
y^2 \text{ and } y^3 \text{-terms negligible} \\
y^{(III)} &= -s|F_1 S(r)|/B_1, \\
m_4^{(III)} &= s|F_1|^2|S(r)|^2/B_1^2 = s \cdot 2.4585 \times 10^{-27}|\mu S(r)|^3.
\end{align*}
\]

(41) \( (42) \) \( (43) \) \( (44) \) \( (45) \) \( (46) \)

Here ranges of validity of \( S(r) \) are equivalent to spatial domains in which solutions are valid. Consequently we have solutions in various disconnected regions and generate much more information than that from (38) and from the preceding section, in which we used solutions fall into case (23), solutions fall into case (I) above if \( S(r) \) is replaced by 6(r) in (42).

In partial solutions above, we assume that \( |S(r)| \) is a smooth continuous function, but its values vary over a great range. Therefore we need to \( \ln[\mu S(r)] \) and \( \alpha \) intrinsically for \( s = +1 \) for two parameters \( A \).
FIG. 1. The fitting of the saturated magnetic spin-density $m$, as a function of the interaction function strength $S(r)$. (a) A draw of the curve defined in (47) but with $S_+ \equiv \lambda S(r) > 0$. The magnitude of $m(r)$ is shown by $\log_{10} m$. The $x$-axis is scaled by $\ln |\mu S(r)|$. (b) The parameter $B$ defined in (47) is plotted. (c) The variation of the parameter $A$ in terms of $\log_{10} A$ is plotted from the definition given in (47). The marks I, II, III in the figure show that near these marked regions, the above three cases are valid correspondingly.

\[ m_0 = A[\lambda S(r)] \delta, \quad (47) \]

\[ \ln(A) \simeq -6.8225 - \frac{662.9}{\ln[\lambda S(r)]} + \frac{1184}{(\ln[\lambda S(r)])^2}, \]

\[ B \simeq 1 + \frac{12.5}{\ln[\lambda S(r)]} + \frac{75}{(\ln[\lambda S(r)])^2} \]

which is estimated as the partial solution inside the nucleus. The variation of $\log|m_0|$ is plotted vs. $\ln|\lambda S(r)|$ in Fig. 1(a). The function $S_+ \equiv \lambda S(r) > 0$. The marks I, II, III mean the valid locations of the above three cases in the figure. Fig. 1(b) and (c) show the variations of $B$ and $A$. Since the hyperfine field distribution has studied intensively [20], the above result can have some comparisons.

IV. Summary

According to the conventional paradigm, two electrons in heliumlike atoms have spins completely aligned in opposite directions which is the standard expectation in relation to
the Pauli exclusion principle, identical particle exchange symmetry, closed-shell structure, zero total angular momentum, zero electron magnetization and minimum energy etc. In this work, we find the decomposition rule for density in the density-functional theory, viz., the density should be decomposed into the spin-up and spin-down densities. The dipole-dipole interaction between electrons in such a system serves as breaking-symmetry to the above standard expectation. Together with the hyperfine interaction, we find that it appears a discrepancy to have the magnetization. As in the Heisenberg ferromagnetism in which the exchange interactions provide ferromagnetic effects in materials, we find that this conclusion is applicable in heliumlike systems [1,2]. The value obtained due to magnetic effects in this paper is actually smaller than experimental findings for the affinity energy of $\text{H}_2^+$. Further investigation is expected.

The dipole-dipole interaction between electrons produces a spin-hole globally when two electrons are in contact. The hyperfine interaction differs in nature because the nuclear spin-hole is centered at the nucleus. We map out the situation qualitatively and its space configuration quantitatively. When the structure function is introduced as in the preceding section, we detect even nuclear structure according to this theory through the hyperfine interaction due to the contact nature (in form of $b$-function) of interactions.

In practice, $\text{H}_2^+$ may have the largest value of the ferromagnetic effect. We expect that it is detectable. The nuclear spin-hole treated in Sec. III implies $^1$ Partial solutions" to be valid in different regions in space. What we have obtained from $^1$ Partial solutions" are that magnetizations exist only in space where the interaction function exists and finite. These quantities reflect the effect of nuclear spatial structure. An estimated solution is given in (47) in a continuation way from solutions derived at discrete portions.

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Appendix A: Investigations of an electron to occupy an energy state

Current physics, especially the semiconductor physics, considers that if there are (band) energy states, there are possibilities to occupy electrons. In terms of the density of states (DOS), when there are higher DOS, we have higher probability to occupy electrons at the same energy (at various space points). What is physics that we can occupy an electron in a quantum state or at an energy level with DOS? We state our recent investigations together with some historical aspects in this appendix. First we review current formalisms in terms of density including DOS. Further we give some troublesome in the DOS formalism in Appendix C. Most important, these formalisms do bring all DOS and density-function together. The foundation of density-functional formalism may roughly be classified into three origins, viz.,

(a) the usual one with the density as the independent variable started from Hohenberg, Kohn and Sham [21,22] (which is commonly referred as the density-functional theory (DFT)).

(b) The second one is from Fano's density-operator with possible mixture states [23]. It also brings the wave function, the state or level, to be occupied by particle, electron say.

(c) The third one is from DOS divided into DOS in energies, in local DOS, in integrated DOS and in sum of states, etc. [24].

To count the number of states equals to count the number of electrons. It arrives at a problem how and when a quantum state is a candidate having a tendency to be occupied? We have investigated its physics in Refs. [3-5,25,26]. Here we use our results from those references to unify conceptually the density formalisms. This report is entirely new. It includes the probability interpretation incorporated with dynamics.

The connection of DOS with the electron number is usually as follows: (i) we employ a minimum energy model, i.e. we fill one possible lowest energy state with one electron until arriving the Fermi energy $E_F$ after all electrons are filled.

(ii) we consider a variation of the total energy. However someone did vary with electron numbers on the Fermi surface from their stationary distribution for transport phenomena. About (i) the same author did borrow the frontier function $f(r)$ or Fukui function [3,4] to investigate how the electron is taking the state to occupy. Actually, for a lowest energy configuration, consisted with $n$ occupied states of $n$ electrons with density $\sum_{occ} |\psi(r)|^2$, we have from Ref. [3]

$$f(r) = \frac{\delta \mu}{\delta v} = \frac{\sum_{occ} |\psi(r)|^2}{n}$$

(48)

for chemical potential $\mu$ and perturbed potential energy $\delta v$. As an example to explain, in the H-like or Slater-type orbitals $2p^6$, there are six states with the same energy. All of them are occupied by a six-electrons configuration. This function denotes the highest occupied orbitals (HOO) for these six electrons. It is the probability to occupy by these electrons by (48) in Ref. [3]. In the example, the $\text{HOO}2p^6$ are in the sum of $f(r)$ in (48). On the contrary, when it is the lowest unoccupied orbitals (LUO), it is the probability to leave the configuration a vacancy. In the example of H-like orbitals, $2p^53s^1$ is the atomic LUO and is involved in $f(r)$ in (48). Note that this is the point (ii) above, i.e. here we vary the total energy. It does not include the vacancy state $3s^1$ for real six-electrons configuration.
for indication $\mu(6)$. However, this occupied $3s^1$ turns out that it represents the occupation possibilities accompanied by electron transfers, say from one occupied state to one vacancy state. It includes to deal with attachment and detachment process with requirement of both occupied and vacancy states. In the above example of six electrons, one $2p$ electron is detached and transferred or attached to $3s^1$ so that it is still considered as one of lowest energy state in calculating $\mu$. The indefiniteness of this occupied or unoccupied possibility in the definition of $f(r)$ is due to the definition of $\mu = \mu(n)$ for the $n$th electron which is defined as the energy difference between $n-1$ and $n$ electrons, and together with a necessity with involvement between $n$ and $n+1$ electrons energy value in commonly accepted cases. This $\mu$ appears in (48) inside $\delta\mu$. In the above $n=6$ example, we measure $\mu$ by taking into account three configurations: $2p^5, 2p^6$ and $2p^53s^1$ this consideration of second lowest energy state (or the first excited state) is exactly the energy variation process of the total energy (ii) above. Therefore $f(r)$ includes a counting on the atomic $\mu_002p$ and the atomic $Luo_0 3s$. It is related to DOS not only for accumulations but also for dissociations. This expresses the following newly discovery fact that the total energy of a system is not conserved but with energy variation. To be explicitly, for two atoms $A$ and $B$, when they are reacted in equilibrium with the compound $A^+6B^-6$ with charge transfers, the total energy of $A$ plus $B$ is not equal to that of $AB$ \cite{5}. More precisely, the variation of energy provides that $\delta E \neq 0, \delta^2 E \neq 0$ in the charge transfer process:

$$A + B = A^{+\delta}B^{-\delta},$$
$$E_{AB} = E_A + E_B + \delta E + \delta^2 E.$$  

One another earlier approach we can find to connect the DOS to electrons is the de Broglie’s guidance wave \cite{25}. An electron does exist inside a state as a guidance of the propagation of this state function. Therefore a single state is equivalent to one electron in number. This is so-called objective representation of the wave function. The author of this paper proved mathematically that the wave field in QM tends to an electron in the classical limit $\hbar \to 0$ \cite{26}. Explicitly the probability in the density-operator measure becomes

$$|<r'|\phi > <\phi|r>|^2 \equiv \phi^*(r')\phi(r) \to H(VW, r) = \begin{pmatrix} \frac{\partial W}{\partial t} \end{pmatrix} \delta(r' - r)$$  \hspace{1cm} (49)

for the Jacobi $W$ function $W(t, r)$. Since

$$H(VW, r) = -\frac{\partial W}{\partial t}$$

is the Hamilton-Jacobi equation, thus along the classical Hamilton-Jacobi trajectory, the probability represents the quantum correspondence of a classical particle, the \textit{quantum particle}. This answers also the Dirac’s question in earlier time for a particle trajectory in QM \cite{27}. All of these considerations connect the number of particle and the DOS. Furthermore they verify also that this connection is a part of QM satisfying the first Postulate in QM. This first Postulate states that a \textit{physical system is described by a wave function which represents the probability amplitude of probability density. All the dynamics are included in the wave function}. This is an accepted Postulate since the development of quantum mechanics \cite{25,28}. Ordinarily, when we study wave function as solutions in QM, no dynamical
picture is given. The above considerations give us not only the probability distributions but also the dynamics, even trajectories picture in our solutions. This not only verifies the correctness of quantum mechanical postulate but also justifies the possibility to have and to use the probability interpretation. This is a further development of density-formalism from its stationary behaviours to time-dependent dynamical behaviours.

Although we can successfully connect the particle picture with the wave function, but among the three origins of DFT given above, they are different connections and only mathematically or conceptually. Here we demonstrate how to unify in our opinions. First we give some pictorial descriptions. We notice that an electron is described by the wave function which is the probability amplitude for a quantum particle [28]. It has not only a distinct classical trajectory, but also has some quantum extents in space in general. The extent of this kind may provide or result from a probability density, or equivalently from an usual density (of mass or particle number). This equivalency is our intuitive identification in most cases. We think that mathematically we have at least one intuitive evidence given in (49). The left hand side of (49) is the Fanol's formalism of density matrix of pure state $|\psi\rangle$ and take the matrix element between $\langle r'| \psi\rangle$ and $| r \rangle$. In the meantime, the right hand side of (49) gives the particle equation of motion as predicted by the guidance waves with distribution $S(r'-r)$. When this $S(r'-r)$ is viewed as the probability distribution, it may have its equivalence to any other probability distribution, such as $|\psi|^2$ in (50) below. Then this picture unifies the objective and the subjective representations of de Broglie's, and verifies the consistency between them with the Fano's formalism mathematically. Some comments about the generalization to mixture states can be found from Ref. [26]. The connection between the DFT with Hartree density of electrons

$$ n \equiv \sum_{\text{occ.}} |\psi_i(r)|^2 $$

and the Fano's formalism is well-known and can be found elsewhere [29]. Even the original formalism of density matrix in the Dirac's book is considered as a part of QM [30].

After some investigations in Refs. [3-5, 26] of the same author, we believe that the third kind of formalism with DOS is consistent with the DFT via the frontier function as demonstrated above. This can be understood that the frontier function represents the probability of occupation per electron and is equal to the wave function square or the probability density per electron if we neglect the detachment of particle in the frontier function $j(r)$. When the probability indicated by the wave function square is expressed in energy values, such as the local DOS

$$ N(E, r) \equiv \sum_{\text{occ.}} |\psi_i(r)|^2 \delta(E-E_i) $$

(50)

is the DOS formalism. In this formalism the sum of wave function squares are the same one as in $f(r)$. Finally as comments here, the indefiniteness of whether the state is attachment or detachment in $f(r)$ is still work of our future investigations.
Appendix B: Total energy in the field theory

In the field theory of many electron system, the Hamiltonian of an N-electrons system in the second quantized form can be written as

\[ \hat{H} = \hat{K} + \hat{V} \]

\[ = \sum_{\tau_1, \tau_2} a_{\tau_1}^* a_{\tau_2} \langle \tau_1 | K | \tau_2 \rangle \delta_{\tau_1, \tau_2} + \frac{1}{2} \sum_{\tau_1, \tau_2, \tau_1', \tau_2'} a_{\tau_1}^* a_{\tau_2'}^* \langle \tau_1, \tau_2 | V | \tau_1', \tau_2' \rangle \delta_{\tau_1, \tau_1'} \delta_{\tau_2, \tau_2'} \]

(51)

for KE \( K \) and potential energy \( V \). For brevity, we borrow the results in Ref. [31]. The present author found that in the free electron model solution of (51), the KE K-part gives exactly the Thomas-Fermi kinetic energy,

\[ \langle N | \hat{K} | N \rangle = N c_k n^\frac{3}{2}, c_k \equiv \frac{3}{10} (3 \pi^2)^{\frac{3}{2}}, \]

(52)

for \( |N\rangle \) the wave function for Fermi sea. This result is verified directly in parallel to the calculation in Ref. [31]. For the potential energy V-part we have put the electron-electron interaction

\[ V = \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}; \]

\[ \langle N | \hat{V} | N \rangle = -N c_k n^\frac{3}{2} \equiv E_{ex}^{S}[n], \]

(53)

the same \( E_{ex}^{S}[n] \) below (6). Therefore for a homogeneous electron gas with a treatment by the field theory, the Coulombic potential of electron-electron interaction for \( n(r) \) and \( N = \int n(r) dr \) gives exactly the exchange energy in DFT, physically and mathematically. From the theory of Ref. [31], we see that the total energy (51) of the N-electrons system has only two terms, viz., the Thomas-Fermi \( \langle N | \hat{K} | N \rangle \)-term given in (52) and the electron-electron \( \langle N | \hat{V} | N \rangle \)-term in (53). That means, the total energy

\[ \langle N | \hat{H} | N \rangle = N c_k n^\frac{3}{2} - N c_e n^\frac{1}{2}. \]

(54)

This is a surprising result: the rigorous field theory implies a total energy for a many-electron system to have a familiar identification in solid state physics. The average energy of an electron is thus well-known as

\[ \frac{\langle N | \hat{H} | N \rangle}{N} = c_k n^\frac{3}{2} - c_e n^\frac{1}{2}. \]

This result is what we use as a daily formula in DFT.

For the discussion of decomposition rules, we obtain a similar decomposition for exchange energies if we decompose the above Fermi sea by spin-up-part and spin-down-part (using exactly the same techniques in Ref. [31]). That means, many-body interaction energies of the spin-independent form can be decomposed into spin-dependent form exactly the same as we did in (4) and (5) for KE.
Here we have derived the conclusion that (a) the total energy of an N-electron system is given by (54) which has only two terms. These two terms are those terms which we are extremely familiar in the local density approximation of DFT. (b) when the spin-up and spin-down parts are decomposed, the potential energy or exchange energy in (54) is decomposed according to (55) together with the decomposition of KE in (6) from (51) and (52).
Appendix C: Troublesome in decomposition of DOS

In Appendix A, we have discussed the physics of occupation of an electron in a state in the DOS. Explicitly, the number density of state represents only the possibility of existence of an energy level at that energy value. What we know from QM is that we can have a wave function (spatial distribution) associated with this energy value. From the de Broglie ideas, we understand that this spatial distribution is only a probability distribution. How and why we can attach a particle or particles onto this state via the spatial distribution of probability is the main point of DFT. It is also a matter of the theoretical foundation of DFT. To author\textsuperscript{5} notice, equation (49) is the only one to accumulate the number of particle inside the wave function. This result is applied widely in semiconductor physics. In semiconductors, a state or a higher DOS means higher possibility to occupy the electrons or holes. Sometimes, we even consider that the DOS means directly equal to the number of particles. In Ref.\textsuperscript{[4]}, the same author did investigate this problem by Fukui function. It is this paper to bring out this problem in a rather systematic way. In our discussion in the text, we have used the number particle density $n$, $n_{\pm}$, $m$ etc. with $n dr$, say, considered as the number of particle existed in the volume element $dr$. No problem for $n$. For $n_k$ in a magnetic field $H$, say, we meet troublesome when the number of particles is identified with the DOS. This is the discussion followed.

Apart from the energy functional decomposition in (2) according to (1), we have another troublesome in decomposition of DOS. For the DOS formalism in Appendix A, we illustrate the decomposition of the DOS by the theory of the Pauli paramagnetism. We use the Thomas statistical model at zero temperature, or simply the Thomas-Fermi kinetic energy. When we are in $k$- or $k$-representation, in other words the states are arranged according to $k$-coordinates, the theory gives DOS of electrons with a parabolic distribution, viz., $n_E(dE)\sim \sqrt{E}$. When a uniform magnetic field $H$ is applied, energies of $n_+$, the spin-up electrons, and $n_-$, the spin-down electrons, become $E(k) \pm \mu_B H$. The DOS is accordingly different as $\sqrt{E(k) \pm \mu_B H}$. They fill up to the same Fermi energy level as their maxima.

The occupations in term of DOS for the SI case in $k$-variable is

$$2 \sqrt{E(k) \neq \sqrt{E(k) + \mu_B H + \sqrt{E(k) - \mu_B H}}}$$

where the right hand side is for the SD case.

In E-distribution, i.e. states are arranged according to E-values, we can still have

$$\int^n_{E_F} 2 \sqrt{E} dE = \int^n_{E_F} \sqrt{E - \mu_B H} d(E - \mu_B H) + \int^n_{E_F} \sqrt{E + \mu_B H} d(E + \mu_B H),$$

which becomes a problem for electrons on Fermi surfaces in the transport discussion. Therefore the spin plays an important differentiation role when the spin-density is concerned. It is noted that Fermi energies in (57) are not the same. Here we have the total energy variation of the whole system including those electrons in low-lying levels. This reviews that we can not consider only electrons near the Fermi levels influenced by the magnetic field. This point is stressed in (ii) in Appendix A. In the derivation of the exchange energy in (53) and (55) from the field theory in Ref.\textsuperscript{[31]}, when there is a magnetic field, we can see easily that the spin-up and spin-down parts must be separated to calculate. The final
results of these spin-up and spin-down parts are exactly the second equation given in (55). This consequence confirms the Heisenberg’s many-body theory of the so-called Heisenberg ferromagnets [32]. From an energy viewpoint, this electron-electron interaction is separable with the separation given in (55). It gives the separability (8) of the total energy given in (51). Our decomposition rule (8) is valid for DOS formalism in this particular way. In addition to these two main terms in the energy functional, another type of energies, such as the DD given below, may not have the decomposition rule of this kind and becomes symmetry-breaking to the decomposition. In this paper, we include the breaking-symmetry of this kind to study what happens to the total energy functional related to the decomposition rule (8) given above.
Appendix D: Variational theory for the ferromagnetic effects of heliumlike atoms

The expression \( E[n, m] \) is evaluated by substituting the electron density (29) and the spin density (30) into the total energy functional (24). We integrate (24) with \( n \) and \( m \) from (26) and (27) and obtain

\[
E[N, M] = \int v_{ext}(\tau) n(\tau) d\tau + 2\mu_B HM + E_{Hartree}[N] + G[N, M],
\]

\[
G[N, M] = \frac{3}{5} A \left[(N + M)\frac{3}{2} + (N - M)\frac{3}{2}\right]^{\frac{1}{2}}
- \frac{3}{4} B \left[(N + M)\frac{3}{2} + (N - M)\frac{3}{2}\right]^{\frac{1}{2}} - \frac{1}{2} CM^2 + FM.
\]

Here the constants are evaluated as

\[
A = \frac{3^{14} 2^7 \pi^2}{500} Z_{eff}^2, \quad B = \frac{3^{10} 2^3}{128 \pi^3} Z_{eff}, \quad C = \frac{4}{3} Z_{eff}^2 \mu_B^2, \quad F = \frac{16}{3} Z_{eff}^2 \mu_B^2.\]

Since the variational principle (21) applies on \( m \), or in turn on \( M \), we obtain finally

\[
\frac{A}{2^{1/3}} \left[(N + M)\frac{3}{2} - (N - M)\frac{3}{2}\right] - \frac{B}{2^{1/3}} \left[(N + M)\frac{3}{2} - (N - M)\frac{3}{2}\right] - CM^2 + F = 0.\]

As a comment, in (60), together with

\[
M_0 \equiv \frac{1}{2} \left[(N + M) - (N - M)\right]
\]

we can see that the decomposition rule is valid here. This leads us to have the possibility of saturation condition below. Explicitly, this leads (62) possible of \( z \) alone below. For instance, if we have a term such as \( l/(N - M)(N - M) \), the coupled factor in terms of \( N - M \) will make the ferromagnetism impossible.

Density-functional formalism after use of the variational method gives a saturated ferromagnetic solution [2]

\[
M_0 = M_0 \equiv - N \equiv -z^3.
\]

This ground state identification leads us to have the \( \delta \)-spin-hole subsystem throughout the paper. This unknown \( z \) is a solution of the cubic equation from (60) and (61)

\[
Ax^2 + Bx + Cz^3 - F = 0.
\]

The orders of magnitude are

\[
A \sim B \gg C \gg |F|; \quad |F| \gg C^2\text{ for non-zero nuclear spin}.
\]

as the Bohr magneton \( \mu_B = (2.137) \times 1 e.u \), and the nuclear magnetic moment \( |\mu| \sim \mu_B/1836 \); we expand our solutions in these orders approximately. With some algebra (62) yields the solutions of three unequal real roots. The dominant terms are
\[ \varepsilon^{(1)} = A/C + O(\mu_B^0) = 68731/Z_{eff} \gg 1 \]

\[ \varepsilon^{(2)} = \left(-M_s^{(2)}\right)^{\frac{1}{2}} = \frac{B^2C}{A^2} - \frac{F}{B} + O(\mu_B^0) = \left(\frac{0.151\mu_B^0}{Z_{eff}}\right)(1 - R_F), \quad (64) \]

\[ \varepsilon^{(3)} = \left(-M_s^{(3)}\right)^{\frac{1}{2}} = \frac{B}{A} - \frac{B^2C}{A^3} + \frac{F}{B} + O(\mu_B^0) \]

\[ = \left(\frac{0.371}{Z_{eff}}\right)[1 - 0.408\mu_B^0(1 - R_F)], \quad (65) \]

\[ R_F \equiv FA^3/(CB^3) = 78.3Z_{eff}^2\mu/\mu_B. \quad (66) \]

Here \( R_F \) is the ratio of the portion due to HI and the portion due to DD in \( \varepsilon^{(2)} \) and \( \varepsilon^{(3)} \). The value of \( \varepsilon^{(1)} \) is unacceptable because it is much larger than unity and lies outside the range of acceptable solutions. As to solutions \( \varepsilon^{(2)} \) and \( \varepsilon^{(3)} \) we cannot judge which is a proper one. For the present theory, we accept \( \varepsilon^{(2)} \), because when \( F = 0, C = 0 \) the energy functional (58) applies to the Thomas-Fermi-Dirac model (TFD). As there are still no ferromagnetic effects nowadays in TFD, we accept \( \varepsilon^{(2)} \). For \( \varepsilon^{(3)} \), it includes the exchange effects and gives information about Heisenberg ferromagnetism. Therefore \( \varepsilon^{(3)} \) includes a larger group of phenomena. It is noticeable to imply a theory of ferromagnetism. This theory is the DFT of TFD itself (here still using \( C = F = 0 \)). It is another kind of ferromagnetism obtained from the exchange effect, different from the deduction of Heisenberg ferromagnets. Here we have actually developed and provided a new theory for (Heisenberg) ferromagnets with entirely different conceptions. Hence we list both two solutions. For various heliumlike

<p>| TABLE I. Values to measure the portion of spin-holes in He-like atoms. Two roots ( \varepsilon^{(2)} ) and ( \varepsilon^{(3)} ) from (64) and (65) and the solutions of portion ( M^{(2)}_s ) and ( M^{(3)}_s ) are given. ( R_F ) indicates the ratio due to hyperfine interaction/dipole-dipole interaction given in (33) and (66). |
|-----------------|-----|----------------|-------------|-----------------|----------------|</p>
<table>
<thead>
<tr>
<th>( \varepsilon^{(2)} ) / ( \mu_B^0 )</th>
<th>( \Delta )</th>
<th>( \varepsilon^{(3)} )</th>
<th>( M^{(2)}_s ) / ( \mu_B^0 )</th>
<th>( M^{(3)}_s )</th>
<th>( \mu_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_F )</td>
<td>0.0385</td>
<td>0</td>
<td>2.70</td>
<td>-2.52</td>
<td>11.8</td>
</tr>
<tr>
<td>( \varepsilon^{(2)} ) / ( \mu_B^0 )</td>
<td>0.211</td>
<td>0.0895</td>
<td>-0.0953</td>
<td>0.144</td>
<td>-0.34</td>
</tr>
<tr>
<td>( \varepsilon^{(3)} )</td>
<td>0.540</td>
<td>0.220</td>
<td>0.138</td>
<td>0.101</td>
<td>0.0792</td>
</tr>
<tr>
<td>( M^{(2)}_s ) / ( \mu_B^0 )</td>
<td>-9.42 \times 10^{-3}</td>
<td>-7.16 \times 10^{-4}</td>
<td>8.65 \times 10^{-4}</td>
<td>-2.99 \times 10^{-3}</td>
<td>0.0422</td>
</tr>
<tr>
<td>( M^{(3)}_s )</td>
<td>-0.157</td>
<td>-0.0106</td>
<td>-2.63 \times 10^{-3}</td>
<td>-1.02 \times 10^{-3}</td>
<td>-4.96 \times 10^{-4}</td>
</tr>
</tbody>
</table>
atoms with \(Z = 1 \rightarrow 5\) we tabulate both \(x^{(2)}\) and \(x^{(3)}\) in Table 1. According to the row of \(M^{(2)}_1\) all solutions of this quantity are small so as to satisfy our stationary concepts in this paper, e.g. for (21). This quantity however increases rapidly with \(Z\). The row of \(M^{(3)}_2\) shows that it has a decreasing magnitude for increasing \(Z\). The largest one, for \(H^-\), has the remarkable value about 16%.

References


