One-electron equation
in terms of equivalent function and phase norm

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\section*{Abstract}

We present an alternative one-electron equation for resolving many-electron problem to one-electron approximation and including the exchange and correlation effects in an analytical way, thereby fulfilling the requirements for ab initio calculation. To derive one-electron equation, we accept a new notion of equivalent function suggestive of the pseudo wavefunction. As a result, we reduce many-electron equation to one-electron including the exchange effect in an analytical method. Moreover we accept the notion of phase norm for two electrons to resolve the electronic correlation problem. The phase norm is used to specify the electron-approachable limit between particles. We take into consideration the electronic correlation with the help of a correlation-hole function in terms of the phase norm, by which multiplying the integrand of the operator term representing the interaction between electrons. Using the phase norm leads to analytical consideration of the electronic correlation without employing in a factitious way the additional term pertaining to correlation, so it embodies the physical essence of electronic correlation. The derived equation becomes an one-electron equation which does not include an additional term pertaining to the exchange and correlation, but takes into consideration the exchange and correlation effects in a rigorous ab initio way.

\keywords{Hartree equation, Hartree-Fock equation, Exchange and correlation, One-electron equation, Density functional theory, Kohn-Sham equation, Pseudopotential method}

\section{1. Introduction}

The main purpose of many-particle theory in non-relativistic quantum mechanics is to study the properties of the solutions of the Schrödinger equation describing the characteristics of many-body interaction including the exchange and correlation effects. The salient problems of ab initio calculation for many-particle system are how to exclude the self-interaction, how to represent the exchange and correlation effects and how to reduce many-particle problem to one-particle one.

According to these criteria, we review the several approaches of ab initio calculation. The complexity of many-electron problems lies in the interaction operator represented by two-particle variables. It makes it impossible to use the variable separation method to solve the Schrödinger equation for many-body systems.

The first approach to the many-electron problem may be considered to be proposed by Hartree, in the very beginnings of the age of quantum mechanics\cite{4}. Hartree’s main assumption is that the many-electron wavefunction can be written as a simple product of one-electron wavefunctions. Hartree justified the self-consistent field(HSCF) approach in a qualitative way\cite{4,44}. Soon after, Slater underpinned the approach in a rigorous mathematical way from the variational principle\cite{5}. Although this approach is not realistic enough for many-body system owing to no consideration of exchange and correlation, it provides the main features of many-electron approach\cite{44}. The set of $N$ coupled partial differential equation representing $N$-particle system can be solved by minimizing the energy with respect to a set of variational parameters in a trial wavefunction or alternatively, by re-calculating the effective potential with

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the help of the previous-step wavefunctions, and solving the Schrödinger equation again. The Hartree approximation
does not contain the feature of antisymmetry of Fermion, as a consequence, the description of many-particle system
in terms of it is incomplete.

To follow Pauli’s principle, there was proposed the Hartree-Fock approximation. Adopting an antisymmetrized
many-particle wavefunction in the form of the Slater determinant makes it possible to take into consideration electronic
exchange in an exact way. In this approximation, what is missing is the electronic correlation.

When neglecting interaction between electrons, from the point of view of mathematics, it is natural to choose
the many-particle wavefunction as a combination of the Slater determinants(SD) that must be determined by means
of variation or other more sophisticated techniques. However, even in the presence of the interaction, the ground
state of the system can be represented by a single Slater determinant. This is the idea of the Hartree-Fock(HF)
theory which aims to describe some physical properties of the system with a wavefunction which is the product of
one-electron functions. The correlation problem which had not been dealt with in the early HF theory was treated and
promoted in the post HF theory. To do this, the post HF theory addresses the electronic correlation by considering
either more than one SD or other anti-symmetric wavefunctions of another type.

The HF theory is applicable only to those systems in which the interaction does not diverge too fast as the inter-
particle distance tends to zero. The strongly repulsive nature of the short-range interactions does not allow direct use
of either mean field theories or ordinary perturbation theory. There have been several evolutions which led to the
considerable improvement of this theory, such as the theory of Brueckner-Hartree-Fock, which is non-divergent and
operates on a non-correlated(mean field) wavefunction.

Parallel to the approaches using the orbital functions, such as the Hartree and Hartree-Fock method, a different
method proposed by Thomas and Fermi takes the full electronic density as the fundamental variable of many-body
problem. The development of this approach was in full swing in 1960s. Hohenberg and Kohn proved in a rigorous
way that the properties of the ground state of an N-particle system can be expressed as functionals of the electronic
density. The density functional theory(DFT) has been applied most of all to electronic systems, such as atoms,
molecules, homogeneous solids, surfaces and interfaces, quantum wells and quantum dots etc, and has provided results
in good accord with experiments. The self-consistent one-electron equation derived from the variational
principle by Kohn and Sham describes the properties of the ground state (energy and density) in the way that, formally,
takes into account all many-body effects. Their solutions are as simple as the Hartree ones but provide
better results than the Hartree-Fock ones, which are much more complicated, in some cases even almost impossible
to obtain. This is because the Kohn-Sham solutions treat accurately, albeit in an empirical way, both exchange and
correlation effects whereas the HF ones treat only exchange exactly, completely neglecting the very correlation.
This equation has the decisive advantage of being framed as an one-electron equation. For this reason great many
use is made of Kohn-Sham equation for the purpose of the calculation of electronic states. It should be noted that
no one can doubt the successes of the modern Kohn-Sham approach to the density functional theory, but this theory
has bottlenecks such as self-interaction, exchange and correlation. Kohn-Sham’s theory does not describe the states
of electronic system with the help of anti-symmetric wavefunctions. Therefore this equation cannot but employ
the additive term relevant to both exchange and correlation more or less in a factitious way. In this connection, the
density functional theory has spawned a multitude of methods such as the local density approximation(LDA) and the
generalized gradient approximation(GGA) distinguished by the exchange and correlation calculations. One of the drawbacks of the theory is that it is difficult to produce correlation functionals compatible with
exact exchange functionals from a definite principle within the framework of the KS theory. Therefore there have
been proposed several improved methods for DFT. One of the methods which have been explored to fix this problem makes use of exact exchange in the KS exchange-correlation calculation. Although there have been a great advances in finding exact exchange functional and the compatible with it, correlation functionals, the exchange-correlation problem also remains as a main challenge to reach the goal of many-body theory. The problem for finding exact exchange requires a very particular kind of correlation. The exact exchange
hole has, from its essence, a non-local character. Contrary to this, the exact correlation hole must be of local nature.
Therefore an incorporated exchange and correlation functional needs the correlation assuming non-local feature. On
this account, representing the exchange and correlation with a hole function undergoes serious difficulties. GGA
of DFT circumvents this problem by using a semi-local exchange and a semi-local correlation which together give
a correct exchange-correlation hole. The method modifies the correlation component of the GGA to introduce a
parameter containing information about the non-locality of the exchange, thereby allowing the correlation to act

2
accordingly in a non-local manner without being rigorously non-local. The correlation is thus compatible with exact exchange.

Such a situation in DFT shows that the proposed approaches are still far from satisfying the requirements of \textit{ab initio} calculation.

It is considered that the main goal of \textit{ab initio} calculations is to obtain an one-electron equation dealing with the exchange and correlation in an analytical way. We understand that the one-electron equation should be taken from the nature of identical-particle system.

What is promising for the Hartree-Fock approach is that in spite of neglecting the electronic correlation and not being framed as one-electron equation, it provides the analytical representation of exchange with the help of antisymmetric wavefunction for a many-electron system.

On the other hand, what is promising for the Kohn-Sham approach is that it furnishes an one-electron equation including exchange and correlation effects, though in a fictitious way. It is desirable to conceive an one-electron equation representing both the exchange and correlation in an analytical way, and in addition, excluding self-interaction. The one-electron equation means that interaction between electrons is included in external potential. The absence of interaction between particles provides the simplest case, namely the independent-particle model (IPM) for which the Hamiltonian operator contains only one-body term. Although this model addresses the simplest case, it would formulate the fundamental framework at which the research on many-particle system should arrive, provided that one could employ the techniques for representing the interaction between particles in the form of one-body potential in the presence of an external field. In this case the problem is how to describe in an one-body context the exchange and correlation effects in a many-body system.

In this work, we adopt the notions of the equivalent function and phase norm. The equivalent function bears the meaning of the pseudo wavefunction. In this context, the pseudo-potential method can be assessed as giving the clue for deriving an one-electron equation. With the help of the idea for the pseudo-potential method, we reduced the equation for many-electron system to an one-electron equation. Our approach does not make use of the electronic density but the one-electron orbital function, thereby excluding the self-interaction and including the exchange. Adopting the phase norm enables to deal with the electronic correlation in accordance with its quantum nature.

In doing so, we reach our goal of reducing the problem of many-electron system to one-electron approximation capable of determining exchange-correlation in an analytical way.

\textbf{2. One-electron equation including exchange effect in terms of antisymmetric wavefunction}

We start to deduce an one-electron equation on the basis of the variational principle of total energy functional. The Hamiltonian operator for a N-electron system can be written as

\[
\hat{H} = \hat{F}_1 + \hat{F}_2, \tag{1}
\]

\[
\hat{F}_1 = \sum_i \hat{A}_i, \tag{2}
\]

\[
\hat{F}_2 = \sum_{i<j} \hat{A}_{ij}, \tag{3}
\]

where \(\hat{F}_1\) is the operator pertaining to single electron which corresponds to the kinetic energy and potential energy of electrons in an external field, and \(\hat{F}_2\) is the operator pertaining to two electrons which corresponds to two-body interaction. By means of these operators, the total energy functional for a N-electron system is written as

\[
\langle H \rangle = \int \Psi^* \hat{H} \Psi d\tau. \tag{4}
\]

Without loss of generality, the total wavefunction \(\Psi\) can be represented by \(\text{SD}\) with the help of one-electron
wavefunctions as
\[ \Psi = (N!)^{\frac{1}{2}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix}. \]  
(5)

Here the particle wavefunction \( \phi_i(j) \) is denoted by the product of the coordinate wavefunction \( \psi_i(r_i) \) and the spin wavefunction \( \chi_j(\sigma) \).

Then the following relations:
\[ \phi_i(j) = \psi_i(r_i) \chi_j(\sigma) \]  
(6)
\[ \sum_{\sigma} \chi_j^*(\sigma) \chi_j(\sigma) = \delta(m_i, m_j) \]  
(7)
should hold true. As regards the wavefunction, we emphasize that the one-electron wavefunctions under consideration do not assume the concrete physical meaning in the sense of the mean field approximation, instead, are taken simply as a mathematical representation for fulfilling the requirement of antisymmetrization of the wavefunction. Now, we can write with the help of one-electron wavefunction the total energy functional for an electronic system as
\[ \langle H \rangle = \langle F_1 \rangle + \langle F_2 \rangle, \]  
(8)
\[ \langle F_1 \rangle = \sum_i \langle \hat{H}_1 | i \rangle = \sum_i \int \, dr \, \psi_i^*(r_i) \hat{H}_1 \psi_i(r_i) \]  
(9)
\[ \langle F_2 \rangle = \sum_{i<j} \langle (i) | \hat{H}_{12} | (j) \rangle = \sum_{i<j} \int \, dr_1 \, dr_2 \, \psi_i^*(r_i) \psi_j^*(r_2) \hat{H}_{12} \psi_i(r_1) \psi_j(r_2) \times | \chi_i^*(\sigma_1) |^2 | \chi_j(\sigma_2) |^2 \]  
(10)
\[ - \sum_{i<j} \int \, dr_1 \, dr_2 \, \psi_i^*(r_1) \psi_j^*(r_2) \hat{H}_{12} \psi_i(r_2) \psi_j(r_1) \times \chi_i^*(\sigma_1) \chi_j^*(\sigma_2) \chi_i(\sigma_2) \chi_j(\sigma_1), \]

where the suffix \( i \) denotes the \( i \)th one-electronic state, the suffixes 1,2, the numbers of electrons. In Eq.(10), the first term represents the direct-interaction energy and the second term, the exchange energy.

Suppose that
\[ \hat{H}_{12} = \frac{\hbar^2}{r_{12}}. \]  
(11)
In this case, we have
\[ \langle F_2 \rangle = \sum_{i<j} \int \, dr_1 \, dr_2 \, | \psi_i(r_1) |^2 | \psi_j(r_2) |^2 \, \hat{H}_{12} \]  
\[ - \sum_{i<j} \delta(m_i, m_j) \times \int \, dr_1 \, dr_2 \, \psi_i^*(r_1) \psi_j^*(r_2) \hat{H}_{12} \psi_i(r_2) \psi_j(r_1). \]  
(12)

The total energy functional for an electronic system, \( \langle H \rangle \) should be minimized under the following normalization condition:
\[ \langle \Psi | \Psi \rangle = 1. \]

Therefore the variational problem to find the minimum of total energy functional leads to the unconditional extreme value problem of the following functional:
\[ \Phi = \langle H \rangle - \epsilon \langle \Psi | \Psi \rangle, \]  
(13)
where $\epsilon$ is an undetermined constant having the meaning of total energy. Varying the functional, $\Phi$ with respect to $i$, namely performing

$$\delta \Phi = \sum_i \delta_i \Phi$$

and assuming the independence of variation with respect to $i$, we get

$$\delta_i \Phi = \int \delta \psi_i^* (r_1) \left\{ \hat{H}_1 \psi_i (r_1) + \sum_{j \neq i} \int \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right\} \psi_i (r_1)$$

$$- \sum_{j \neq i} \left[ \delta (m_{ii}, m_{ij}) \times \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right] \psi_j (r_1)$$

$$- \epsilon \int \delta \psi_i^* (r_1) \psi_i (r_1) \, dr_1 + c.c = 0,$$

where $c.c$ is the complex conjugate. Hence we obtain

$$\hat{H}_1 \psi_i (r_1) + \sum_{j \neq i} \int \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right\} \psi_i (r_1)$$

$$- \sum_{j \neq i} \left[ \delta (m_{ii}, m_{ij}) \times \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right] \psi_j (r_1)$$

$$- \epsilon \int \delta \psi_i^* (r_1) \psi_i (r_1) \, dr_1 + c.c = 0,$$

In Eq.(16), the expression in the bracket of the second term represents direct-interaction energy and that of the third term, the exchange energy. In order to change Eq.(16) to the eigen equation with respect to the $i$th one-electronic wavefunction, we modify the third term to have

$$\hat{H}_1 \psi_i (r_1) + \sum_{j \neq i} \int \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right\} \psi_i (r_1)$$

$$- \sum_{j \neq i} \left[ \delta (m_{ii}, m_{ij}) \times \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right] \psi_j (r_1)$$

$$- \epsilon \int \delta \psi_i^* (r_1) \psi_i (r_1) \, dr_1 + c.c = 0,$$

For convenience, we shall denote

$$\left\{ - \sum_{j \neq i} \left[ \delta (m_{ii}, m_{ij}) \times \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2 \right] \psi_j (r_1) \right\}$$

in Eq.(17) by $E^{(i)}_{\text{exc}} (r_1)$ and $\sum_{j \neq i} \int \psi_j^* (r_2) \hat{H}_{ij} \psi_j (r_2) \, dr_2$ in Eq.(16) by $E^{(i)}_{\text{int}} (r_1)$. Then Eq.(16) is written in a compact shape as

$$\hat{H}_1 \psi_i (r_1) + E^{(i)}_{\text{exc}} (r_1) \psi_i (r_1) + E^{(i)}_{\text{int}} (r_1) \psi_i (r_1) = \epsilon \psi_i (r_1).$$

This is nothing but the Hartree-Fock equation. Eq.(18) can be considered as the eigen equation for the $i$th one-electron state. The eigen equation varies with $i$. Therefore every eigen equation does not give the same eigenfunctions as those the others yield, and thus in general an eigenfunction of a given eigen equation is not orthogonal to eigenfunctions of other eigen equation.

It is considered that electrons are not distinguished, being identical particles and consequently, are in the same quantum-mechanical state through exchange. Therefore we require that for an electronic system an eigen equation
should be determined so that it can yield a definite set of eigen functions \( \psi_i \) describing not an electron but the electronic system to agree with the identity principle.

It is obvious that the variation of an eigenfunction is not independent of the others and consequently the variation of functional \( \Phi \) as a whole should be considered. Namely,

\[
\delta \Phi = \sum_i \delta \psi_i \Phi = 0. \tag{19}
\]

Now, it is necessary to find a single eigen equation from the variational Eq.(19) without performing the separation of variation. It is the mathematical requirement originating from the identity principle.

To resolve this problem, we consider in a different way the variation with respect to

\[
\{ \psi_i (r_1) | i = 0, 1, 2, \cdots, N \}. \tag{20}
\]

Obviously, it is impossible to perform arbitrary independent variations with respect to \( \{ \psi_i (r_1) | i = 0, 1, 2, \cdots, N \} \) and the admissible variation is subject only to the unitary transformation.

Performing the variation, \( \{ \delta \psi_i (r_1), \delta \psi_j (r_1) | i = 0, 1, 2, \cdots, N \} \), we get the following equation:

\[
\sum_i \delta \psi_i (r_1) \left\{ \hat{H}_1 + E^{(i)}_{\text{int}} (r_1) + E^{(i)}_{\text{exc}} (r_1) - \epsilon_i \right\} \psi_i (r_1) \, dr_1 + c.c. = 0. \tag{21}
\]

To deduce one-electron equation describing electronic system, we introduce a definite equivalent function \( \psi (r_1) \) determined by \( \{ \psi_i (r_1) | i = 0, 1, 2, \cdots, N \} \) and a definite equivalent energy \( \epsilon \) determined by \( \{ \epsilon_i (r_1) | i = 0, 1, 2, \cdots, N \} \).

For the equivalent function \( \psi (r_1) \) and equivalent energy \( \epsilon \), it is assumed that the following relations:

\[
\sum_{i=1}^{N} \delta \psi_i^* (r_1) \hat{H}_1 \psi_i (r_1) = \delta \psi^* (r_1) \left[ N\hat{H}_1 \right] \psi (r_1), \tag{22a}
\]

\[
\sum_{i=1}^{N} \delta \psi_i^* (r_1) E^{(i)}_{\text{int}} \psi_i (r_1) = \delta \psi^* (r_1) \left[ \sum_{i=1}^{N} E^{(i)}_{\text{int}} \right] \psi (r_1), \tag{22b}
\]

\[
\sum_{i=1}^{N} \delta \psi_i^* (r_1) E^{(i)}_{\text{exc}} \psi_i (r_1) = \delta \psi^* (r_1) \left[ \sum_{i=1}^{N} E^{(i)}_{\text{exc}} \right] \psi (r_1), \tag{22c}
\]

\[
\sum_{i=1}^{N} \delta \psi_i^* (r_1) \epsilon_i \psi_i (r_1) = \delta \psi^* (r_1) \left[ N\epsilon \right] \psi (r_1) \tag{22d}
\]

should hold. Then \( \{ \psi_i (r_1) | i = 0, 1, 2, \cdots, N \} \) in the operator terms are the eigenfunctions for \( \psi (r_1) \).

As a result, the equation for the equivalent function satisfying the extremum condition for total energy can be represented as

\[
\int \delta \psi^* (r_1) \left\{ N\hat{H}_1 + \sum_i E^{(i)}_{\text{int}} (r_1) + \sum_i E^{(i)}_{\text{exc}} (r_1) - N\epsilon \right\} \psi (r_1) \, dr_1 = 0. \tag{23}
\]

Here the exchange operator is written as

\[
E^{(i)}_{\text{exc}} (r_1) = - \sum_{j \neq i} \left[ \delta (m_x, m_y) \int \psi_j^* (r_2) \hat{H}_1 \psi_i (r_2) \, dr_2 \right] \frac{\psi_j (r_1)}{\psi_i (r_1)} \tag{24}
\]
the direct-interaction operator, as
\[ \sum_{j=1}^{N} E_{\text{int}}^{(j)}(\mathbf{r}_1) = (N - 1) \sum_{j=1}^{N} \int \psi_j^*(\mathbf{r}_2) \hat{H}_{12} \psi_j(\mathbf{r}_2) \, d\mathbf{r}_2 = (N - 1) \sum_{j=1}^{N} \int \rho_j(\mathbf{r}_2) \, d\mathbf{r}_2. \] (25)

From Eq.(23), we derive the single equation for N-electron system:
\[ N\hat{H}_1\psi(\mathbf{r}_1) + \sum_i E_{\text{int}}^{(i)}(\mathbf{r}_1) \psi(\mathbf{r}_1) + \sum_i E_{\text{exc}}^{(i)}(\mathbf{r}_1) \psi(\mathbf{r}_1) = N\varepsilon\psi(\mathbf{r}_1). \] (26)

Finally, we obtain the one-electron equation:
\[ \hat{H}_1\psi(\mathbf{r}_1) + \frac{N - 1}{N} \sum_{j=1}^{N} \int \psi_j^*(\mathbf{r}_2) \hat{H}_{12} \psi_j(\mathbf{r}_2) \, d\mathbf{r}_2 \psi(\mathbf{r}_1) + \frac{1}{N} \sum_{i=1}^{N} E_{\text{exc}}^{(i)}(\mathbf{r}_1) \psi(\mathbf{r}_1) = \varepsilon\psi(\mathbf{r}_1). \] (27)

In the physical sense, we can interpret Eq.(27) as follows. To begin with, Eq.(18) can be considered as the system of eigen equations a bit different from one another. Namely,
\[ \hat{H}_1\psi(\mathbf{r}_1) + E_{\text{int}}^{(i)}(\mathbf{r}_1) \psi(\mathbf{r}_1) + E_{\text{exc}}^{(i)}(\mathbf{r}_1) \psi(\mathbf{r}_1) = \varepsilon\psi(\mathbf{r}_1). \] (28)

In this case, the eigen equations vary with \( E_{\text{int}}^{(i)}(\mathbf{r}_1) \) and \( E_{\text{exc}}^{(i)}(\mathbf{r}_1) \). Then the eigen equations produce different systems of eigen functions. As a result, every eigen equation can be thought of as the deviation from the exact one-electron equation for N-electron system. To relieve the differences, we introduce the mean operator given by Eq.(28). As a consequence, we obtain the one-electron Eq.(27).

By using the one-electron wavefunctions given by the eigen Eq.(27), we can calculate the total energy of a many-electron system on
\[ E = \sum_{k=1}^{N} \int \psi_k^*(\mathbf{r}_1) \left[ \hat{H}_1 + \frac{N - 1}{N} \sum_{j=1}^{N} \int \psi_j^*(\mathbf{r}_2) \hat{H}_{12} \psi_j(\mathbf{r}_2) \, d\mathbf{r}_2 \right] \psi_k(\mathbf{r}_1) \, d\mathbf{r}_1 \]
\[ = \sum_{k=1}^{N} \int \psi_k^*(\mathbf{r}_1) \varepsilon_k \psi_k(\mathbf{r}_1) \, d\mathbf{r}_1 = \sum_{k=1}^{N} \varepsilon_k. \] (29)

The eigen Eq.(27) becomes the wave equation for N-electron system in the one-electron approximation and the system of eigenfunctions describes the quantum-mechanical states of the electronic system with the help of one-electron wavefunctions.

3. Consideration of electronic correlation in terms of phase norm

The correlation is defined as the deviation of real wavefunction from the product of single-particle wavefunctions. The terminology, the correlation means inseparable, dependent relation between particles. Generally, it is considered that the correlation in a wavefunction is represented as the difference between exact wavefunction and the Hartree-Fock wavefunction. Now, how can one find the exact wavefunction? To answer this question, it is necessary to understand the quantum nature of the electronic correlation. The correlation in a wavefunction is not ascribed only to the Coulomb interaction.

The electronic correlation is ascribed to the limitation on the configuration of electrons arising from the reason that electrons are impossible to get infinitely close to one another due to quantum as well as classical cause. It is considered that in the sense of quantum mechanics, the correlation between electrons is attributed to the uncertainty relation and Pauli’s principle.

A variety of the methods for taking account of the electronic correlation has been proposed but the present situation of the correlation theory seems to be not in perfect harmony with the nature of electronic correlation. Since the
correlation is originally relevant to the approachable limit of particles, it is consistent to take account of it through the integral of the operator term by restricting the approach of particles in a quantum-mechanical way. We have solved this matter by inserting a correlation hole function in terms of the phase norm into the integral of two-body operator term in the present one-electron equation. The correlation hole function gives the value 0 within a given range and the value 1 out of the range. The key problem lies in from what principle to specify the approachable limit of particles.

We have specified the approachable limit of particles by using phase space. If two electrons are involved in the same volume as $\hbar$ in phase space, it is proved that they are in the same quantum-mechanical state. Accordingly, such an approach is prohibited by Pauli’s principle and the uncertainty principle. The main point of the method consists in multiplying the integrand of the two-body operator term by a hole function determined by evaluating the phase norm for two electrons. Using the hole function $\theta(r_1, r_2)$, we can rewrite the one-electron equation as

\[
\hat{H}_1\psi(r_1) + \frac{N-1}{N} \sum_{j=1}^{N} \int \psi_j^*(r_2) \hat{H}_{12} \psi_j(r_2) \theta(r_1, r_2) \, dr_2 \psi(r_1)
\]

\[
\frac{1}{N} \left\{ -\sum_{m_{i_s}, m_{s_i}} \delta(m_{i_s}, m_{s_i}) \int \psi_j^*(r_2) \hat{H}_{12} \psi_i(r_2) \theta(r_1, r_2) \, dr_2 \frac{\psi_j(r_1)}{\psi_i(r_1)} \right\} \psi(r_1) = \varepsilon \psi(r_1). \tag{30}
\]

In practice, we should evaluate whether the states of two electrons are identical or not. For this purpose, we define the distance between two states in phase space. First of all, for two particles we determine the magnitude of momentum of a particle with respect to the other and the distance from the particle to the other as

\[
\Delta p = |p_1 - p_2|, \tag{31}
\]

\[
\Delta r = |r_1 - r_2|. \tag{32}
\]

Next, we adopt the phase norm as

\[
\varrho = \Delta r \cdot \Delta p. \tag{33}
\]

It indicates the distance in phase space between the states of two particles.

Next, we represent the momentum of a particle with the help of the wavefunction. Taking into consideration the relation between probability density and probability current density, we have

\[
j = \rho v = \frac{\rho \mathbf{v}}{m}. \tag{34}
\]

where $v$ is the velocity of an electron and $m$, the mass of the electron. Accordingly, we get the following expression for momentum:

\[
p = \frac{mj}{\rho}. \tag{35}
\]

With the help of wavefunction, we represent the momentum of an electron as

\[
p_i(r) = \frac{i\hbar}{2\psi_i^* \psi_j} (\psi_i^* \nabla \psi_j - \psi_j^* \nabla \psi_i)
= \frac{i\hbar}{2} \left( \frac{1}{\psi_i^*} \nabla \psi_j^* - \frac{1}{\psi_j^*} \nabla \psi_i \right) = \hbar \text{Im} \left( \frac{1}{\psi_i} \nabla \psi_i \right). \tag{36}
\]

where $r$ is the position variable of an electron, $i$ denotes the $i$th electronic state and $\text{Im}$, the imaginary part of a complex number.

It is natural to consider that the correlation hole function in terms of the phase norm should be the following two-value function:

\[
\theta = \begin{cases} 
0 & : \varrho < \hbar \\
1 & : \varrho \geq \hbar
\end{cases}. \tag{37}
\]
In practice, we can introduce a fitting constant $\alpha$ so as to have the following relation:

$$\theta = \begin{cases} 0 & ; \alpha \rho < \hbar \\ 1 & ; \alpha \rho \geq \hbar \end{cases}.$$  

(38)

This definition leads to fulfilling the requirement that the approach of particles should be admitted under the condition that the volume element in phase space assigned to every particle is $\hbar^3$.

In this way, we have introduced a kind of correlation hole function in terms of the phase norm to take into consideration the correlation effect in an analytical way in accordance of the quantum nature of correlation.

4. Summary and discussion

We summarize the main results.

First, we have obtained an alternative one-electron equation for many-particle system, which describes the exchange effect in an analytical way. It is due to the deduction of this equation with the help of antisymmetric wavefunction. This equation uses the orbital functions instead of the density in DFT and has the feature of one-electron equation analogous to the Kohn-Sham equation.

Second, we have shown that it is feasible to introduce the correlation-hole function in terms of the phase norm to consider the correlation effect in an analytical way. This method addresses the cause of pure quantum correlation by introducing the notion of phase norm.

In conclusion, this equation resolves the self-interaction, exchange and correlation, one-electron equation problems in a mathematically consistent ways. In doing so, we reached the goal of obtaining self-consistent one-electron equation including exchange and correlation effects in an analytical way.

The features and interpretations of this approach can be understood as follows.

This approach employs orbital functions. As a result, the self-interaction is automatically excluded within the framework of this approach in contrast to the Kohn-Sham equation employing the electronic density.

One problem in understanding quantum many-particle theory is whether the one-electron state is real. The obtained equation does not describe the real one-electron states in the presence of electron interaction. In the exact sense, this equation can be considered to describe states of quasi-particles or electronic plasmon standing for a many-particle system. We consider that the real one-electron state loses its meaning because electrons are not distinguished from one another due to the identity principle. Therefore we do not accept the meaning of one-electron state in the sense of physical reality. However, for many-electron systems the one-electron state has an exact and feasible meaning since it helps to consider a real interacting many-particle system as a non-interacting quasi-particle system[45] which yields the same result as real one for the collective behavior of the electron system.

One idea for endowing this scheme with characters of generalized formalism is to consider the Slater determinant as the mathematically optimized choice for the antisymmetrization of wavefunction, and not to assume the one-electron wavefunction in the sense of mean field approximation. In fact, the Slater determinant does not assume the property of variable separation, and can be considered as a purely mathematical selection for antisymmetrized wavefunction.

To deduce one-electron equation, we introduced the notion of equivalent function suggestive of pseudo wavefunction. It makes us shun many hardships to be faced with in manipulating many-electron equation. Generally, an one-electron equation should be given as

$$\hat{H}\psi(r) = \varepsilon \psi(r),$$  

(39)

$$\varepsilon = \sum_{i} \epsilon_i.$$  

(40)

Here $\varepsilon$ is the total energy of an electronic system and $\epsilon_i$ is the $i$th eigenvalue of the eigen Eq.(39).

It is obvious that according to this criterion, the Kohn-Sham equation is an one-electron equation whereas the Hartree equation and the Hartree-Fock equation are otherwise. Evidently, the present equation is an one-electron equation using the orbital functions.
The method of this scheme for dealing with the electronic correlation is distinguished from the others since its methodology originates from one of the principles of quantum mechanics, namely the uncertainty principle and Pauli’s principle. Initiated by Gouy and Chapman, and introduced into elucidation of many-body effects by Debye and Hückel, the electronic correlation is a non-trivial problem and a great challenge to resolving many-electron problem \[2, 1, 3\]. The electronic correlation can be understood to have classical plus quantum cause. Our approach for considering the electronic correlation focuses on its quantal cause. The present approach lets one avoid assuming the additional correlation term in the wave equation for many-electron system. We claim that since the phase norm enables to explain the possible electron-approachable limit from the principle of quantum mechanics, the present approach provides the possibility of revealing the electronic correlation in line with the quantum nature. Within the KS approach, finding the exact exchange-correlation functional requires painful processes of modeling. The different understandings of the electronic exchange and correlation have yielded a great diversity of calculation approaches \[14, 21, 24, 27, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43\]. Such a situation shows that there is not seen the prospect of finding the final solution to the exchange and correlation problem by manipulating within DFT. The present method circumvents the obstacles of DFT and HF theory, by employing the equivalent function and phase norm. It is concluded that the derived equation amounts to an one-electron equation which does not include any additional term pertaining to the exchange and correlation, but takes into consideration the exchange and correlation effects in an ab initio way. Therefore this equation can elucidate properties of many-particle systems in the ground state in a new way. The equation addresses electronic states of a many-electron system with orbital functions and yields the eigen functions and energy eigenvalues of the many-electron system. In essence it is an equation for many-electron system written in the form of one-electron equation similar to the Kohn-Sham equation.

The present equation employs the form of one-electron equation from the Kohn-Sham equation, anti-symmetric property from the Hartree-Fock equation and the trick of the reduction of many-electron equation to one-electron equation from pseudo-potential method.

This formalism is possible to be easily extended to time-dependent case and excited states, since it has the advantage of one-electron equation and analytical representation of exchange-correlation.

5. Conclusion

The obtained one-electron equation takes into consideration exchange and correlation effects in an analytical way. The goal of obtaining the one-electron equation of desired characteristics has been achieved by introducing the equivalent function and the correlation hole function in terms of the phase norm.

Unlike the Hartree-Fock equation, it is an one-electron equation, which fulfills the requirement that electronic states of many-electron system should be determined by an eigen equation since identical particles are not distinguished from one another. Moreover, it includes the correlation effect in an analytical way. What is better, compared to HF theory using the complicated methods with combination of SDs to explain electronic correlation, is that this method approaches the nature of electronic correlation.

Unlike the KS equation that adopts several formal ways to take into consideration exchange and correlation effects, this equation does not include the additional exchange-correlation term inaccessible to physical nature. Although there has been considerable progress in investigating the exchange and correlation, it still remains as a core problem in the first principles calculation. Thanks to methodological characteristics, the present work is considered to contribute to exploring a new avenue towards the decisive solution of the exchange and correlation.

In conclusion, the derived equation does not adopt any empirical method and fulfills all the requirements for selfinteraction, exchange and correlation, and one-electron equation. We have plans to show at the next stage that this approach can be easily extended to time-dependent and excited state since it is an one-electron equation using the orbital functions.

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