Computational schemes for the ground-state pair density

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Abstract
We reconfirm the performance of the initial scheme for calculating the ground-state pair density
(Higuchi and Higuchi 2007 *Physica* B **387** 117, 2008 *Phys. Rev.* B **78** 125101) by using the
alternative approximation of the correlating kinetic energy functional. It is shown that about
20% of the correlation energy can be reproduced by the initial scheme, irrespective of the
approximate form of the correlating kinetic energy functional. On the basis of the initial
scheme, various kinds of schemes that go beyond the initial one can be developed. We illustrate
two kinds of computational schemes.

1. Introduction

The pair density (PD) functional theory is expected to be one
of the most promising theories beyond the density functional
theory, because the PD has a larger amount of information
than the electron density. The PD functional theory itself
was first proposed by Ziesche [1, 2], and was followed by
many other contributions [3–19]. However, there are two
problems for the practical use of the theory. One is concerned
with the fact that the variational principle with respect to the
PD should be performed within the set of N-representable
PDs. Although many attempts have been made to obtain
the necessary and sufficient conditions for N-representable
PDs [20–27], they have not yet been obtained in a practical
form. This is a longstanding problem. Another problem is
concerned with the approximate form of the kinetic energy
functional. Through the constrained-search method the kinetic
energy is a functional of the PD. Unfortunately this functional
is unknown and has to be approximated. Several approximate
forms have been proposed so far [5, 6, 11, 28].

Due to the above problems, few computational schemes of
the PD functional theory have been reported so far. Recently,
we have proposed a computational scheme for calculating
the ground-state PD [16, 18] on the basis of the extended
constrained-search (ECS) theory [29–34]. In this scheme,
in order to avoid the N-representability problem, the search
region of PDs is restricted in the set of PDs that are constructed
from the single Slater determinants (SSDs). Namely, the best
solution is searched within the set of restricted but definitely

N-representable PDs. For the development of the kinetic
energy functional, the sum of the kinetic energy functional of
a noninteracting reference system and the correlating kinetic
energy functional is used as the approximate form of the kinetic
energy functional [16, 18]. Since this scheme is perhaps the
first one to provide a practical scheme that incorporates both
of the above-mentioned problems, this is regarded as the initial
scheme for calculating the ground-state pair density [16, 18].
Very recently, we have performed actual calculations on the
basis of this initial scheme. For the Ne atom it is illustrated
that about 20% of the correlation energy is reproduced by this
scheme [18].

In this paper, we shall reconfirm the performance of the
initial scheme by using the alternative approximation of the
correlating kinetic energy functional. Based on the results
obtained by the initial scheme, it is expected that various kinds
of effective schemes that go beyond the initial scheme can be
developed. We shall review our recent attempt [17] and discuss
other possibilities to go beyond the initial scheme.

2. PD functional theory by means of the single Slater determinant

2.1. Overview of the initial scheme

In this section, we shall overview the initial scheme. We shall
consider the many-body system, the Hamiltonian of which is
given by

$$\hat{H} = \hat{T} + \hat{W} + \int \hat{\rho}(r)v_{\text{ext}}(r)\,dr, \qquad (1)$$

where $v_{\mathrm{ext}}(\boldsymbol{r})$ is an external potential, and where $\hat{T}$, $\hat{W}$, and $\hat{\rho}(\boldsymbol{r})$ are the operators of the kinetic energy, electron–electron interaction energy, and electron density, respectively. The PD is defined as

$$\gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'})$$
$$= \langle \Psi | \tfrac{1}{2} \int \int \psi^{\dagger}(x) \psi^{\dagger}(x') \psi(x') \psi(x) \, \mathrm{d}\eta \, \mathrm{d}\eta' | \Psi \rangle, \qquad (2)$$

where $\psi(x)$ and $\psi^{\dagger}(x)$ are field operators of electrons, Ψ is the antisymmetric wavefunction, and x is the coordinate including the spatial coordinate $\boldsymbol{r}$ and spin coordinate η. According to the ECS theory [29–34], the universal functional can be defined by

$$F[\gamma^{(2)}] = \mathop{\mathrm{Min}}_{\Psi \to \gamma^{(2)}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle, \qquad (3)$$

where $\Psi \to \gamma^{(2)}$ denotes the searching over all antisymmetric wavefunctions that yield a prescribed $\gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'})$. By means of the universal functional, we can give the theorem of the one-to-one correspondence between the ground-state PD and ground-state wavefunction, and the variational principle with respect to the PD [16, 18].

In order to perform the variational principle, it is necessary to restrict the search region within the set of N-representable PDs. Our strategy is to restrict the region within the N-representable PDs which are constructed from SSDs [16, 18]. Searching the best solution within such a restricted region results in the single-particle equation:

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + v_{\mathrm{ext}}(\boldsymbol{r}) \right\} \phi_{\xi}(x)$$
$$+ \int \mathrm{d}x' \left\{ \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r'}|} + \frac{1}{2} \frac{\delta \Delta T_{xc}[\gamma^{(2)}]}{\delta \gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'})} \Big|_{\gamma_0^{(2)}} \right.$$
$$+ \frac{1}{2} \frac{\delta \Delta T_{xc}[\gamma^{(2)}]}{\delta \gamma^{(2)}(\boldsymbol{r'r}; \boldsymbol{r'r})} \Big|_{\gamma_0^{(2)}} \right\} \sum_{\nu=1}^{N} \{ \phi_{\nu}^*(x') \phi_{\nu}(x') \phi_{\xi}(x)$$
$$- \phi_{\nu}^*(x') \phi_{\xi}(x') \phi_{\nu}(x) \} = \varepsilon_{\xi} \phi_{\xi}(x), \qquad (4)$$

where $\Delta T_{xc}[\gamma^{(2)}]$ is the correlating kinetic energy functional that is defined as the difference between the kinetic energy of the many-body system and that of the noninteracting reference system [16, 18]. The reproduced form of the PD is given by

$$\gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'}) = \tfrac{1}{2} \sum_{\mu,\nu=1}^{N} \int \int \{ \phi_{\mu}^*(x) \phi_{\nu}^*(x') \phi_{\mu}(x) \phi_{\nu}(x')$$
$$- \phi_{\mu}^*(x) \phi_{\nu}^*(x') \phi_{\nu}(x) \phi_{\mu}(x') \} \, \mathrm{d}\eta \, \mathrm{d}\eta'. \qquad (5)$$

Equations (4) and (5) are the self-consistent single-particle equations. Equation (4) can be regarded as a modified Hartree–Fock (HF) equation, in which $\Delta T_{xc}[\gamma^{(2)}]$ terms are included as the correlation potentials. Namely, if $\Delta T_{xc}[\gamma^{(2)}]$ terms are neglected, the equation exactly coincides with the HF equation. Due to $\Delta T_{xc}[\gamma^{(2)}]$ terms, spin orbitals deviate from the solutions of the HF equation. Not only the additional terms but also values of the Hartree and Fock potentials are differences of this equation and the HF equation. All of these differences come from $\Delta T_{xc}[\gamma^{(2)}]$ terms, which should be recognized as the correlation effects.

In order to solve the single-particle equation, we need the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$. To this end, with the aid

of the scaling properties of $\Delta T_{xc}[\gamma^{(2)}]$ [16], we have already developed two kinds of approximate forms:

$$\Delta T_{xc}[\gamma^{(2)}] = K_1 \int \int \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r'} \frac{\gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'})^{7/6}}{|\boldsymbol{r} - \boldsymbol{r'}|} \qquad (6)$$

or

$$\Delta T_{xc}[\gamma^{(2)}] = K_2 \int \int \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r'} \gamma^{(2)}(\boldsymbol{rr'}; \boldsymbol{rr'})^{4/3}, \qquad (7)$$

where K_1 and K_2 are arbitrary constants [16, 18].

As mentioned in section 1, the PD functional theory is not yet a fully formed field. Therefore, it is important as a first step toward developing the PD functional theory to present an initial standard scheme which just corresponds to the HF approximation of the wavefunction theory. As is well known, the HF approximation gives the best solution within the set of SSDs. In a similar way to that, the present scheme gives the best PD within the restricted search region consisting of the SSD-representable PDs. In addition, the single-particle equation of the present scheme is computationally tractable like the HF equation. Thus, the position of the scheme in the PD functional theory just corresponds to that of the HF approximation in the wavefunction theory. There is no doubt that the HF approximation can be regarded as an initial standard in the wavefunction theory. Correspondingly, the scheme may be regarded as an initial standard in the PD functional theory. Furthermore, although the search region is restricted, we can say from the formal viewpoint that the scheme may contain the correlation effects [16, 18]. This fact is also the reason why the present scheme may be regarded as an initial standard of the PD functional theory.

2.2. Reconfirmation of the performance of the initial scheme

In order to evaluate the initial scheme, actual calculations have already been performed for the neutral neon atom [18], in which it is shown that the initial scheme reproduces 22.8% of the correlation energy. In the test calculations, we have used equation (6) as the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$. It is also meaningful to check the performance of the initial scheme by using the alternative approximate form of $\Delta T_{xc}[\gamma^{(2)}]$, i.e. equation (7).

The parameter K_2 is determined by fitting the electron density of the present scheme to that of the configuration interaction (CI) method, similarly to the parameter K_1 [18]. The electron density that is calculated with $K_2 = -0.002$ is in good agreement with the CI electron density. The root-mean-square error is 0.04. The total energy of the present scheme is calculated as -257.237 Ryd. This is lower than that of the HF approximation (-257.094 Ryd) [35] and higher than that of the CI method (-257.856 Ryd) [36] (see table 1). The correlation energy, which is calculated as the difference between the total energy of the HF approximation and that of the present one, is obtained as -0.142 Ryd. This value corresponds to 18.7% of the correlation energy that is calculated by the CI method. Also, the percentage 18.7% is comparable to the previous result (22.8%) that is obtained by using equation (6). Thus, we can reconfirm the performance of the initial scheme. Namely, from the viewpoint of the correlation energy, about

Table 1. Atomic structure calculations for a neutral neon atom.

	K_1 or K_2	RMSE[a]	Total energy (Ryd)	Correlation energy (Ryd)
Initial-1[b]	-1.6×10^{-3}	0.04	-257.268	-0.174 (22.8%)
Initial-2[c]	-2.0×10^{-3}	0.04	-257.237	-0.142 (18.7%)
CI method	—	—	-257.856 [d]	-0.762 [d]

[a] The root-mean-square error for the electron density.

[b] Equation (6) is utilized as the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$ [18].

[c] Equation (7) is utilized as the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$.

[d] Reference [36].

20% of correlation effects can be covered by the initial scheme, irrespective of the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$. Judging from the fact that two different approximations lead to the same order of the correlation energy, it seems that the remaining error is caused from the restricted search region of the PD.

3. Attempts beyond the initial scheme

As mentioned in the previous section, the initial scheme can reproduce about 20% of the correlation energy, irrespective of the approximate form of $\Delta T_{xc}[\gamma^{(2)}]$. So, the remaining parts of the correlation effects may be covered only by extending the search region substantially. In order to extend the search region, we have already proposed the PD functional theory that yields the best PD within the set of the Jastrow wavefunction PDs of the lowest-order (LO-Jastrow PDs) [17]. In a previous paper [17], we adopted the correlation function that depends only on the electron–electron separations. However, it is pointed out that one needs the correlation function that depends not only on the electron–electron separations but also on the electron–nucleus separations [37]. Taking this into account, the LO-Jastrow PD is generally given by

$$\gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}'; \boldsymbol{r}\boldsymbol{r}') = \tfrac{1}{2}|f(\boldsymbol{r}, \boldsymbol{r}', \{\boldsymbol{R}_i\})|^2$$
$$\times \sum_{\mu,\nu=1}^{N} \int\int \{\phi_\mu^*(x)\phi_\nu^*(x')\phi_\mu(x)\phi_\nu(x')$$
$$- \phi_\mu^*(x)\phi_\nu^*(x')\phi_\nu(x)\phi_\mu(x')\} \, d\eta \, d\eta', \tag{8}$$

where $f(\boldsymbol{r}, \boldsymbol{r}', \{\boldsymbol{R}_i\})$ is the correlation function, $\{\boldsymbol{R}_i\}$ denotes the coordinates of nuclei, and $\phi_\mu(x)$ ($\mu = 1, \ldots, N$) denote constituent orbitals of the SSD of the Jastrow wavefunction.

Using equation (8), the variational principle with respect to the PD leads to the following single-particle equation:

$$\{F(\boldsymbol{r}) - \varepsilon_\delta\} \phi_\delta(x) = G_\delta(x) \tag{9}$$

with

$$F(\boldsymbol{r}) = \int dx_1 |f(\boldsymbol{r}, \boldsymbol{r}_1, \{\boldsymbol{R}_i\})|^2 \sum_{\nu=1}^{N} |\phi_\nu(x_1)|^2$$
$$\times \left\{ \frac{4K}{3} \gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}_1; \boldsymbol{r}\boldsymbol{r}_1)^{1/3} + \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_1|} \right.$$
$$\left. + \frac{v_{\text{ext}}(\boldsymbol{r}) + v_{\text{ext}}(\boldsymbol{r}_1)}{N - 1} \right\}, \tag{10}$$

$$G_\delta(x) = \int dx_1 |f(\boldsymbol{r}, \boldsymbol{r}_1, \{\boldsymbol{R}_i\})|^2 \sum_{\nu=1}^{N} \phi_\nu^*(x_1)\phi_\delta(x_1)\phi_\nu(x)$$
$$\times \left\{ \frac{4K}{3} \gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}_1; \boldsymbol{r}\boldsymbol{r}_1)^{1/3} + \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_1|} \right.$$
$$\left. + \frac{v_{\text{ext}}(\boldsymbol{r}) + v_{\text{ext}}(\boldsymbol{r}_1)}{N - 1} \right\}, \tag{11}$$

where ε_δ's in equation (9) are the Lagrange multipliers, which are determined by requiring that $\phi_\mu(x)$ ($\mu = 1, \ldots, N$) are orthonormal to each other. Since the resultant equations are quite tractable, the present scheme, as well as the initial scheme mentioned in the previous section, is a computational approach.

Are there any ways of going beyond the initial scheme besides the above-mentioned scheme? Here, let us recall that we have obtained the initial scheme that corresponds to the HF approximation. With reference to the wavefunction theory, in which various kinds of schemes have been developed on the basis of the HF approximation, we can develop the other computational schemes for the PD. In the wavefunction theory, the Møller–Plesset perturbation method is one of the successful schemes to deal with the correlation effects systematically [38, 39]. In the Møller–Plesset perturbation method, the HF equation is treated as the unperturbed one for the system. Similarly to this method, the perturbation method may be developed by treating the single-particle equation (4) as the unperturbed one. Since the spin orbitals of the initial scheme contain the correlation effects as shown in the previous section, the correlation effects are expected to be more efficiently included in the perturbation expansion than the Møller–Plesset perturbation method.

Furthermore, with reference to the CI method, it may be possible to devise the variational method by utilizing the spin orbitals of the initial scheme as the basis functions. Thus, by referring to the wavefunction theory, various kinds of computational schemes for calculating the ground-state PD can be developed on the basis of the initial scheme.

4. Concluding remarks

We check the performance of the initial scheme by performing actual calculations with the alternative approximation of the correlating kinetic energy functional. It is shown that the initial scheme can cover about 20% of correlation effects from the viewpoint of the correlation energy, irrespective of the approximate form of the correlating kinetic energy functional. This means that we get an established initial scheme in the sense that it can more or less cover the correlation effects (definitely about 20% of the correlation energy). On the basis of the initial scheme, it is possible to develop a variety of computational schemes for the PD functional theory. This is analogous to the wavefunctional theory, in which various computational schemes have been developed on the basis of the Hartree–Fock approximation.

Acknowledgments

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