



Pair density functional theory

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ABSTRACT

The pair density (PD) functional theory is regarded as not only an extension of the density functional theory but also one of the reduced density matrix theories. The main feature of the PD functional theory is that the PD, as a basic variable, essentially contains more information on the electron–electron interaction than the electron density. In order to develop the PD functional theory, there exist two kinds of problems to solve. In this paper, we review our recent approaches about how to tackle with these problems, and show the latest results of the atomic structure calculations for Ne.

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1. Introduction

The density functional theory (DFT) is one of the first-principles methods that can formally reduce the many-body problem to the single-particle problem under the effective potential [1,2]. The Hohenberg–Kohn (HK) theorem and the introduction of the noninteracting reference system enable such a reduction [1,2]. With the progresses of the computational techniques and computers, the DFT has been extensively applied to various systems including larger-size systems such as molecules and solids.

The exchange–correlation (xc) energy functional is a key quantity of the DFT [2]. Namely, the accuracy of the DFT calculation is explicitly dependent on whether the xc energy functional is reasonably approximated or not. The history of approximations of the xc energy functional has started from the local density approximation (LDA) which appeared in the original paper of the DFT [2]. After the LDA, a lot of sophisticated approximations have been proposed in an effort to attain the chemical accuracy of calculations. This developing process of the xc energy functional is likened to “Jacob’s ladder” by Perdew [3]. Among approximations, it is especially worth noting that the GGA [4] and related approximations [5,6] have been much utilized due to their validity and simplicity of the expressions.

However, if one aims at explaining and/or predicting quantitatively the various physical quantities besides the electron density and total energy, the conventional DFT seems to be insufficient

to be applied. This is because the DFT guarantees the reproductions of the electron density and total energy of the ground state but does not do the other physical quantities in principle. Namely, when we intend to reproduce the physical quantities other than the electron density and total energy, we cannot reach the goal of the first-principles calculations along Jacob’s ladder of the xc energy functional of the DFT.

The reduced density matrix (RDM) has more information than the electron density. The first-principles calculation methods that pursue the RDM have been developed by many challengers and pioneers including Coleman [7–13]. The greatest merit of these RDM theories is the ability to predict not only the electron density but also the other physical quantities via the RDM. For example, the expectation value of the one-particle operator such as the kinetic energy (KE) can be calculated from the first-order RDM (1-RDM). Similarly, that of the two-particle operator such as the xc energy can be calculated from the second-order RDM (2-RDM) [14]. Since these merits are quite attractive, the direct calculation methods of the 2-RDM have been developed by Nakatsuji [15], Valdemoro [16], Mazziotti [17–19].

On the other hand, it is pointed out as a demerit that the calculation load of the RDM theory is generally larger than that of the DFT. The applications have been so far restricted to smaller-size systems. This is because the number of variables for the RDM (6–12 variables) is larger than that of the electron density (three variables). In general, the more number of variables a function has, the heavier the calculation to determine its spatial shapes becomes [20]. However, with the recent developments of the calculation

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methods, it is becoming possible to apply the 1-RDM theory to larger-size systems such as molecules and solids [22–31].

The pair density (PD) is the diagonal elements of the 2-RDM. Similarly to the 1-RDM, the PD is a 6-variables function, so that it is expected that the PD functional theory would also be applicable to larger-size systems [32]. The PD functional theory was first proposed by Ziesche [33,34]. After his proposal, many workers have studied it extensively [35–64]. The PD has more information than the electron density, namely, the expectation value of an arbitrary two-particle operator can be obtained only by using this. In addition to this merit, the PD functional theory has another merit which is related to the development of the approximate functional. That is to say, in the PD functional theory, only development required is the approximate form of the KE functional, because the xc energy functional can rigorously be expressed by the PD [65].

For developing the PD functional theory, as mentioned in the subsequent section, there exist two kinds of problems to solve. In this paper, we present our recent approaches mainly about the way to overcome these problems.

Organization of this paper is as follows: In Section 2, we outline the PD functional theory, and refer to two kinds of problems to the development of it. In Section 3, our recent approaches are presented, and especially an effective extension method of the search region of PDs is explained. Finally, concluding remarks are given in Section 4.

2. Outline of the Pair density functional theory

In this section, we shall sketch the outline of the PD functional theory. The PD is defined as:

$$\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \frac{N(N-1)}{2} \int |\Psi(\mathbf{r}\zeta_1, \mathbf{r}'\zeta'_1, \mathbf{r}_2\zeta_2, \dots, \mathbf{r}_N\zeta_N)|^2 d\zeta_1 d\zeta'_1 d\zeta_2 d\zeta'_2 \dots d\zeta_N d\zeta'_N, \quad (1)$$

where \mathbf{r}_j and ζ_j are spatial and spin coordinates of the j th electron, respectively, and where $\Psi(\mathbf{r}_1\zeta_1, \mathbf{r}_2\zeta_2, \dots, \mathbf{r}_N\zeta_N)$ is the antisymmetric wave function. The universal energy functional of the PD functional theory is defined as

$$F[\gamma^{(2)}] = \text{Min}_{\Psi \rightarrow \gamma^{(2)}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = \langle \Psi[\gamma^{(2)}] | \hat{T} + \hat{W} | \Psi[\gamma^{(2)}] \rangle, \quad (2)$$

where \hat{T} and \hat{W} are operators of the KE and electron–electron interaction energy, respectively. The right-hand side of the first line of Eq. (2) denotes the searching of the minimum for the expectation value of $\hat{T} + \hat{W}$ over all antisymmetric wave functions that yield a prescribed $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$, and $\Psi[\gamma^{(2)}]$ which appears in the second line is the minimizing wave function.

Using this functional, the HK theorem with respect to the PD can be proven in a similar way to the DFT [1,2] and extended constrained-search theory [66–71]. The first theorem is one-to-one correspondence between the ground-state PD and ground-state wave function. The second theorem is the variational principle with respect to the PD. According to the second theorem, the ground-state PD gives the minimum of the following total energy functional:

$$\begin{aligned} E[\gamma^{(2)}] &= F[\gamma^{(2)}] + \frac{1}{N-1} \int \{v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}')\} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r d^3r' \\ &= T[\gamma^{(2)}] + e^2 \int \frac{\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \\ &\quad + \frac{1}{N-1} \int \{v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}')\} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r d^3r', \end{aligned} \quad (3)$$

with

$$T[\gamma^{(2)}] = \langle \Psi[\gamma^{(2)}] | \hat{T} | \Psi[\gamma^{(2)}] \rangle, \quad (4)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential. It should be noted that the PD functional theory does not need to introduce the xc energy

functional since the electron–electron interaction energy can be written exactly by using the PD. In the conventional DFT, it is indispensable to approximate both KE and xc energy [2]. On the other hand, in the PD functional theory, only the KE is needed to be approximated. This is also a merit of the PD functional theory.

As is already known, there exist two kinds of problems for developing the PD functional theory [46]. One is that necessary and sufficient conditions for the N -representability of the PD have not yet been known in a practical form. Namely, we have to devise how the search region of PDs is extended sufficiently with preserving the N -representability of PDs [7–11,53–64]. The other is the approximate form of the KE functional. The KE can be written by the 1-RDM, but not by the PD alone [72]. As a result, we have to devise the approximate KE in a form of the functional with respect to the PD [73–77].

In order to develop the PD functional theory, the above-mentioned problems should be considered simultaneously. This is because we cannot check the validity of either one without checking that of the other. So far, we have attempted several approaches in an effort to overcome or reduce above problems. Let us mention them in the next section.

3. Our recent approaches

3.1. KE functional

First we shall show our strategy for developing the approximate form of the KE functional. In the conventional DFT, methods for the development of the approximate xc energy functional are classified into two groups. One is the method to develop the approximate form on the basis of the coupling-constant expression for the xc energy functional [78]. This is rigorously written by introducing the varying coupling-constant of the electron–electron interaction [78]. Another is to develop the approximate form by utilizing as the restrictive conditions the relations to be fulfilled by the xc energy functional. Such relations have been derived by scaling the coordinates of electrons uniformly and nonuniformly [79,80].

It is expected that similar methods may be effective for the KE functional of the PD functional theory. We have recently derived the coupling-constant expression for the KE functional [77], and several types of relations to be fulfilled by the KE functional [51,77]. In the former case, the difference between the KE functional of the noninteracting fictitious system and that of the real system is renormalized into the coupling-constant integration [77]. On the basis of this expression we also propose the approximate form of the KE functional of the PD functional theory [77]. In the latter case, exact relations that are fulfilled by the KE functional are derived by means of the HK theorem and scaling properties of the KE functional [51]. By imposing these relations as the restrictive conditions to the KE functional, the approximate forms have also been obtained [51]. One of them is illustrated as [51]

$$\iint \left\{ K \left(\frac{1}{r^2} + \frac{1}{r'^2} \right) + \frac{K'}{rr'} \right\} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r d^3r', \quad (5)$$

where K and K' are constants. Combining these approximate KE functionals with the idea which is related to the search region of PDs, atomic structure calculations have been performed so as to confirm the validities of our PD functional theories [46–48,50–52,81]. Concerning the idea about the search region of PDs, we will explain just below.

3.2. Search region of PDs

The other problem of the PD functional theory is the necessary and sufficient conditions for the N -representability of the PD. As

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