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A self-consistent first-principles calculation scheme for correlated electron systems

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Abstract

A self-consistent calculation scheme for correlated electron systems is created based on the density-functional theory (DFT). Our scheme is a multi-reference DFT (MR-DFT) calculation in which the electron charge density is reproduced by an auxiliary interacting fermion system. A short-range Hubbard-type interaction is introduced in a rigorous manner with a residual term for the exchange–correlation energy. The Hubbard term is determined uniquely by referencing the density fluctuation at a selected localized orbital. This strategy to obtain an extension of the Kohn–Sham scheme provides a self-consistent electronic structure calculation for the materials design. Introducing two approximations for the residual exchange–correlation energy functional, we have the LDA + U energy functional. Practical self-consistent calculations are exemplified by simulations of hydrogen systems, i.e. a molecule and a periodic one-dimensional array, which is a proof of existence of the interaction strength U as a continuous function of the local fluctuation and structural parameters of the system.

1. Introduction

Inclusion of the short-range correlation effect (SRCE) is a long-term quest for first-principles electronic structure calculations based on the density-functional theory (DFT) [1, 2]. In principle, this is possible, since the strategy introduced by Hohenberg, Kohn and Sham was shown to be given by a rigorous variational principle [3–6]. Although the method should give formally an exact calculation scheme for the Coulomb system, the energy density functional

is not perfectly known at present. Plausible approximation schemes have been proposed and utilized [2, 7–9]. However, they have their own limitations. For example, the local-density approximation (LDA) is known to give a metallic ground state for the Mott insulator La_2CuO_4 [10–16]. This failure of LDA is a central problem of DFT, for which we hope the inclusion of SRCE to be a solution. In particular, when LDA gives near degeneracy in the ground state, appropriate treatment of the SRCE can lift the degeneracy to have a non-degenerated ground state, implying formation of the Mott gap. This assumption may be widely accepted as a natural conclusion according to the study of the Hubbard models [17, 18].

Here we should note that the Kohn–Sham scheme has flexibility and can be adjusted even for the Mott insulator. If we introduce the wavefunction of an entangled state as the Kohn–Sham ground-state wavefunction, the excitation spectrum for the Kohn–Sham system may change. This implies that the response of the system has changed. Considering the adiabatic shift in the ground state as a function of some outer parameters like the external electro-magnetic field, there should be an essential change as a consequence of the introduction of the SRCE in the Kohn–Sham scheme. Even if we consider the density-functional theory for the ground state of the Coulomb system, this extended scheme allows us to handle the correlated electron system using the density-functional theory.

Thus we still have many possible approaches for practical computation as a realization of the Kohn–Sham scheme in an extended formulation. Actually, the Kohn–Sham equation is regarded as an auxiliary equation for realizing the optimization process of the single-particle density $n(\mathbf{r})$. In this paper, we consider this physical quantity as a central order parameter of the electron system. Usually, a system of non-interacting fermions is utilized to describe $n(\mathbf{r})$ in the Kohn–Sham scheme. Interestingly, we are allowed to consider interacting fermion systems, which can be used to replace the non-interacting Kohn–Sham system. This is called the multi-reference density-functional theory (MR-DFT) [19–25]. To develop a direct description of a Mott insulating state, one of the authors defined a kind of MR-DFT [26]. Utilizing this formulation, called the extended Kohn–Sham scheme (EKSS), one has a chance of detecting Coulomb suppression of the fluctuation, which is not directly found in $n(\mathbf{r})$.

The interacting Kohn–Sham system was originally motivated by a hybrid approach with a configuration interaction (CI) scheme in the theory of quantum chemistry [19–25]. In the hybrid density-functional theory, people utilized (1) all or part of the elements of the density matrix [22] or (2) restriction of the search space [23] in the constrained minimization to define the energy density functional. Knowledge of the modified energy density functional, however, is not enough. Proof of existence of a minimum in the constrained search is required. In contrast, it is possible to formulate MR-DFT in another way by referring to the original Levy–Lieb energy functional [26, 27].

In this paper, focusing on the fluctuation reference method [27], we will discuss a self-consistent calculation scheme of MR-DFT. The method is shown to be a kind of renormalization method for finding a fixed effective interacting Hamiltonian. A practical approximation for the residual exchange–correlation energy functional allows us to confirm that the scheme does give a self-consistent solution. We will give a report of the first application of our scheme in two types of hydrogen systems. If we introduce a local-density approximation after replacing the residual exchange–correlation energy functional by the ordinal exchange–correlation energy functional, the obtained energy functional is a kind of LDA + U energy functional. However, our approach is different from the former LDA + U approaches [28–30], because we follow the fluctuation reference method and we are not primarily looking at the excitation spectrum. A clear difference from the LDA + U approach can be seen in the fact that we are able to avoid the indicated approximation, replacing the residual exchange–correlation energy functional by the ordinal exchange–correlation energy functional.

The structure of the paper is as follows. In section 2, we introduce our energy functional. The functional is a wavefunction functional. The variational principle is shown. In section 3, the idea of the fluctuation reference is introduced. The uniqueness theorem of the U term is briefly reviewed. We discuss the extended Kohn–Sham Hamiltonian as a fixed-point Hamiltonian in MR-DFT in section 4. In section 5, the importance of the density fluctuation in determining the correlated nature of electron systems is discussed. In section 6, we introduce a practical application of the method with two hydrogen systems. A final discussion and summary is given in section 7.

2. Energy functional

We review the formal theory of the extended Kohn–Sham scheme (EKSS) [26]. We consider a non-relativistic electron system with N electrons in an external scalar potential $v_{\text{ext}}(\mathbf{r})$. The Hamiltonian operator that we consider is

$$\hat{\mathcal{H}}_C = \hat{T} + \hat{V}_{\text{ee}} + \int d^3r v_{\text{ext}}(\mathbf{r})\hat{n}(\mathbf{r}). \quad (1)$$

The kinetic-energy operator is given by,

$$\hat{T} = -\frac{\hbar^2}{2m} \int d^3r \sum_{\sigma} \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}') \Delta_{\mathbf{r}} \hat{\psi}_{\sigma}(\mathbf{r}),$$

and the inter-electron repulsion is

$$\hat{V}_{\text{ee}} = \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \sum_{\sigma, \sigma'} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}).$$

The ground state $|\Psi_{\text{GS}}\rangle$ of the system exists and gives the lowest energy E_0 and the single particle density as,

$$E_0 = \langle \Psi_{\text{GS}} | \hat{\mathcal{H}}_C | \Psi_{\text{GS}} \rangle. \quad (2)$$

$$n_{\text{GS}}(\mathbf{r}) = \langle \Psi_{\text{GS}} | \hat{n}(\mathbf{r}) | \Psi_{\text{GS}} \rangle. \quad (3)$$

Here $\hat{n}(\mathbf{r}) \equiv \sum_{\sigma} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r})$, with the electron field operator $\hat{\psi}_{\sigma}(\mathbf{r})$ satisfying $[\hat{\psi}_{\sigma}(\mathbf{r}), \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}') \delta_{\sigma, \sigma'}$.

We know the following density-functional theory [5]. For a normalizable wavefunction Ψ with a finite kinetic energy, the single-particle density $n(\mathbf{r})$ of Ψ and $|\nabla(n(\mathbf{r}))^{1/2}|^2$ are in a set of integrable functions in \mathbb{R}^3 . A set H^1 is a set of functions f for which $\int f^2$ and $\int |\nabla f|^2$ are finite. We consider a minimization scheme with respect to $n(\mathbf{r}) > 0$ such that $n(\mathbf{r})^{1/2} \in H^1(\mathbb{R}^3)$ and $\int n(\mathbf{r}) d^3r = N$. This class of functions is called \mathcal{I}_N .

Since a minimizing sequence of a positive quadratic form in $H_1(\mathbb{R}^{3N})$ has a limit, and since the Harriman construction [31, 5] ensures the existence of Ψ giving $n(\mathbf{r}) \in \mathcal{I}_N$, one can introduce a universal energy functional $F[n]$ which is called the Levy–Lieb energy functional and is defined by

$$F[n] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle. \quad (4)$$

Utilizing this energy functional, we can construct the minimization process of EKSS. To formulate it, let us consider a set of orthogonalized normalizable functions $\{\phi_i(\mathbf{r})\}$, the creation and annihilation operator $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$, and a number operator $\hat{n}_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ with respect to $\phi_i(\mathbf{r})$. Expectation values $\bar{n}_{i\sigma} = \langle \Psi' | \hat{n}_{i\sigma} | \Psi' \rangle$ are given for a state $|\Psi'\rangle$. We introduce another density functional

$$F_U[n] = \min_{\Psi' \rightarrow n(\mathbf{r})} \langle \Psi' | \hat{T} + \frac{U}{2} \sum_i (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} - \bar{n}_{i\uparrow} - \bar{n}_{i\downarrow})^2 | \Psi' \rangle. \quad (5)$$

There is a minimizing state for any $n(\mathbf{r}) \in \mathcal{I}_N$.

As the ordinal Kohn–Sham scheme, EKSS ensures that the total energy E_0 and the single-particle density $n_{\text{GS}}(\mathbf{r})$ of the ground state are reproduced. This is due to the definition of the optimization process utilizing the Levy–Lieb energy functional. The physical phase space of $|\Psi\rangle$ is divided into pieces specified by their single-particle density $n(\mathbf{r})$. Then, the minimization process is decomposed into the inner process with respect to $|\Psi\rangle$ within the subspace given by $n(\mathbf{r})$ and the outer process with respect to $n(\mathbf{r})$.

If we further pay attention to the Hadjisavvas–Theophilou scheme [6], we can show EKSS in a rigorous manner. This process is easily shown in the following equality:

$$\begin{aligned}
E_0 &= \langle \Psi_{\text{GS}} | \hat{T} + \hat{V}_{\text{ee}} | \Psi_{\text{GS}} \rangle + \int n_{\text{GS}}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d^3r \\
&= \min_n \left\{ \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d^3r \right\} \\
&= \min_n \left\{ \min_{\Psi' \rightarrow n(\mathbf{r})} \langle \Psi' | \hat{T} + \frac{U}{2} \sum_i (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} - \bar{n}_{i\uparrow} - \bar{n}_{i\downarrow})^2 | \Psi' \rangle \right. \\
&\quad \left. + F[n] - F_U[n] + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d^3r \right\} \\
&= \min_{\Psi'} \left\{ \langle \Psi' | \hat{T} + \frac{U}{2} \sum_i (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} - \bar{n}_{i\uparrow} - \bar{n}_{i\downarrow})^2 | \Psi' \rangle \right. \\
&\quad + \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + F[n_{\Psi'}] \\
&\quad \left. - \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' - F_U[n_{\Psi'}] + \int n_{\Psi'}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d^3r \right\} \\
&= \min_{\Psi'} \left\{ \langle \Psi' | \hat{T} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} | \Psi' \rangle + \frac{U}{2} \sum_i (\bar{n}_i - \bar{n}_i^2) \right. \\
&\quad \left. + \frac{e^2}{2} \int \frac{n_{\Psi'}(\mathbf{r}) n_{\Psi'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{rxc}}[n_{\Psi'}] + \int n_{\Psi'}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d^3r \right\} \\
&= \min_{\Psi'} \bar{G}_U[\Psi']. \tag{6}
\end{aligned}$$

Here, n_{Ψ} is the density associated with Ψ' ,

$$n_{\Psi'}(\mathbf{r}) = \langle \Psi' | \hat{n}(\mathbf{r}) | \Psi' \rangle.$$

Thus we have found that the minimization process of a wavefunction functional $\bar{G}_U[\Psi']$ gives the exact value of the total energy of the system.

In a general form, the energy functional $\bar{G}_{\text{EKS}}[\Psi]$ of EKSS is given in the following formula.

$$\begin{aligned}
\bar{G}_{\text{EKS}}[\Psi] &= \langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle - \min_{\Psi' \rightarrow n_{\Psi}} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle + F[n_{\Psi}] + \int d^3r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}) \\
&= \langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle + \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r}) n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \\
&\quad + E_{\text{rxc}}[n_{\Psi}] + \int d^3r v_{\text{ext}}(\mathbf{r}) n_{\Psi}(\mathbf{r}). \tag{7}
\end{aligned}$$

Here the operator \hat{V}_{red} denotes a generalized operator counting fluctuation or hidden order parameters which are of a higher order than that of $n(\mathbf{r})$. The operator has to be positive semi-definite and be bounded from above. When minimizing $\bar{G}_{\text{EKS}}[\Psi]$ with respect to Ψ , which is

an auxiliary wavefunction, the value of $\bar{G}_{\text{EKS}}[\Psi]$ becomes E_0 . This is easily seen by looking at the first line of equation (7), in which $\langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle - \min_{\Psi' \rightarrow n_\Psi} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle \geq 0$ becomes zero at the minimum. At this minimum point, Ψ gives the minimum value of the expectation value $\langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle$ within a phase space of wavefunctions whose single-particle density is n_Ψ . Now, the density functional $F[n_\Psi] + \int d^3r v_{\text{ext}}(\mathbf{r})n_\Psi(\mathbf{r})$ becomes a minimum when $n_\Psi(\mathbf{r})$ is equal to the single-particle density of the true ground state $n_{\text{GS}}(\mathbf{r})$. Thus, the total minimization is achieved only if $n_\Psi(\mathbf{r}) = n_{\text{GS}}(\mathbf{r})$ and if Ψ gives the minimum of $\langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle$ within the phase space of wavefunctions which give $n_{\text{GS}}(\mathbf{r})$.

One would find that equation (7) is nothing but the definition of $E_{\text{rxc}}[n_\Psi]$. Formally, \hat{V}_{red} is arbitrary, since redefinition of $E_{\text{rxc}}[n_\Psi]$ keeps the equality. Moreover, the kinetic term and the Hartree term are not necessarily given by the formula in equation (7). At present, we just follow the conventional idea that the Hartree-type approximation would be close to the answer, when we know *a priori* the density $n(\mathbf{r})$. Using the usual kinetic energy of fermions with the electron mass, we have determined $E_{\text{rxc}}[n_\Psi]$. This guideline may be explained in the following manner. If we know that $n(\mathbf{r})$ is the appropriate order parameter, it would be natural to expect that the explicit energy functional written in $n(\mathbf{r})$ with the Hartree term reflects a dependence on the structure of the materials at the first stage. The electron charge density acts as a source and creates the scalar Coulombic field. In addition, introduction of the fermion kinetic energy $\langle \Psi | \hat{T} | \Psi \rangle$ keeps the system from collapse to the bosonic solution. The reason why we conclude the above statement is that the variable of the theory is $n(\mathbf{r})$. The kinetic energy functional, however, has another meaning, as discussed in section 7.

An important point for the density-functional theory is that we can find continual refinement for the improvement. The introduction of $\langle \Psi | \hat{V}_{\text{red}} | \Psi \rangle$ shifts the energy functional so that $|\Psi\rangle$ represents a correlated electron state. Using the entangled state, the expression of the energy functional is modified. In the new description, explicit evaluation of the energy is performed with the Hartree term, the kinetic energy and the fluctuation. If the residual correlation energy functional $E_{\text{rxc}}[n_\Psi]$ becomes small in ratio to the total energy by this modification, we notice that the fluctuation has emerged. Now we start to explain the idea in detail.

To proceed, we need to consider functional differentiability [9]. For this purpose, all of the energy functional defined above should be replaced by the Legendre transforms of them. The technique was introduced by Lieb [5]. To specify the problem, we consider $\bar{G}_U[\Psi]$. By making a variation with respect to $\langle \Psi |$, we have an extended-Kohn–Sham equation (EKSE):

$$\left[\hat{T} + \int v_{\text{eff}}(\mathbf{r})\hat{n}(\mathbf{r})d^3r \right] |\Psi\rangle + \sum_i U \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} |\Psi\rangle + \sum_i \frac{U}{2} (1 - 2\bar{n}_i) \sum_\sigma \hat{n}_{i,\sigma} |\Psi\rangle = E |\Psi\rangle. \quad (8)$$

Here $\bar{n}_i = \sum_\sigma \bar{n}_{i,\sigma}$. A Lagrange multiplier E is introduced to keep the norm of $|\Psi\rangle$ to 1. Here the effective single-particle potential $v_{\text{eff}}(\mathbf{r})$ is given by

$$v_{\text{eff}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \frac{\delta E_{\text{rxc}}[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}). \quad (9)$$

The charge density $n(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \sum_\sigma \langle \Psi | \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) | \Psi \rangle. \quad (10)$$

Please note that we have not yet given a determination method for $\{\phi_i(\mathbf{r})\}$, but that the variational principle always holds rigorously.

We solve the auxiliary one-body problem given by v_{eff} as

$$\left\{ -\frac{\hbar^2}{2m} \Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r}) \right\} \chi_l(\mathbf{r}) = \varepsilon_l \chi_l(\mathbf{r}), \quad (11)$$

in which the $\chi_l(\mathbf{r})$ are determined to be normalized and orthonormal. If we construct a set of creation and annihilation operators $d_{l,\sigma}^\dagger$ and $d_{l,\sigma}$ associated with $\chi_l(\mathbf{r})$, the effective many-body problem is found:

$$\left\{ \sum_{l,\sigma} \varepsilon_l d_{l,\sigma}^\dagger d_{l,\sigma} + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} + \sum_i \frac{U}{2} (1 - 2\bar{n}_i) \sum_\sigma \hat{n}_{i,\sigma} \right\} |\Psi\rangle = E|\Psi\rangle. \quad (12)$$

Note again that $\hat{n}_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ is defined by $\phi_i(\mathbf{r})$. In a crystal, the index l may be a combined index of the crystal momentum \mathbf{k} and the band index n . One may call EKSE defined by equations (11) and (12) a first-principles Anderson model or a first-principles Hubbard model.

3. A comment on the uniqueness of the model

In principle, EKSS works irrespective of the form of \hat{V}_{red} , if we can check the existence of the minimum of $\langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle$ and its bound. This fact tells us about the flexibility of the theory. A large class of effective Hamiltonians exists and each auxiliary system is an extended Kohn–Sham model. Thus, we need to have a rule for selecting an appropriately chosen effective model for practical calculation. In other words, there should be a guiding principle to determine $\bar{G}_U[\Psi]$. The idea is that there has to be a physical quantity which is in a higher order than $n(\mathbf{r})$ and which specifies the model.

At the beginning, we need to understand the nature of $\bar{G}_U[\Psi]$ to construct the best-fitting model. To make the discussion concrete, let us consider a U term in our theory. For a given normalizable localized orbital $\phi_i(\mathbf{r})$, density fluctuation is determined as follows:

$$\langle \underline{n}_i^2 \rangle \equiv \langle (n_{i,\uparrow} + n_{i,\downarrow} - \bar{n}_{i,\uparrow} - \bar{n}_{i,\downarrow})^2 \rangle. \quad (13)$$

A key observation is that the fluctuation counted by the model may be suppressed, if the minimizing Ψ changes when the value of U is increased in equation (12).

The U term in $\bar{G}_U[\Psi]$ is given by the following energy functional:

$$\langle \Psi | \hat{V}_{\text{red}} | \Psi \rangle = \frac{U}{2} \langle \Psi | \underline{n}_i^2 | \Psi \rangle. \quad (14)$$

A requirement is that the U term has to be bounded from below and from above. This is guaranteed in the above expression, since the quadratic form is positive-semi-definite and the lemma below holds [27].

Lemma 1. $\langle \underline{n}_i^2 \rangle$ is real. The following inequality holds:

$$0 \leq \langle \underline{n}_i^2 \rangle \leq 1. \quad (15)$$

We also have the following few statements, which are given here without proof.

Lemma 2. Assume that the ground state of a Coulomb system given by $v_{\text{ext}}(\mathbf{r})$ exists. (i) The ground state $|\Psi\rangle$ of a corresponding extended-Kohn–Sham model $\bar{G}_U[\Psi]$ with a given positive U exists. (ii) For fixed $n(\mathbf{r})$, $\bar{F}(U) = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \frac{U}{2} \underline{n}_i^2 | \Psi \rangle$ is a continuous function of U . (iii) If a state $|\Psi\rangle$ is the ground state of $\bar{G}_{U_1}[\Psi]$ and $\bar{G}_{U_2}[\Psi]$ with $0 \leq U_1 < U_2$ simultaneously, $|\Psi\rangle$ is the ground state of $\bar{G}_U[\Psi]$ in a finite range $[U_1, U_2]$ of U .

The proofs are given in another paper [27]. Finiteness of $\langle n_i^2 \rangle$ is utilized for the proof of continuity. The constraint for the degeneracy of the Coulomb system is not required in lemma 2.

If we increase U from zero, the effective interaction in equation (8) brings the system into a correlated regime. The change results in the suppression of the fluctuation considered. Thus, the U term can control the value of $\langle n_i^2 \rangle$. For the original Coulomb system, we can also determine $\langle n_i^2 \rangle_{\text{GS}}$ in principle, once we fix $\phi_i(\mathbf{r})$. We are thus allowed to compare the fluctuation of the original system and the extended Kohn–Sham system. There could be an adjusted value of U for which $\langle n_i^2 \rangle$ of EKSS is identical to that of the Coulomb system.

At a first glance, this point is not so important, since the density-functional theory tells us nothing about fluctuation or correlation functions. The Kohn–Sham wavefunction is introduced to determine the minimization process with respect to $n(\mathbf{r})$ and does not have a direct relevance in itself. However, if the given extended Kohn–Sham system is properly written in a multi-reference description, and if the obtained extended Kohn–Sham model reproduces an essential nature of the original system, the theory may have gone beyond the original concept of the density-functional theory.

For example, the introduction of U can make the extended Kohn–Sham system the Mott insulator. The solidification caused by the suppression of the density fluctuation given by $\langle n_i^2 \rangle$ may be detected in practical calculations. As discussed in sections 6 and 7, we can judge whether the system is a Mott insulator or not. Thus, reproduction of important fluctuation can be a key procedure for having a good description of some materials.

In a previous work, Kusakabe has shown a statement on uniqueness of the U term. We have the following exact statement.

Theorem 3. *Assume that the ground state of a Coulomb system is non-degenerate. An appropriate extended Kohn–Sham model given by $\hat{G}_U[\Psi]$ which has a non-degenerate ground state and reproduces both $n_{\text{GS}}(\mathbf{r})$ and $\langle n_i^2 \rangle_{\text{GS}}$ is uniquely determined, or it does not exist.*

This is a principle of our fluctuation reference method.

The restriction on the degeneracy of the Coulomb ground state is strict in the above theorem. Some systems are known to have degeneracy in the ground state. As for the degeneracy due to the spatial symmetry, the condition may not be a problem, since we are allowed to consider an outer scalar field which breaks the symmetry. Internal symmetry considered of the present description of the many-electron system with equation (1) as the electron spin. We may have degeneracy due to the internal symmetry of this spin degrees of freedom. As for the trivial degeneracy coming from the $SU(2)$ symmetry of the total spin, an external magnetic field will lift the degeneracy via the Zeeman splitting. If we change the structure of atomic configuration, effective spin interactions in the system change to lift the degeneracy in some cases.

4. Renormalization of the extended Kohn–Sham model

We now clarify that the self-consistent determination of the extended Kohn–Sham model is a sort of renormalization process. We consider equation (8) or (12). The set of solutions of equation (11), $\chi_l(\mathbf{r})$, can be used to create $\phi_i(\mathbf{r})$. In each step in the self-consistent loop, $n(\mathbf{r})$ is changing gradually and thus $\chi_l(\mathbf{r})$ is too. What can be fixed in the process is an algorithm to make $\phi_i(\mathbf{r})$ from $\chi_l(\mathbf{r})$.

More precisely, considering a lattice structure, we can diagonalize the single-particle part using Bloch waves $\chi_l(\mathbf{r}) = \chi_{n,\mathbf{k}}(\mathbf{r})$. The orbital is at first specified by a combined index l with band index n and crystal momentum \mathbf{k} . A unitary transformation from the Bloch states to the Wannier states may be useful to define $\phi_i(\mathbf{r})$ as $\phi_m(\mathbf{r} - \mathbf{R}_j)$. We suppose that i denotes an m th

localized orbital at a Wannier centre \mathbf{R}_j [32, 33]. If we fix the selection of the relevant bands to create the Wannier states, the self-consistency loop for finding a solution of equations (11) and (12) is well defined and it may converge.

In the model of equation (8), the scattering channels given by the effective interaction term are open only within a subset of $\chi_l(\mathbf{r})$, which is determined by the selection of $\phi_i(\mathbf{r})$. In other words, $c_{i\sigma}^\dagger$ is expanded in $d_{l\sigma}^\dagger$ in a specified n th band only. The scattering by the U term is restricted within this band and no direct interaction with other bands exists. Thus the definition gives a separable form of the effective interaction. If scattering processes due to the effective interaction are completely restricted within selected bands, the form is called separable.

If the effective interaction is written in terms of the field operators $\hat{\psi}_\sigma(\mathbf{r})$, and if the interaction strength $g(\mathbf{r}, \mathbf{r}')$ is not written in a separable form, there should be a finite amplitude for the scattering channel from one band to all the other bands. Thus, solving the obtained EKSE is as hard as the original Coulomb problem. But if the fermion scattering processes due to the effective interaction are restricted in a specified sub-space of the whole phase space, a reduction in the many-body description is achieved. If relevant scattering processes are appropriately chosen in the effective model, and if total self-consistency is achieved, then the obtained Hamiltonian should be a fixed Hamiltonian. The point is that the orbitals for describing the effective interaction have to be determined self-consistently.

The arbitrary nature of $\phi_i(\mathbf{r})$ actually allows us to have a fixed Hamiltonian. We can redefine the U term in an optimization process of $\bar{G}_U[\Psi]$ by making use of $\phi_i(\mathbf{r})$ given by the selected n th band in the calculation. If $\phi_i(\mathbf{r})$, given in a step of the self-consistency loop, is not perfectly expanded in the former set of wavefunctions in the n th band of equation (11), we can reconstruct $\phi_i(\mathbf{r})$ as a new Wannier orbital in the next step, starting from the obtained n th band. This approach to redefining the effective interaction is regarded as a renormalization process. The final fixed-point Hamiltonian would be described in a specified relevant sub-space whose dimension is much smaller than the original problem. Irrelevant scattering processes are smeared out from the theory. As for the electronic charge density $n(\mathbf{r})$, which is an essential quantity for determining the structure or the atomic configuration of a material, introduction of the renormalization process does nothing harmful, since the obtained effective Hamiltonian gives the ground-state charge density and the ground-state energy.

5. Density fluctuation

The density fluctuation $\langle n_i^2 \rangle$ plays an important role in our theory. The reason why we select this quantity as a physical quantity second to $n(\mathbf{r})$ may be explained as follows.

This quantity has a value depending on the environment around $\phi_i(\mathbf{r})$. Consider a d orbital of a copper atom as an example. The fluctuation on the orbital would not be small when copper atoms form a bulk metal. But, if the atom is in a copper oxide, the fluctuation should be reduced on it due to the SRCE.

In an ideal case, we can have a correlated electron state as the ground state, whose electron density $n(\mathbf{r})$ is the same as another uncorrelated state but has a different fluctuation on $\phi_i(\mathbf{r})$. The theory in section 3 tells us that an effective many-body system properly describing both $n(\mathbf{r})$ and the fluctuation $\langle n_i^2 \rangle$ on $\phi_i(\mathbf{r})$ is uniquely determined, if it exists. The ground state of the model would have a correlated state and sometimes it even becomes a Mott insulator. A typical example may be the Heitler–London state, which is an entangled singlet state.

Considering both the uncorrelated metallic state and the entangled state in a correlated regime, we can easily understand the essential behaviour of $\langle n_i^2 \rangle$ as follows. For a nearly uncorrelated metal, it is easy to show that $\langle n_i^2 \rangle = 0.5$. However, it should be zero for the Heitler–London state of the hydrogen molecule, as exemplified in section 6.

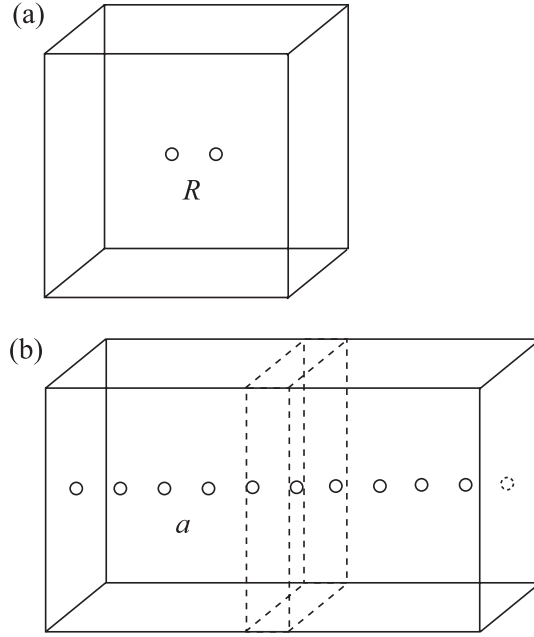


Figure 1. The calculation cell of the hydrogen systems: (a) the hydrogen molecule and (b) a hydrogen chain. The inter-atomic distance is R (\AA) or a (\AA) for the molecule or the chain. The system in (b) consists of ten atoms with a periodic boundary condition. The outer cell is for the many-body calculation. The inner cell denoted by the dashed lines is for the determination of the single-particle orbital $\chi_l(\mathbf{r})$.

We may define the Fermi level E_F for convenience, once equation (11) is solved with a fixed number of electrons. The wavefunctions $\chi_l(\mathbf{r})$ are grouped in bands. For each band, a unitary transformation to a localized orbital $\phi_i(\mathbf{r})$ is given. The typical value of the fluctuation on it is classified in the following list:

- (i) If $\phi_i(\mathbf{r})$ is deep below E_F , $\langle n_i^2 \rangle = 0$. This is because the orbital is doubly occupied.
- (ii) If $\phi_i(\mathbf{r})$ is far above E_F , $\langle n_i^2 \rangle = 0$. This is because the orbital is empty.
- (iii) If $\phi_i(\mathbf{r})$ is around E_F and if the state is uncorrelated, $\langle n_i^2 \rangle = 0.5$.
- (iv) If $\phi_i(\mathbf{r})$ is around E_F and if the state is correlated, $\langle n_i^2 \rangle = 0$.

We have to select $\phi_i(\mathbf{r})$ to keep the symmetry of the system, otherwise we will encounter difficulty in description of the system. Another important comment is that, if we choose an extended wavefunction as $\phi_i(\mathbf{r})$, the fluctuation on it may approach $\langle n_i^2 \rangle = 1$ in a correlated regime.

6. Determination of U in the hydrogen systems

In this paper, we consider hydrogen systems to demonstrate that it is possible to determine (1) the self-consistent solution of the extended Kohn–Sham scheme, and (2) the interaction parameter U , in practical calculations. Since the relevant orbitals are only 1s orbitals in the hydrogen systems, the electronic structure is easily tractable. We select two systems, i.e. the hydrogen molecule and a one-dimensional lattice structure (figure 1). The former example shows that an entangled state is obtained as a self-consistent solution of the extended

Kohn–Sham model. The U term is determined by fitting the local fluctuation of an accurate CI calculation for the hydrogen molecule. The latter seemingly artificial configuration of a hydrogen chain with a periodic boundary condition is introduced to show that a Mott-insulating state is obtained as a self-consistent solution.

For both of these systems, the extended Kohn–Sham equation is given in equation (8). The value of U is identical for every site indexed by i , because of the symmetry of the system. More precisely there are the C_2 symmetry (the mirror symmetry with respect to the centre of the molecule) for H_2 and the translational symmetry (invariance for uniform shift by the lattice constant a) for the chain. For both of the system, we have no spontaneous symmetry breaking causing the charge density wave, because the final solution of EKSE is non-degenerate.

6.1. Self-consistent calculation method

The self-consistent calculation is realized by adopting an algorithm with two nested loops. The outer loop is the determination of the CI configuration of the effective many-body problem. The inner loop is the diagonalization of equation (11) to obtain $\chi_l(\mathbf{r})$. The index l is $l = 1, 2$ for a bonding state and an anti-bonding state in the molecule. Meanwhile, it is $l = (n, k)$ with $n = 1$ and $k = 0, \dots, N - 1$ for the chain. $n = 1$ corresponds to the 1s band. We define ϕ_i by

$$\begin{aligned}\phi_1 &= \frac{1}{\sqrt{2}}(\chi_1 + \chi_2), \\ \phi_2 &= \frac{1}{\sqrt{2}}(\chi_1 - \chi_2),\end{aligned}$$

for the molecule and the Wannier state

$$\phi_i = \frac{1}{\sqrt{N}} \sum_{k=1}^N \exp\left(i \frac{2\pi}{Na} k x_i\right) \chi_{1,k},$$

for a chain with N atoms. Note that the size of the outer cell in the x direction is Na . $\chi_{1,k}$ is the Bloch wave in the first 1s band with the crystal momentum $p = 2\pi k/(Na)$ in the chain direction. $x_i = ai$ is the x -coordinate of the i th atom (figure 1). In the present systems, we can determine the transfer matrix element by

$$t_{ij} = \int \phi_i^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r}) \right\} \phi_j(\mathbf{r}) d\mathbf{r}. \quad (16)$$

Here, σ dependence does not appear because the system is non-magnetic. We select a typical transfer energy t_0 as that between the nearest-neighbour pair of orbitals. The U term is then introduced and equation (12) is diagonalized. For the case of the chain, we utilize a numerical diagonalization with the Lanczos algorithm. Here, the problem is solved for a fixed U/t_0 . Fixing the CI configuration, the one-body problem of equation (11) is solved self-consistently. Then, using the determined new χ_l , the effective Hubbard model is rebuilt. The self-consistency of the CI configuration is checked in the outer loop. Actually, we can reach a totally self-consistent solution.

The residual exchange–correlation energy functional is rewritten as follows:

$$\begin{aligned}E_{\text{rxc}}[n_{\Psi}] &= F[n_{\Psi}] - \min_{\Psi' \rightarrow n_{\Psi}} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle - \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r}) n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \\ &= F[n_{\Psi}] - \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r}) n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \\ &\quad + \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \min_{\Psi' \rightarrow n_{\Psi}} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle \\ &= E_{\text{xc}}[n_{\Psi}] + \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \min_{\Psi' \rightarrow n_{\Psi}} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle.\end{aligned} \quad (17)$$

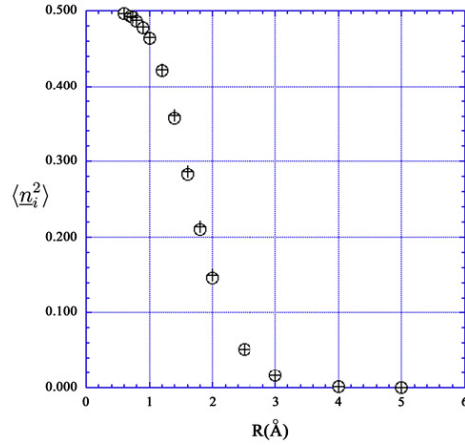


Figure 2. The density fluctuation $\langle n_i^2 \rangle$ at a 1s orbital of the hydrogen molecule. For the inter-atomic distance R (Å), $\langle n_i^2 \rangle$ is obtained using the CAS–CI calculation (circles) and the CAS–CI–DFT calculation (crosses).

(This figure is in colour only in the electronic version)

One way to treat the above expression is utilizing the following approximation [34]:

$$\begin{aligned} \min_{\Psi' \rightarrow n_\Psi} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle &\simeq \min_{\Psi' \rightarrow n_\Psi} \langle \Psi' | \hat{T} | \Psi' \rangle + \min_{\Psi' \rightarrow n_\Psi} \frac{U}{2} \sum_i \langle \Psi' | n_i^2 | \Psi' \rangle \\ &= \min_{\Psi' \rightarrow n_\Psi} \langle \Psi' | \hat{T} | \Psi' \rangle. \end{aligned} \quad (18)$$

If the search space of Φ' in equation (17) is the set of the single Slater determinant ϕ' , and if $\min_{\phi' \rightarrow n_\Psi} \langle \phi' | \hat{T} | \phi' \rangle = \min_{\Psi' \rightarrow n_\Psi} \langle \Psi' | \hat{T} | \Psi' \rangle$, then $E_{\text{xc}}[n_\Psi]$ is the same as the ordinal exchange–correlation energy functional. Note that Ψ' and Φ' are multi-Slater determinants. This is true if we consider the Legendre transform of each expression. If equation (18) is adopted, we see that $E_{\text{rxc}}[n_\Psi] \simeq E_{\text{xc}}[n_\Psi]$. Then, $E_{\text{xc}}[n_\Psi]$ is approximated by the local-density approximation [36]. The treatment of equation (17) will be reconsidered in section 7. For the actual calculation in the inner loop, we utilized the plane-wave expansion technique with the soft pseudo-potential [37]. To use the pseudo-potential with LDA does not harm the purpose of the present MR–DFT calculation, which is planned to show the existence of self-consistent solutions. The cutoff energy is set to be 40 (Ryd). The conjugate-gradient technique is used to optimize the Kohn–Sham orbitals $\chi_l(\mathbf{r})$. The actual calculation was performed using a computation code called ESopt, which was originally developed by Ogitsu and maintained by KK.

6.2. Reference calculation

As the reference calculation, we refer to the result obtained by the complete-active-space configuration–interaction (CASCI) theory [19] for the hydrogen molecule. The Gaussian basis set is utilized. The CAS wavefunction is prepared to incorporate all the resonating features arising in the H_2 molecule. Another MR–DFT approach, the CASCI density-functional theory (CASCI–DFT), was also examined. In the CASCI–DFT calculation, the CI configuration is taken from the CASCI calculation. The detailed description of the exchange–correlation energy functional used in CASCI–DFT is seen in [25]. The fluctuation on the 1s orbital is obtained as a function of the inter-atomic distance, as shown in figure 2.

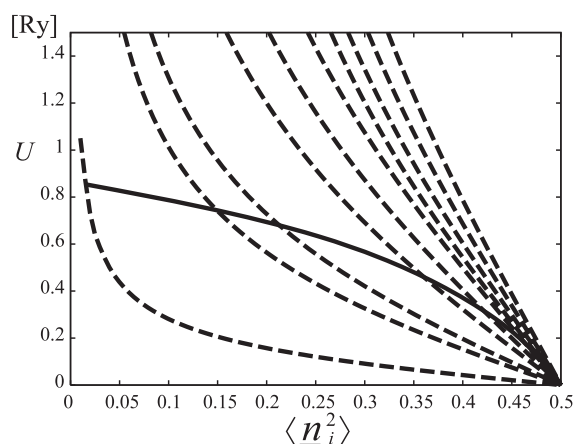


Figure 3. The effective interaction parameter U obtained using the extended Kohn–Sham calculation for the hydrogen molecule. The dashed lines are the values of U for $R = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8, 2.0, \text{ and } 3.0$ (Å), from top to bottom. The density fluctuation $\langle n_i^2 \rangle$ is counted on a $1s$ orbital of a hydrogen atom. By adjusting $\langle n_i^2 \rangle$ to the result in figure 2 for each value of R , the optimized U is obtained (the solid line).

When the inter-atomic distance is the equilibrium value $R = 0.740$ Å, the fluctuation is close to 0.5. This result tells us that the two-electron system of the hydrogen molecule is in a weak correlated regime, when the system is in equilibrium. However, when R becomes larger than 1 Å, the fluctuation is rapidly suppressed. This is seemingly natural, since the system should approach the Heitler–London limit when $R \gg 0.740$ Å. The crossover region is thus shown to be $R \simeq 2$ Å.

6.3. EKSS calculation of the hydrogen molecule

The MR-DFT using the extended Kohn–Sham scheme is applied to the hydrogen molecule [35]. Formally, the value of the fluctuation should be given as a function of R (Å) and U (Ryd). However, we obtained U for a given R (Å) and $\langle n_i^2 \rangle$ (figure 3). In this case, fixing $\langle n_i^2 \rangle$ is equivalent to fixing $\tilde{U} = U/t_0$. The value of t_0 is given when the inner loop is converged. The value of $U = \tilde{U}t_0$ is thus known after finding a self-consistent solution. The solution is obtained for each fixed \tilde{U} and R . By comparing $\langle n_i^2 \rangle$ of the effective model with that obtained by CASCI, U is determined uniquely (the solid line in figure 3).

Since we utilize the pseudo-potential method, the obtained $\phi_i(\mathbf{r})$ in the model is not the same as that given by CASCI. Thus the estimated value is an approximate value. In principle, the evaluation of $\langle n_i^2 \rangle$ using $\phi_i(\mathbf{r})$ in CASCI is possible. An important point is that the obtained value of U changes continuously and monotonously. Thus, in this numerical evaluation, the determination of U is possible.

6.4. A one-dimensional hydrogen array

As the second test calculation, we consider an array of hydrogen atoms. The configuration is imaginary, since the structure is not stable and inter-atomic forces are finite. But, to consider a simple Mott insulator, this artificial configuration is very useful.

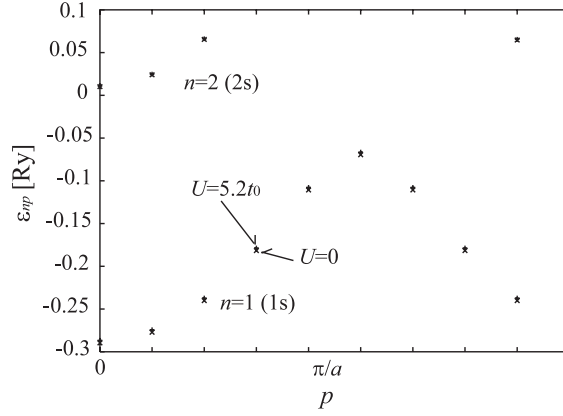


Figure 4. The Kohn–Sham eigenvalues $\varepsilon(n, p)$ of equation (11), which gives the single-particle dispersion of a hydrogen chain, the value of $U/t_0 = 0$ (crosses) or $5.2t_0$ with t_0 (pluses) being the transfer energy between neighbouring atoms.

We consider a periodic boundary condition with ten atoms ($N = 10$) in an outer simulation cell (figure 1). Since the system does not show spontaneous charge ordering, the electron charge density $n(\mathbf{r})$ has a periodicity that is same as that of the array. Thus, we can consider an inner unit cell containing a single atom in it. Within the second unit cell, $n(\mathbf{r})$ is kept in the simulation.

For a multi-reference state, we have an expansion:

$$|\Psi\rangle = \sum_{\alpha} C_{\alpha} |\Psi_{\alpha}\rangle, \quad (19)$$

$$|\Psi_{\alpha}\rangle = \prod_{m=1}^{N_u} c_{u_{\alpha,m}\uparrow}^{\dagger} \prod_{n=1}^{N_d} c_{d_{\alpha,n}\downarrow}^{\dagger} |0\rangle. \quad (20)$$

Here, α is an index specifying the CI configuration. Considering N_u up electrons and N_d down electrons, we need to specify the positions of up electrons as $u_{\alpha,m}$ ($m = 1, \dots, N_u$) and those of the down electrons as $d_{\alpha,n}$ ($n = 1, \dots, N_d$). They satisfy $1 \leq u_{\alpha,1} < u_{\alpha,2} < \dots < u_{\alpha,N_u} \leq N$ and $1 \leq d_{\alpha,1} < d_{\alpha,2} < \dots < d_{\alpha,N_d} \leq N$. In the present case, we have a half-filled Hubbard model whose ground state is given with $N_u = N_d = N/2$.

Note that, for a pair of different k points $k \neq k'$, $\langle \Psi | c_{k,\sigma}^{\dagger} c_{k',\sigma} | \Psi \rangle = \langle k, \sigma | k', \sigma \rangle = 0$. The charge density is thus represented as,

$$\begin{aligned} n(\mathbf{r}) &= \sum_{\sigma} \langle \Psi | \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma}(\mathbf{r}) | \Psi \rangle = \sum_{\sigma} \sum_{k,k'} \phi_k^*(\mathbf{r}) \phi_{k'}(\mathbf{r}) \langle \Psi | c_{k,\sigma}^{\dagger} c_{k',\sigma} | \Psi \rangle \\ &= \sum_{\sigma} \sum_k |\phi_k(\mathbf{r})|^2 \langle \Psi | c_{k,\sigma}^{\dagger} c_{k,\sigma} | \Psi \rangle = \sum_{\sigma} \sum_k |\phi_k(\mathbf{r})|^2 n(k, \sigma) \end{aligned} \quad (21)$$

where $n(k, \sigma)$ is the momentum distribution given by $|\Psi\rangle$. The system is found in a paramagnetic state and $\phi_k(\mathbf{r})$ and $n(k, \sigma) = n(p)$ lose their spin dependence, in which the crystal momentum $p = 2\pi k/(Na)$ is used.

In this simulation, the value of U is approximated to be $U = 5.2t_0$, which is roughly estimated from the result of the hydrogen molecule in section 6.3. In the obtained self-consistent solution, the transfer terms $t_{i,j}$ are given by the Fourier transformation of the Kohn–Sham eigenvalues $\varepsilon(n, p)$. Only the 1s band ($n = 1$) is used to construct $t_{i,j}$.

We show the single-particle dispersion of equation (11) and the momentum distribution of the obtained self-consistent solution in figures 4 and 5, respectively. The many-body model

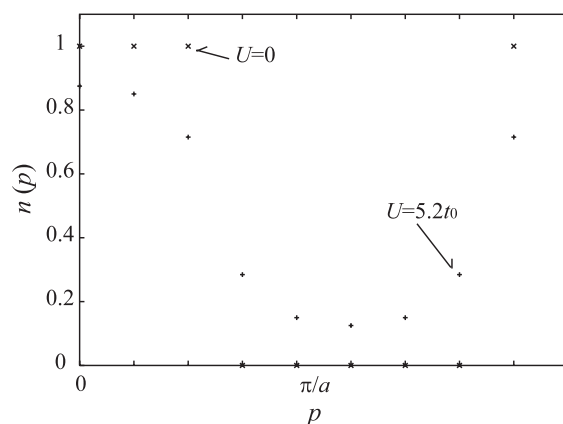


Figure 5. The fermion momentum distribution $n(p)$ of the hydrogen chain with $N = 10$ atoms, the value of $U/t_0 = 0$ (crosses) or $5.2t_0$ with t_0 (pluses) being the transfer energy between neighbouring atoms.

equation (12) becomes a kind of one-dimensional Hubbard model. We can see that $n(\mathbf{r})$ is almost unchanged by the introduction of U , while $\langle n_i^2 \rangle$ is suppressed by the U term. This is seen in the dispersion relation of $\varepsilon(n, p)$, which is almost the same for cases with a finite U and without U . On the other hand, when $U = 5.2t_0$, $n(p)$ is completely different from that of the free fermion. The feature of $n(p)$ as well as the filling factor of the system tells that the system is in a Mott insulating phase.

7. Discussion

We have a concept of the fixed-point Hamiltonian in our theory, which is defined in the whole phase space of the original problem. This fact is in contrast to the usual idea of the renormalization group. The smearing process in our formulation is the self-consistency loop, in which effective interaction processes are rebuilt via the redefinition of $\phi_i(\mathbf{r})$. In contrast to the usual renormalization group analysis, in which the zooming-out process inevitably smears out microscopic details of the order parameter, the central order parameter $n(\mathbf{r})$ keeps its microscopic structure in the present formulation of MR-DFT. A reason why we can reconstruct the effective many-body Hamiltonian comes from the flexibility of EKSS based on the density-functional theory.

In the present formulation of EKSS, people might think that the reference calculation is inevitable for obtaining the value of U . If we utilize LDA for the residual exchange–correlation energy functional, the approach may seem close to the established LDA + U . Now, we will propose an indicator to find out the clue of the change in fluctuation appearing in the system. We also discuss a method for detecting the Mott insulating transition in MR-DFT. Due to these characteristic factors, EKSS is qualitatively and quantitatively different from the known LDA + U approaches.

7.1. An indicator for fluctuation suppression

We analyse the EKSS result of the hydrogen molecule to test the refinement of the residual exchange–correlation energy functional. In figures 6–8, we show the total energy, the kinetic

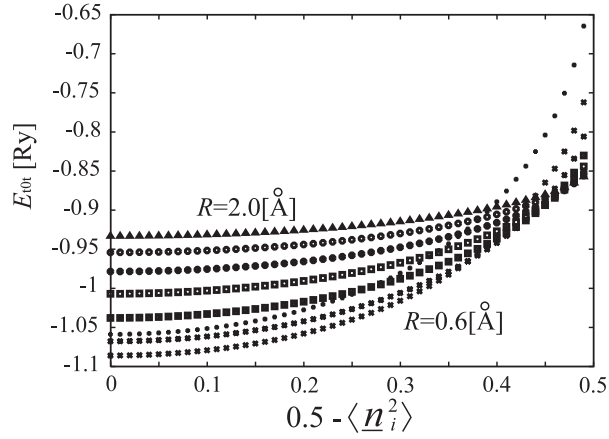


Figure 6. The total energy E_{tot} for the hydrogen molecule with the inter-atomic distance R (Å) obtained by EKSS. Depending on the fluctuation $\langle \underline{n}_i^2 \rangle$, E_{tot} increases monotonically.

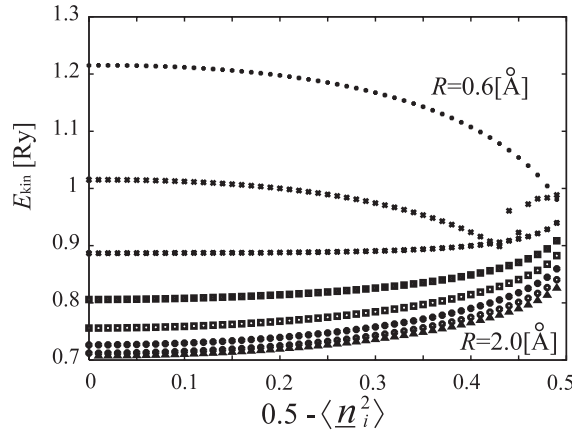


Figure 7. The kinetic energy E_{kin} for the hydrogen molecule with the inter-atomic distance R (Å) obtained by EKSS. The value is written as a function of $\langle \underline{n}_i^2 \rangle$, which is controlled by U .

energy and the Hartree term of the system. Here, the definition of the total energy is

$$E_{\text{tot}} = \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r})n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[n_{\Psi}] + \int d^3r v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r}) \quad (22)$$

in which the contribution of the U term is omitted. $|\Psi\rangle$ is obtained by solving equation (12), so that the state is a correlated fermion state. The kinetic energy and the Hartree term denote $E_{\text{kin}} = \langle \Psi | \hat{T} | \Psi \rangle$ and

$$E_{\text{Hartree}} = \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r})n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'.$$

Now, we have another expression for E_0 . Consider the minimizing $|\Psi\rangle$ of $\langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle$ which gives $n_{\text{GS}}(\mathbf{r})$ and is the solution of equation (12). Then, we have

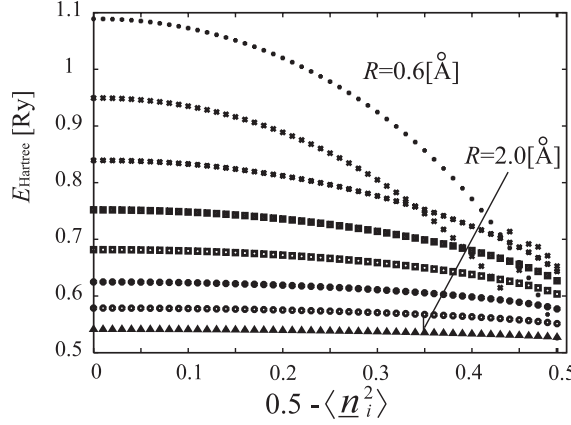


Figure 8. The Hartree term E_{Hartree} for the hydrogen molecule with the inter-atomic distance R (Å) obtained by EKSS. The value is written as a function of $\langle n_i^2 \rangle$, which is controlled by U .

$$\begin{aligned}
 E_0 &= \langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle + \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r})n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{rxc}}[n_{\Psi}] + \int d^3r v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r}) \\
 &= \langle \Psi | \hat{T} + \hat{V}_{\text{red}} | \Psi \rangle + \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r})n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[n_{\Psi}] \\
 &\quad + \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \min_{\Psi' \rightarrow n_{\Psi}} \langle \Psi' | \hat{T} + \hat{V}_{\text{red}} | \Psi' \rangle + \int d^3r v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r}) \\
 &= \langle \Psi | \hat{T} | \Psi \rangle + \frac{1}{2} \int \frac{n_{\Psi}(\mathbf{r})n_{\Psi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[n_{\Psi}] \\
 &\quad + \int d^3r v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r}) + \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \langle \Psi | \hat{T} | \Psi \rangle. \tag{23}
 \end{aligned}$$

Thus we may write E_0 as

$$E_0 = E_{\text{tot}} + \min_{\Phi' \rightarrow n_{\Psi}} \langle \Phi' | \hat{T} | \Phi' \rangle - \langle \Psi | \hat{T} | \Psi \rangle. \tag{24}$$

This is another exact expression for the true total energy of the electron system. Note that the U term does not appear in the formula, although it affects $|\Psi\rangle$. People might find that the above expression can be used to avoid the double-counting problem. Let us evaluate E_0 within the approximation utilized in section 6. Now, look at the kinetic energy E_{kin} for the hydrogen molecule (figure 7). When $R < 1.0$ (Å), the value decreases with decreasing $\langle n_i^2 \rangle$, which is controlled by increasing U . Namely, the horizontal axis is the direction of increasing U . This reduction in the kinetic energy is caused by expansion of the wavefunction in the real space. Actually, the Hartree term decreases and the electron–ion potential terms reduce their absolute values. In this range, as seen in the shift in the Hartree term, $n(\mathbf{r})$ expands with increasing U . Thus, we find that E_{kin} decreases in a weakly correlated regime ($R < 1.0$ (Å)) by increasing U .

Let us compare the result with the cases with $R \geq 1.0$ (Å). In this region, E_{kin} increases by increasing U . If we look at E_{Hartree} , we see that the value does not change so much and is almost constant, when $R \geq 2.0$ (Å). This fact means that $n(\mathbf{r})$ is nearly unchanged. What the U term does in this regime is that it only shifts the internal fluctuation. Thus, the value of E_{kin} increases. Now look at the expression of equation (24). The true value of E_0 is estimated by adding the kinetic energy of an uncorrelated fermion system $\langle \Phi' | \hat{T} | \Phi' \rangle$, which has $n(\mathbf{r}) = n_{\Psi}(\mathbf{r})$, and subtracting $\langle \Psi | \hat{T} | \Psi \rangle$ from E_{tot} . In this example, since $n(\mathbf{r})$ is nearly unchanged against a shift

in U for $R \gg 1.0$ (Å), $\min_{\Phi' \rightarrow n_\Psi} \langle \Phi' | \hat{T} | \Phi' \rangle$ for finite U may be approximated by E_{kin} for $U = 0$. The result suggests that E_0 is almost unchanged by increasing U , while the state $|\Psi\rangle$ becomes a correlated state.

On the other hand, if we detect a decrease in E_{kin} by increasing U , this suggests that minimizing the Φ' of $\langle \Phi' | \hat{T} | \Phi' \rangle$ should be close to Ψ . We have an inequality, $\min_{\Phi' \rightarrow n_\Psi} \langle \Phi' | \hat{T} | \Phi' \rangle \leq \langle \Psi | \hat{T} | \Psi \rangle$. Thus, E_0 evaluated for finite U is nearly the same as E_{tot} . However, E_{tot} increases through the introduction of U . When we have the weakly correlated regime $R < 1.0$ (Å), the U term is not necessary for an appropriate description of the system.

As a result, we conclude that we can utilize the U -dependence of $E_{\text{kin}} = \langle \Psi | \hat{T} | \Psi \rangle$ to detect the occurrence of Coulomb suppression in a correlated electron system. Once we have a properly designed method for estimating $\min_{\Phi' \rightarrow n_\Psi} \langle \Phi' | \hat{T} | \Phi' \rangle$, EKSS works as a first-principles calculation method for the correlated electron system in general, even without a reference calculation prepared for each individual problem. The target systems for EKSS include the Mott insulating state. Actually, we know a numerical algorithm [38] for obtaining the Legendre transform:

$$\tilde{T}[n] = \sup_v \left[\min_{\Psi} \langle \Psi | \left\{ \hat{T} + \int d\mathbf{r} v(\mathbf{r}) (\hat{n}(\mathbf{r}) - n(\mathbf{r})) \right\} | \Psi \rangle \middle| v \in L^{3/2} + L^\infty \right].$$

7.2. A test for the Mott insulator

To test the conduction property of the system within DFT, we may be able to utilize the following technique for the momentum boost. Let us consider a twisted boundary condition for our simulation:

$$\Psi(\mathbf{r} + L_x \mathbf{e}_x) = \exp(i\theta) \Psi(\mathbf{r}), \quad \Psi(\mathbf{r} + L_y \mathbf{e}_y) = \Psi(\mathbf{r}), \quad \Psi(\mathbf{r} + L_z \mathbf{e}_z) = \Psi(\mathbf{r}),$$

where \mathbf{e}_i and L_i ($i = x, y, z$) are the unit vectors and the length of a simulation cell, respectively. The density-functional theory holds for any fixed θ . Let us shift θ from zero to 2π adiabatically and obtain the lowest energy eigenvalue $E_0(\theta)$. Then we can connect $E_0(\theta)$ and draw a graph of $E_0(\theta)$ as a function of θ .

According to the Kohn argument [39], we can identify the Mott insulating state by looking at the period of $E_0(\theta)$, although we may see only the lowest edge of the whole $E_0(\theta)$. If formation of a gap in the flow of $E_0(\theta)$ is detected by changing the lattice constant, for example, the system undergoes a Mott transition. Actually, a complete test using the one-dimensional Hubbard model showed the period 2π for the half-filled band, which is useful for characterization of the ground state [40]. If the system is described in the Kohn–Sham scheme with LDA, however, the period would not change from the value of a metallic state. This failure would be recovered by the introduction of the U term in the Kohn–Sham scheme. If we ask the system to reproduce the local fluctuation, modification of the Kohn–Sham system naturally makes the system interacting. This is a way to model the stiffness of the Mott insulating state against the boost induced by the imaginative magnetic flux, which amounts to $\frac{\theta}{2\pi} \Phi_0$ with the unit flux Φ_0 . The nature of the ground state is modified via a change in the charge fluctuation.

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