Density-functional theory based on the electron distribution on the energy coordinate

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Abstract
We developed an electronic density functional theory utilizing a novel electron distribution \( n(e) \) as a basic variable to compute ground state energy of a system. \( n(e) \) is obtained by projecting the electron density \( n(r) \) defined on the space coordinate \( r \) onto the energy coordinate \( e \) specified with the external potential \( v_{\text{ext}}(r) \) of interest. It was demonstrated that the Kohn–Sham equation can also be formulated with the exchange-correlation functional \( E_{\text{xc}}[n(e)] \) that employs the density \( n(e) \) as an argument. It turned out an exchange functional proposed in our preliminary development suffices to describe properly the potential energies of several types of chemical bonds with comparable accuracies to the corresponding functional based on local density approximation. As a remarkable feature of the distribution \( n(e) \) it inherently involves the spatially non-local information of the exchange hole at the bond dissociation limit in contrast to conventional approximate functionals. By taking advantage of this property we also developed a prototype of the static correlation functional \( E_{\text{sc}} \) including no empirical parameters, which showed marked improvements in describing the dissociations of covalent bonds in \( \text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \) molecules.

Keywords: density functional theory, exchange energy, static correlation, energy electron density

(Some figures may appear in colour only in the online journal)

1. Introduction

Kohn–Sham density-functional theory (KS-DFT) [1] has been successfully utilized to study various properties of molecule, cluster, and solid. It offers a versatile framework for describing the electronic correlations in terms of electron density \( n \). It, however, suffers from critical problems, referred to as ‘static correlation error (SCE)’ [2–4] and ‘self-interaction error (SIE)’ [2, 5–8], that emerge in the dissociations of chemical bonds even in simplest molecules, e.g. \( \text{H}_2 \) or \( \text{H}_2^+ \). As reviewed in [2], the former gives rise to serious destabilization in the electronic energy of a system with fractional spins at atomic sites, and it also leads to qualitative failures in nearly degenerate electronic states. The latter manifests itself as erroneous stabilization for a system with fractional charges, and consequently, tends to delocalize electrons over the system artificially. Importantly, it is diagnosed that the problematic situations arising in the applications of KS-DFT have their origins in these errors [2]. Thus, eliminating the root of errors will extend the frontier of DFT. The source of the failures lies not in the formalism of DFT, but in the fundamental framework of the approximate exchange-correlation functional \( E_{\text{xc}}[n] \) which carries the complex effects of electron repulsions. The Kohn–Sham equation for the non-interacting electrons involves the local potential defined as \( v_{\text{xc}}[n](r) = \delta E_{\text{xc}}[n]/\delta n(r) \) at position \( r \). In principle, it is possible to incorporate the non-local information of the electron density in the construction of \( v_{\text{xc}}(r) \). In practice, however, due to the local density approximation (LDA) on which the basic framework of the approximate functionals is founded, only local or semi-local properties at \( r \) \((n(r), \nabla n(r), \text{ and } \nabla^2 n(r), \ldots)\) are utilized to yield the
potential $v_{ex}(r)$. Here, we briefly illustrate the SCE which arises in describing a bond dissociation with LDA. Suppose that the chemical bond of $H_2$ is stretched, the exchange hole associated with a reference point $r_{ref}$ on an atomic site is split over two separated atoms. Unfortunately, it is unlikely that the local or semi-local quantities at $r_{ref}$ can take into consideration the other exchange hole shifted on the distal site. Thus, the hole depth at $r_{ref}$ is to be estimated as half of the density $n(r_{ref})$, which causes erroneously high dissociation limit of $H_2$ within the LDA-based approach [3]. The underlying mechanism in SIE can also be described in terms of the inherent defect in LDA. A new framework of approximation based on a different starting point is, therefore, needed to overcome these problems.

In this paper we formulate a DFT based on the electron distribution on the energy coordinate defined through the external potential of interest. In the following we will provide the explicit definition of the energy electron density and discuss the advantage of the use of the distribution in the calculation of the static correlation (SC). The proof is presented for the existence of the one-to-one correspondence between the energy distribution and the potential energy defined on the energy coordinate. A formulation is then, given to adapt the energy distribution to the Kohn–Sham SCF procedure. A prototype of a functional which includes the SC is also developed on the basis of the linear-response regime. As benchmark tests of the present theory the potential energy curves for some diatomic molecules and organic molecules with $\pi$ electrons are calculated using our method and compared with those obtained by a conventional exchange functional. Finally, we make conclusions and discuss the prospect of the method.

2. Theory and formulation

2.1. Energy electron distribution

First, we define the energy electron distribution $n(\epsilon)$ which serves as a fundamental variable in the present DFT. $n(\epsilon)$ is being constructed by projecting the electron density $n_s(r)$ ($\sigma = \alpha$ or $\beta$) onto an energy coordinate $\epsilon$, thus,

$$n^\sigma_s[v_{\text{def}}](\epsilon) = \int dr \delta(\epsilon - v_{\text{def}}(r)) n_s(r),$$

where $v_{\text{def}}$ is the potential function introduced to define energy coordinate $\epsilon$ for electrons. Usually, the external potential $v_{\text{ext}}$ of interest is taken as the potential $v_{\text{def}}$, thus

$$v_{\text{def}}(r) = -\sum_A \frac{Z_A}{|r - R_A|},$$

where $Z_A$ and $R_A$ are the charge and the position vector of the nucleus $A$ in the molecule of interest. Hereafter, the dependence of the density $n^\sigma_s(\epsilon)$ on the potential $v_{\text{def}}$ is not explicitly indicated for the sake of brevity. $\epsilon$ is a well-defined variable for a molecular system. In an H atom, for instance, the electron has the normalized density $n_{1\alpha}(r) = (1/8\pi) \exp(-r)$ and the corresponding energy density is $n^\alpha_{1\alpha}(\epsilon) = 0.5 e^{-4\epsilon} \exp(1/\epsilon)$ where $\epsilon$ is defined as $\epsilon = -1/r$ ($r$ is the distance of the electron from the nucleus). $n^\alpha_{1\alpha}(\epsilon)$ is apparently integrable and, hence, normalizable. Equation (1) is parallel in form to the definition of the solvent distribution function utilized in a novel theory of solutions in energy representation developed by Matubayasi et al [9]. Their approach has been successfully applied to the calculation of solvation free energies of various solutes in solutions.

As will be demonstrated in the next subsection a rigorous framework of the electronic DFT can be found in terms of the total energy distribution $n^\alpha(\epsilon)$ without a spin index. In practice, however, a spin-dependent density $n^\sigma_s(\epsilon)$ will be used as an input to some explicit functional $E_{xc}^\sigma[n^\sigma_s]$ in the Kohn–Sham procedure. The projection of the spatial distribution $n$ onto the energy coordinate $\epsilon$ of one dimension (equation (1)) smears the details of the density used to build the exchange hole function. However, as investigated by Parr and Berk in [10], the electron densities in molecules as well as in atoms have contours nearly parallel to those of bare-nuclear Coulomb potentials. From the statistical point of view it is quite natural to consider that the electron population is reasonably constant on the equi-energy surface of the external potential. The advantage of introducing the distribution of equation (1), which is vital for the present development, is that the energy distribution can take into consideration the spatially non-local population of electrons. We illustrate in figure 1 the electron densities $n^\beta_s(r)$ and $n^\beta_s(r)$ yielded, respectively, with spin-restricted and unrestricted KS-DFT for a dissociated $H_2$ molecule. These distributions completely differ from each other in their spatial behaviors. The projections of these onto the energy coordinate $\epsilon$, however, provides exactly the same distribution $n^\beta_s(\epsilon)$ when $2n^\beta_s(\epsilon) = n^\beta_s(\epsilon)$ is satisfied on site $H_A$. Thus, the symmetry-broken solution gives the same energy distribution as the symmetry-adapted density. Therefore, $E_{xc}^\sigma[n^\sigma_s]$ is in principle same as $E_{xc}^\sigma[n^\sigma_s]$, for any choice of approximate functional. A ‘strong correlation test’ advocated by Becke in [11] requires that a perfect density-functional methodology should give the same energy and the total density both in the restricted and unrestricted dissociations of $H_2$ molecule for instance. Our approach enables ones to deal with such a stringent test by virtue of the property of the energy density.
2.2. One-to-one correspondence

Hohenberg-Kohn (HK) theorem proved in 1964 [12] states that one-to-one correspondence is established between the set of external potentials and that of densities of $N$-electrons systems. From a historical viewpoint HK theorem played a critical role in the development of DFT since it provides a justification for the density functional approach. It should be reminded, however, that the HK theorem is valid only for the set of $\nu$-representable electron densities. Hence, the energy functional $E_{\text{HK}}[\nu]$ is defined only for $\nu$-rep. densities. We discuss below the one-to-one mapping between the energy electron densities and the corresponding potentials, that is partially parallel to the original HK theorem.

We partition the set $\{\nu(r)\}$ of the external potentials into the subsets $\{\nu(r)\}_l$ ($l = 1, 2, 3, \ldots$) where the isosurfaces of the potential energies of the elements are mutually parallel within each subset $\{\nu(r)\}_l$. More precisely, the definition of this subset can be expressed as follows. Provided some two potentials $\nu$ and $\nu'$ belong to the same subset $\{\nu(r)\}_l$, the relation $\nu(r_1) = \nu'(r_2)$ holds for any points $r_1$ and $r_2$ which satisfy the equality $\nu(r_1) = \nu(r_2)$. It should be noted that it is always possible to find any external potential within a certain subset. Thus, the whole set $\{\nu(r)\}$ can be expressed by the sum (union) of the subsets $\{\nu(r)\}_l$, thus,

$$\{\nu(r)\} = \{\nu(r)\}_1 \cup \{\nu(r)\}_2 \cdots \cup \{\nu(r)\}_l \cdots .$$  \hspace{1cm} (3)

Of course, the intersection of any pair of the subset is the empty set,

$$\{\nu(r)\}_l \cap \{\nu(r)\}_j = \emptyset. \hspace{1cm} (4)$$

Any element in each subset $\{\nu(r)\}_l$ can be chosen as a defining potential to represent the potentials in the subset and the corresponding energy electron densities as well. That is, any element in each subset indexed by $I$ can be represented by a single defining potential $\nu_{\text{def}}(r)$ in $\{\nu(r)\}_l$. Since the one-to-one correspondence is established between the set of external potentials and that of $\nu$-rep. electron densities [12], the set of $\nu$-rep. densities $\nu(r)$ can also be partitioned into subsets in a way completely parallel to equation (3), thus,

$$\{\nu(r)\} = \{\nu(r)\}_1 \cup \{\nu(r)\}_2 \cdots \cup \{\nu(r)\}_l \cdots .$$  \hspace{1cm} (5)

The one-to-one mapping is also established between the subset $\{\nu(r)\}_l$ and the subset $\{\nu(r)\}_l$ with the same index $I$. We construct the set of energy electron density $\{\nu'(e)\}_l$ by projecting the set of the electron density $\{\nu(r)\}_l$ with a defining potential $\nu_{\text{def}}(r)$ in it. Hereafter, the energy electron density $\{\nu'(e)\}_l$ is thus introduced to refer to as a set of $\nu$-rep. electron energy density. The $\nu$-rep. condition for the energy electron density is also unknown as in the case of density $\nu(r)$ [13]. Anyway, it is straightforward to prove the one-to-one mapping between the subset of the potentials and that of the $\nu$-rep. energy electron densities with the same index $l$ as shown below.

As mentioned above it is always premised that some defining potential $\nu_{\text{def}}(r)$ is given from the outset in the DFT based on the energy electron density. Then, a certain subset $\{\nu(r)\}_l$ is uniquely determined depending on the choice of $\nu_{\text{def}}(r)$. The one-to-one mapping between $\nu$-rep. $\{\nu'(e)\}_l$ and $\{\nu(r)\}_l$ can, then, be shown below in the same way as the proof of HK theorem [12].

We first assume that there exists within a subset $\{\nu(r)\}_l$ different potentials $\nu$ and $\nu'$ which yield the same energy electron density $\nu'(e)$ associated with a defining potential $\nu_{\text{def}}(r)$. The Hamiltonian $H$ and $H'$ of the interacting $N$-electron systems are defined as,

$$H = T + V_{ee} + \nu.$$  \hspace{1cm} (6)

$$H' = T + V_{ee} + \nu'.$$  \hspace{1cm} (7)

The corresponding ground state wave functions are denoted as $\Psi_0$ and $\Psi'_0$ for the Hamiltonian $H$ and $H'$, respectively. For the expectation value $E_0$ for $\Psi_0$ we have an inequality,

$$E_0 < \langle \Psi'_0 | H | \Psi'_0 \rangle = \langle \Psi'_0 | H' | \Psi'_0 \rangle + \langle \Psi'_0 | H - H' | \Psi'_0 \rangle = E'_0 + \int d\nu \nu'(e)(\nu(e) - \nu'(e)).$$  \hspace{1cm} (8)

Similarly, for the energy $E'_0$, we have

$$E'_0 < \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | H' | \Psi_0 \rangle + \langle \Psi_0 | H' - H | \Psi_0 \rangle = E_0 + \int d\nu \nu'(e)(\nu'(e) - \nu(e)).$$  \hspace{1cm} (9)

The sum of these inequalities leads to a contradiction and hence the assumption we made must be dismissed. Thus, the one-to-one correspondence between $\nu$-rep. $\{\nu'(e)\}_l$ and $\{\nu(r)\}_l$ is proved.

We close this subsection by summarizing the one-to-one mapping in energy electron density. For a given potential $\nu_{\text{def}}$ introduced to define the energy coordinate, the subset of the external potentials $\{\nu(r)\}_l$ and also the corresponding subset of $\nu$-rep. electron density $\{\nu(r)\}_l$ are uniquely specified. For each subset we construct the set of energy electron density $\{\nu'(e)\}_l$ through the projection of equation (1). Then, the mapping from the energy electron density $\{\nu'(e)\}_l$ to $\{\nu(r)\}_l$ or $\{\nu(r)\}_l$ is unique. Therefore, the HK functional $F_{\text{HK}}[\nu]$ exists for $\nu$-rep. energy electron density though it is not universal and dependent on the defining potential $\nu_{\text{def}}$. The domain of the variable $\nu'$ for the functional can be extended from $\nu$-rep. to $N$-rep. energy electron density with the similar manner to the Levy’s constraint search [14].

2.3. Levy’s constraint search

In this subsection we formulate Levy’s constraint search [14] in the space of the energy electron density $\nu'(e)$ which serves as a fundamental variable in the present framework of DFT. It should be kept in mind that an energy distribution is constructed using a potential $\nu_{\text{def}}$ and, hence, the information contents of an energy distribution differs from others associated with different $\nu_{\text{def}}$. For a given external potential $\tilde{\nu}_{\text{ext}}$ the Hamiltonian $\hat{H}$ for the $N$-electron system is given by

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \tilde{\nu}_{\text{ext}},$$  \hspace{1cm} (10)
where \( \hat{T} \) and \( \hat{V}_e \) are, respectively, the kinetic energy and electron repulsion operators. The ground state energy \( E_0 \) of a system can be derived in the way parallel to the original Levy’s constraint search [14] for the N-electron system, thus,

\[
E_0 = \min_{n' \rightarrow N} \left\{ \min_{\psi \rightarrow n'} \langle \psi | \hat{H} | \psi \rangle \right\}
\]
\[
= \min_{n' \rightarrow N} \left\{ \min_{\psi \rightarrow n'} \langle \psi | \hat{T} + \hat{V}_e | \psi \rangle + \int d\mathbf{r} \ n'(\mathbf{r}) v_{\text{ext}}'(\mathbf{r}) \right\}
\]
\[
= \min_{n' \rightarrow N} \left\{ F_v[n'] + \int d\mathbf{r} \ n'(\mathbf{r}) v_{\text{ext}}'(\mathbf{r}) \right\}.
\]  (11)

The first line in equation (11) expresses a minimization of the energy in the space of N-rep. energy electron density \( n' \) combined with the variational search in the N-rep. wave function that yields \( n' \). In the second line the external potential \( v' \) is also represented on the energy coordinate defined by the potential \( v_{\text{ext}} \) in equation (1). Then, the second equality is derived from the transformation,

\[
\int d\mathbf{r} \ v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) = \int d\mathbf{r} \int d\mathbf{r} \ \delta(\epsilon - v_{\text{def}}(\mathbf{r})) v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})
\]
\[
= \int d\mathbf{r} \ v_{\text{ext}}'(\mathbf{r}) \int d\mathbf{r} \ \delta(\epsilon - v_{\text{def}}(\mathbf{r})) n(\mathbf{r})
\]
\[
= \int d\mathbf{r} \ v_{\text{ext}}'(\mathbf{r}) n'(\mathbf{r}).
\]  (12)

In equation (12) it is assumed that \( v_{\text{ext}}(\mathbf{r}) \) and \( v_{\text{def}}(\mathbf{r}) \) belong to the same subset in equation (3). Specifically, if \( v_{\text{ext}}(\mathbf{r}) \) itself is taken as \( v_{\text{def}}(\mathbf{r}) \), we have \( v_{\text{ext}}'(\mathbf{r}) = \epsilon \). In the third line in equation (11) we introduced a functional \( F_v[n'] \) which represents the sum of kinetic and electronic energies of \( \Psi_{\text{min}} \) that yields the energy density \( n'(\mathbf{r}) \). It should be noted, however, that \( F_v[n'] \) is not universal since the energy distribution \( n' \) is specific to the choice of \( v_{\text{def}} \). Later, we will demonstrate that some \( v \)-dependent exchange-correlation functional \( E_{xc}[n'] \) can actually be constructed. The functionals for kinetic energy and electron repulsion can be defined using the wave function \( \Psi_{\text{min}}[n'] \) which minimizes the expectation value of \( \hat{T} + \hat{V}_e \) as

\[
T'[n'] = \langle \Psi_{\text{min}} | \hat{T} | \Psi_{\text{min}} \rangle
\]
\[
V_{xc}^v[n'] = \langle \Psi_{\text{min}} | \hat{V}_e | \Psi_{\text{min}} \rangle.
\]  (13)

The superscripts \( v \) in equations (13) and (14) are attached to clarify that these functionals are dependent on the defining potential and not universal.

2.4. Kohn–Sham procedure

Next, we formulate the variational search of equation (11) through the Kohn–Sham procedure [1]. Introducing a single determinant wave function \( \Psi_{\text{SD}} \) of a non-interacting system we define a functional \( G[n'] \), thus,

\[
G[n'] = \min_{n' \rightarrow n} \left\{ \min_{\Psi_{\text{SD}} \rightarrow n} \langle \Psi_{\text{SD}} | \hat{T} | \Psi_{\text{SD}} \rangle + J[n] \right\}.
\]  (15)

In equation (15), \( J[n] \) is the Hartree energy of the electron density \( n(\mathbf{r}) \) which yields \( n' \). Then, the kinetic energy \( T_v[n'] \) of the non-interacting system can be represented as

\[
T_v[n'] = \langle \Psi_{\text{SD}}^{\text{min}} | \hat{T} | \Psi_{\text{SD}}^{\text{min}} \rangle,
\]  (16)

where \( \Psi_{\text{SD}}^{\text{min}} \) is the wave function which minimizes \( T + J \) in equation (15) under the constraint that its electron density gives \( n' \). We define the Hartree energy \( J'[n'] \) as a functional of \( n' \) as

\[
J'[n'] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \ n_{\text{SD}}(\mathbf{r}_1) n_{\text{SD}}(\mathbf{r}_2) \left| \mathbf{r}_1 - \mathbf{r}_2 \right|,
\]  (17)

where \( n_{\text{SD}} \) is the density constructed from \( \Psi_{\text{SD}}^{\text{min}} \). With the definitions equations (13), (14), (16), and (17), we define the exchange-correlation functional \( E_{xc}[n'] \) as

\[
E_{xc}[n'] = T'[n'] - T_v[n'] + V_{xc}^v[n'] - J'[n'].
\]  (18)

The Kohn–Sham energy minimization with the functional \( E_{xc}[n'] \) can be expressed as

\[
E_0 = \min_{n' \rightarrow N} \left\{ G[n'] + E_{xc}[n'] \right\} = \min_{\Psi_{\text{SD}}} \left\{ \langle \Psi_{\text{SD}} | \hat{T} | \Psi_{\text{SD}} \rangle + J[n] \right\}
\]
\[
= \langle \Psi_{\text{SD}}^{\text{min}} | \hat{T} | \Psi_{\text{SD}}^{\text{min}} \rangle + \int d\mathbf{r} \ n'(\mathbf{r}) v(\mathbf{r}).
\]  (19)

In the second equality in equation (19) the minimization with respect to \( n' \) is replaced by a search in the space of non-interacting wave function \( \Psi_{\text{SD}} \). Since arbitrary N-rep. electron density can be constructed from some \( N \) orthonormal orbitals [15], any N-rep. energy electron density defined in equation (1) is also given in terms of \( \Psi_{\text{SD}} \). To derive the Kohn–Sham equation we formulate functional derivative of \( E_{xc}[n'] \) with respect to one-electron wave function \( \phi(\mathbf{r}) \), thus,

\[
\frac{\delta E_{xc}[n']}{\delta \phi_v(\mathbf{r})} = \int d\mathbf{r} \ \delta E_{xc}^v \left( \frac{\delta n'(\mathbf{r}')}{\delta n'(\mathbf{r})} \right) \frac{\delta n(\mathbf{r})}{\delta \phi_v(\mathbf{r})}
\]
\[
= \int d\mathbf{r} \ v_{xc}[n'(\mathbf{r})] \left( \delta(\epsilon - v(\mathbf{r})) \right) \phi_v(\mathbf{r})
\]
\[
= v_{xc}[n'(\mathbf{r})] \left( \delta(\epsilon - v(\mathbf{r})) \right) \phi_v(\mathbf{r}).
\]  (20)

where \( v_{xc}[n'(\mathbf{r})] \equiv \delta E_{xc}^v \left( \frac{\delta n'(\mathbf{r})}{\delta n'(\mathbf{r})} \right) \) is the exchange-correlation potential for an electron on the energy coordinate \( \epsilon \). The definitions equation (1) and \( n(\mathbf{r}) = \sum \left| \phi_v(\mathbf{r}) \right|^2 \) are used to derive the second equality in equation (20). Now we have the Kohn–Sham equation parallel to the conventional theory, thus,

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \right] \phi_v(\mathbf{r}) = \eta \phi_v(\mathbf{r}),
\]  (21)

where the first and second terms in the square bracket are, respectively, the kinetic and Hartree potential operators. We note that the exchange potential \( v_{\text{xc}}(\mathbf{r}) \) in equation (21) is constant on the isovalue surface of the external potential \( v_{\text{ext}}(\mathbf{r}) \) taken as the defining potential.
3. Functional development and its applications

In this section some exchange functionals \( E_x[n]\) are developed as an exploratory work and applied to the calculation of potential energy curves of exchangable bonds in simple molecules (\( \text{H}_2, \text{HF}, \text{LiH}, \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \)). Further, a prototype of the functional that realizes SC is also proposed and is applied to the dissociations of chemical bonds in molecules \( \text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \). The numerical details for these implementations and applications are provided at first.

3.1. Numerical details

We first summarize computational details of the calculations done in the following subsections for later references. Basically, all the calculations were performed using our KS-DFT program ‘Vmol’ [16–18] based on the real-space grid (RSG) approach [19, 20]. The one-electron wave functions of equation (21) were accommodated in a cubic real-space cell, where each axis of the cell was discretized by equally spaced 80 grid points. The grid spacing \( h \) was set at 0.222 a.u. In the RSG method the external potential \( u_{\text{ext}} \) is represented by the pseudopotentials in the Kleinman-Bylander form [21] reinforced by the double grid technique [22]. The width of the dense grid was set at \( h/3 \). The kinetic energy operator was described by the 4th-order finite difference approach [20].

The potential \( u_{\text{def}}(r) \) in equation (1) that defines the energy coordinate \( \epsilon \) was given by

\[
u_{\text{def}}(r) = \sum_A \frac{Z_A}{|r - \mathbf{R}_A|},
\]

where \( Z_A \) and \( \mathbf{R}_A \) are the charge of the ion core \( A \) and its position vector, respectively. Then, the energy electron distribution \( n^x(\epsilon) \) was constructed by a discrete sum of electron density \( n(r) \) on the grids in the cell through equation (1). To increase the number of sampling points we introduce dense grids at each coarse grid in the real-space cell. The width of the dense grid was set to \( h/N_0 \). The values of the electron densities on the dense grids were evaluated by 4th-order polynomial interpolation for the densities on coarse grids.

Two types of bin were prepared on the energy coordinate to accumulate the electron densities. In the energy region of \( \epsilon_{\text{min}} \leq \epsilon \leq \epsilon_{\text{core}} \) equally spaced \( N_1 \) grids were introduced on the energy coordinate to form uniform bins, while \( N_2 \) grids were placed in the region of \( \epsilon_{\text{core}} \leq \epsilon \leq \epsilon_{\text{max}} \) with the same interval on the log-scale energy coordinate. In the following we provide the energy specifications with the units of a.u. For \( \text{H}_2 \) and \( \text{LiH} \) molecules we used the set of \( N_0 = 5, \epsilon_{\text{min}} = 0.1, \epsilon_{\text{core}} = 0.8, \epsilon_{\text{max}} = 3 \times 10^2, N_1 = 100, \) and \( N_2 = 300 \), while for \( \text{HF}, \text{C}_2\text{H}_4, \) and \( \text{C}_2\text{H}_2 \) molecules we employed the set of \( N_0 = 10, \epsilon_{\text{min}} = 0.3, \epsilon_{\text{core}} = 5.0, \epsilon_{\text{max}} = 3 \times 10^3, N_1 = 300 \) and \( N_2 = 500 \). Fortunately, the numerical results are not sensitive to the choice of the setup for construction of the energy distributions. We note that substantial computational load is required in yielding the distributions since the 4th-order polynomial interpolation is performed at each dense grid as mentioned above. However, the cost increases only linearly with the system size and can be fairly decreased when some atomic basis set is utilized because the electron densities on the dense grids can be evaluated analytically.

3.2. LDA on energy coordinate

In this subsection we present an exchange functional \( E_x[n^x] \). To this end we introduce the average electron density \( \bar{n}^x(\epsilon) \) on the energy coordinate \( \epsilon \) by dividing \( n^x(\epsilon) \) with the spatial volume \( \Omega(\epsilon) \) of the region with the energy coordinate \( \epsilon \). Explicitly, \( \bar{n}^x(\epsilon) \) is given by

\[
\bar{n}^x(\epsilon) = n^x(\epsilon)/\Omega(\epsilon)
\]

\[
\Omega(\epsilon) = \int dr \delta(\epsilon - u_{\text{def}}(r)).
\]

An ad hoc construction of the functional is to employ average density \( \bar{n}^x(\epsilon) \) as a variable for some current density functional \( E_x[n] \). The simplest exchange functional can be constructed in terms of the exchange energy of the homogeneous electron gas (HEG) [23], thus,

\[
E_x^{\text{HEG}}[n^x] = C_x \int d\epsilon \ n^x(\epsilon)\bar{n}^x(\epsilon)^{1/3}
\]

with theoretical coefficient \( C_x = \frac{3}{4\pi^2} \) for each spin. We note that the functional is also dependent on the potential \( u_{\text{def}}(r) \) of interest through equations (22) and (23). This approach can be referred to as the LDA on the energy coordinate. Provided the average of the density gradient \( \nabla n(r)|_{\epsilon=\epsilon_{\text{rep}}} \) over the energy coordinate \( \epsilon \) is given, it is also possible to apply a generalized gradient approximations (GGA) as a correction to \( E_x^{\text{HEG}}[n^x] \). Below, we provide an exchange functional based on the Becke–Roussel (BRx) approach [24, 25]. The BRx functional utilizes electron density of the hydrogenic atom as a model exchange hole for the real system. In constructing the BR exchange hole function the quantity called exchange hole curvature \( Q_\sigma \) have to be calculated besides the gradient of the electron density. Explicitly, \( Q_\sigma \) is defined as

\[
Q_\sigma = \frac{1}{6}(\nabla^2 n_\sigma - 2D_\sigma),
\]

where \( D_\sigma \) is expressed by

\[
D_\sigma = \tau_\sigma - \frac{1}{4} \frac{(\nabla n_\sigma)^2}{n_\sigma}
\]

and \( \tau_\sigma \) is the kinetic energy density. In applying the BR method to the functional using \( n^x \) we take the average of \( Q_\sigma \) over the surface with the same energy coordinate. We employ this functional combined with the LYP correlation functional [26] to calculate the potential energy curve of an \( \text{H}_2 \) molecule.

The result is shown in figure 2, where it is also compared with the results of BRx-LYP and BLYP functionals [26, 27] employing the ordinary electron density \( n(r) \) as an argument. All of these calculations were performed using RSG approach [17–20]. The electron density and wave functions for the BRx-LYP calculations were yielded by BLYP functional using conventional electron density. It is realized in the figure that the potential energy of the present work which employs \( n^x(\epsilon) \) gives the result reasonably close to the original BRx-LYP functional. The difference is smaller than that of GGA functional (BLYP) from the original BRx-LYP. Thus, it is clearly demonstrated that the projection of the electron
density $n(\tau)$ to the energy coordinate does not degrade the potential energy of $H_2$ seriously.

We also applied our method to other molecules. In this early stage of the development of a functional utilizing a new variable, a detailed assessment would not be required. Hence, we focus our attention only on the comparisons in LDA-based functionals hereafter. In the following calculations done in this subsection, the energy electron density $\tilde{n}(\epsilon)$ is constructed from the density $n(\tau)$ yielded by an SCF calculation with the LDA functional. Our next interest is placed on a hetero-diatomic molecule $H-F$ with a significant electronic polarization. As shown in [10] the electron density of $H-F$ has the contour nearly parallel to that of the bare-nuclear potential. As mentioned the exchange functional $E_{\text{x}}^{\text{HEG}}[n^r]$ gives completely the same result with the conventional LDA functional when the contour of the electron density is exactly parallel to that of the nuclear potential. The potential energies for $H-F$ around its equilibrium bond distance are presented in figure 3. It is shown that the potential energy $E_{\text{x}}^{\text{HEG}}[n^r]$ given by equation (24) is very close to that by the conventional functional $E_{\text{x}}^{\text{HEG}}[n]$ based on LDA though the total energy is slightly shifted upward. When the pseudopotential is being used along with the present approach, a care must be taken for the evaluation of a total energy. Since core electrons are not explicitly involved in a KS-DFT calculation using pseudo-potentials, the electron density $n(\tau)$ on atomic cores for heavy atoms are depleted. This directly causes the underestimation of the exchange energy density on hydrogen atoms in the same system. Since the atomic core of fluoride has the same energy coordinate $\epsilon$ with that of hydrogen, deficit of core electrons in the F atom leads to the lowering of $\tilde{n}(\epsilon)$ and also the decrease in the exchange energy density on the hydrogen core as a consequence. Thus, the calculation of the atomization energies for molecules will not be performed correctly with the present approach combined with the pseudopotential method. A possible remedy for this problem is to compensate some rigid core densities at the atomic centers. Of course, when all electrons are considered using e.g. linear-combination-of-atomic-orbitals approach, the present method will give the total energies that can be compared with those obtained by the conventional approach. Anyway, the electron density near the hydrogen core will not be changed largely with respect to the variation of the bond length. Hence, the use of pseudopotential will cause only a constant shift of the potential energy curve.

Thus, we found that the exchange functional using $n^p(\epsilon)$ as an argument also works soundly for the diatomic molecule where the electrons are highly localized on an atom. Actually, it is shown in figures 3 and 4 in [10] the contour of the bare potential (BP) of HF resembles that of the electron density. However, for the lithium hydride Li–H, the contour of BP is rather different from that of the electron density. Thus, calculation of the potential of Li–H can be a severe test of our approach. The potential energy curves for Li–H are displayed in figure 4, where we see the equilibrium bond distance given by $E_{\text{x}}^{\text{HEG}}[n^r]$ is elongated by $\sim 0.1$ a.u. as compared to the curve given by the ordinary LDA functional. Such a difference can be attributed to the distinct discrepancy in the contour of BP of Li–H and that of the electron density. Obviously it is desirable to develop a correction to alleviate the deficiency.

Our next issue is to assess the applicability of the method to the description of the chemical bonds of the systems with double and triple bonds. To this end we computed the potential energies of ethylene $C_2H_4$ and acetylene $C_2H_2$ using the functionals $E_{\text{x}}^{\text{HEG}}[n^r]$ and $E_{\text{x}}^{\text{HEG}}[n]$. In constructing these potential energy curves only the distance of C–C bonds was varied with other internal coordinates frozen. As shown in figure 5 the functional based on the energy electron density
is a spin-adapted symmetric density, though molecule computed with

ead

Figure 6. Potential energy curves of LiH molecule computed with the Kohn–Sham DFT utilizing the exchange energy functionals $E_{\text{HEG}}^{\text{xc}}[\rho]$ (This work) and $E_{\text{LDA}}^{\text{xc}}[\rho]$ (LDA). The specifications for the axes are synonymous with those for figure 3.

Figure 5. Potential energy curves of $C_2H_4$ molecule computed with the Kohn–Sham DFT utilizing the exchange energy functionals $E_{\text{HEG}}^{\text{xc}}[\rho]$ (This work) and $E_{\text{LDA}}^{\text{xc}}[\rho]$ (LDA). The specifications for the axes are synonymous with those for figure 3.

Figure 4. Potential energy curves of $C_2H_2$ molecule computed with the Kohn–Sham DFT utilizing the exchange energy functionals $E_{\text{HEG}}^{\text{xc}}[\rho]$ (This work) and $E_{\text{LDA}}^{\text{xc}}[\rho]$ (LDA). The specifications for the axes are synonymous with those for figure 3.

$n(\epsilon)$ faithfully reproduces the behavior of the potential energy curve given by the original LDA functional. Thus, it was demonstrated that the present method can also describe the double bond of a $\pi$ electron system soundly. We also show potential energy curves for $C_2H_2$ in figure 6. Again, we found the potential energies by LDA around the equilibrium C–C distance can be successfully realized by the method using the energy distribution.

3.3. Static correlation

We, next, consider the method to incorporate the SC into the exchange-correlation functional, which constitutes the major issue in this work. Unfortunately, when we use the variable $\tilde{\rho}(\epsilon)$ defined in equations (22) and (23) the dissociation curves of the UKS as well as RKS converge to the dissociation limit of the RKS energy produced with the conventional exchange functional. Since the volume $\Omega(\epsilon)$ at some coordinate $\epsilon$ of dissociated H$_2$ amounts to twice of the single atom, average electron density at $\epsilon$ becomes half of the corresponding density of the isolated atom. To resolve this problem we introduce an intermediate state of which total electron density $n_0(r)$ is expressed in terms of the density $n_0$ of the isolated fragment $p$. Explicitly, $n_0(r)$ is given by

$$n_0(r) = \sum_p n_0^p(r).$$

(27)

The choice of this reference state is motivated by Harris functional [29], the frozen density functional approach [30] or the partition DFT [31] where the total electron density of an interacting system is built from the overlap of densities of partitioned molecular regions. In the present work the density of equation (27) serves to construct the exchange-correlation energy $E_{\text{xc}}[n_0]$ of the intermediate state. Then, the total exchange-correlation energy is expressed by sum of $E_{\text{xc}}[n_0]$ and the relaxation term $\Delta E^\text{relax}_{\text{xc}}$, thus,

$$E_{\text{xc}}[n, n_0] = E_{\text{xc}}[n_0] + \Delta E^\text{relax}_{\text{xc}}[n^*, n_0^*].$$

(28)

where the subscript ‘xc’ in $E_{\text{xc}}$ denotes the exchange and SCs, $n(r)$ is a spin-adapted symmetric density, though $n_0(r)$ is not. The energy distributions $n^*(\epsilon)$ and $n_0^*(\epsilon)$ are, respectively, constructed from $n(r)$ and $n_0(r)$ through equation (1). The term $\Delta E^\text{relax}_{\text{xc}}$ in equation (28) describes the difference in the exchange energy between the states which correspond to the densities $n$ and $n_0$. In our approach $\Delta E^\text{relax}_{\text{xc}}$ is evaluated by a functional of the energy electron density, thus,

$$\Delta E^\text{relax}_{\text{xc}} = E_{\text{xc}}[n^*] - E_{\text{xc}}[n_0^*],$$

(29)

where $n^*$ is derived from the ‘spin-adapted’ wave function. In the construction of equation (28) we eventually attain the symmetric electron density by bypassing the spin-unrestricted intermediate state of which density is given by $n_0$. Within this scheme the SC $E_{\text{sc}}$ is being expressed by the difference in the exchange energy for the reference densities $n_0$ and $n_0^*$, thus,

$$E_{\text{sc}} = E_{\text{xc}}[n_0] - E_{\text{xc}}[n_0^*].$$

(30)

We consider here the two extremes in the dissociations of diatomic systems. At the dissociation limit the exact spin-restricted energy density $n^*$ coincides with the fragment density $n_0^*$ as illustrated in figure 1. Therefore, the relaxation term $\Delta E^\text{relax}_{\text{xc}}$ in equation (28) completely vanishes at the dissociation and only the energy $E_{\text{xc}}[n_0]$ remains, which guarantees the correct asymptotic energy. At the other
Figure 7. H₂ dissociation curves calculated by spin restricted KS-DFT with the Slater’s exchange functional E₁[ρ ] (LDA) and with the corresponding functional using energy electron density E₁[ρ ] (LDA-E). The results which involve the static correlations (SC) employing equations (28) and (33) are also presented for comparisions. The electron density yielded by the conventional LDA functional was adopted to all the calculations except for LDA-E with SC (equation (33)).

The positions of the two atoms are identical in a diatomic molecule, the external potential of the molecule gets isotropic and as a consequence Eₙₐ(n₀) becomes equal to E₁[ρ ] resulting Eₙₐ = 0. Thus, it is readily understood equation (28) is designed to work correctly at the two extremes by virtue of the property of the energy distribution n'. The density n₀ is actually necessitated in the evaluation of Eₙₐ by equation (30). We note, however, it is also true that its projected density nₐ plays a decisive role in formulating Eₙₐ for the spin-adapted electron density.

We apply equation (28) to calculate the dissociation curves for H₂, the double bond in ethylene C₂H₄, and C–H bond in methane CH₄. In order to envelop the wave functions of the stretched bonds in these molecules we prepared larger sizes of the real-space cells. Explicitly, the width h of the grid was increased to 0.287 a.u. and the number of the grids N_grid along each axis of the cell was also increased to 128. In the computations for ethylene and methane, however, N_grid was set to 100 due to the limitation of the memory size. The number of the dense grids for the construction of the energy densities was decreased to 5 to expedite the calculations. The result for H₂ dissociation is presented in figure 7, where we employ the Slater’s LDA exchange functional E₁[ρ ] that uses energy electron density n₀ or nₐ as an argument. The atomization energy is evaluated as 109.4 kcal mol⁻¹ which shows rather good agreement with the experimental value of 109 kcal mol⁻¹. We emphasize that no adjustable parameter was introduced to the functional. It should be kept in mind, however, that the calculation did not involve the dynamic correlation energy Eₙₐ that exists in the chemical bond in H₂. In this subsection we will not employ a conventional correlation functional to avoid the double counting of the SC. Inclusion of dynamical correlation Eₙₐ will lower the potential energy of the bonding region in relative to the dissociated state, which gives rise to the increase in the dissociation energy. The major source of the error would be the overestimation of Eₙₐ in the region around the equilibrium bond distance. This also causes the unfavorable elongation of the equilibrium bond distance as shown in figure 7.

A drawback in the method described above is that the density n itself is determined independently of Eₙₐ because Eₙₐ employs only the reference density n₀ as an argument. To incorporate the effect of SC in the variational calculation we next consider an approach where the potential vₙₐ is constructed through the linear response scheme. Explicitly, vₙₐ(n') is given as

\[ \nu_{n_{0}}(n')(\epsilon) = \nu_{n_{0}}(n_{0})(\epsilon) + \int d\epsilon' \frac{\delta \nu_{n_{0}}(n'')(\epsilon)}{\delta n_{0}(\epsilon')} |_{n_0} \delta n_{0}(\epsilon'), \]

(31)

where \( n' = n' (\epsilon) - n_{0}(\epsilon) \) represents the density shift on the energy coordinate. The existence of the exchange kernel \( \delta \nu_{n_{0}}(\epsilon)/\delta n(\epsilon') \) is guaranteed by the one-to-one correspondence between the energy density and the external potential defined with some defining potential. We note \( \delta n_{0} \) can be an adequate variable for the Taylor expansion since \( n' \) would be reasonably close to \( n_{0} \). Importantly, the exchange potential \( \nu_{n_{0}}(n')(\epsilon) \) as well as \( n' \) is optimized self-consistently through equations (21) and (31). In order to apply equation (31) to numerical calculations, we adopted the exchange kernel for HEG to equation (31), thus,

\[ \frac{\delta \nu_{n_{0}}(n_{0})(\epsilon)}{\delta n_{0}(\epsilon)} = \frac{4}{9} C_{x} \bar{n}_{0}(\epsilon) \hat{n}_{0}(\epsilon) n_{0}(\epsilon)^{-1}. \]

(32)

Correspondingly, the exchange energy \( E_{x}[n'] \) is given as

\[ E_{x}[n'] = E_{x}[n_{0}] \]

+ \[ \int d\epsilon' \delta n(\epsilon') \left\{ \frac{4}{3} C_{x} \bar{n}_{0}(\epsilon) n_{0}^{-1} \hat{n}_{0}(\epsilon) \right\} \]

(33)

The potential energy curve computed by equations (31)–(33) for H₂ dissociation is also plotted in figure 7. The result obtained by using equation (33) and that given by equation (28) are hardly discernible, which implies the robustness of the linear-response approach represented with equation (31).

Equation (33) was also applied to the dissociation of the double bond in ethylene C₂H₄, where the carbons in triplets (\( \tilde{B}_1 \)) were supposed to be the fragments. The computed potential energy curves are presented in figure 8. The dissociation energy \( \Delta E_{\text{diss}} \) without zero-point energy correction was evaluated as 214.1 kcal mol⁻¹ by the present approach, which made a significant improvement on \( \Delta E_{\text{diss}} \) given by the conventional LDA functional (262.4 kcal mol⁻¹). However, it still overestimates \( \Delta E_{\text{diss}} \) by ~40 kcal mol⁻¹ since spin-unrestricted LDA approach gives \( \Delta E_{\text{diss}} = 173.1 \) kcal mol⁻¹. Again the error could be attributed to the overestimation of \( E_{n_{0}} \) near the C–C bonding region.

So far, we examined the dissociations that provide identical fragments. In these cases \( n_{0}^{\pm} \) is automatically equal to \( n_{0}^{\pm,1} \) and hence the exchange potential in equation (31) for
of an H₂ molecule. It was, thus, demonstrated that equation (33) can also be applied to heterolytic dissociations.

Here, we summarize the calculation of \( E_{\text{sc}} \) where the energy distribution \( n'(\epsilon) \) plays a major role. It was demonstrated that the variational approach (equation (33)) as well as the non-variational method (equation (28)) made a significant contribution to realize \( E_{\text{sc}} \) associated with the bond dissociations in \( \text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \) in spite of their marked simplicities. However, \( E_{\text{sc}} \) are erroneously stabilized in the middle ranges of the bond distances of these molecules, which gives rise to the overestimations of the dissociation energies \( \Delta E_{\text{diss}} \) and unfavorable elongations of the equilibrium bond distances. Solving this problem is a major issue of the next stage in the development of the DFT based on the energy electron density \( n'(\epsilon) \). In the following we provide a possible remedy for the deficiency of the method.

A straightforward solution to the problem is to attenuate \( E_{\text{sc}} \) for the region where the exchange hole is not delocalized seriously. For this purpose we first formulate the exchange-correlation energy \( E_{\text{sc}} \) in equation (28) in terms of the exchange energy density \( U_x \), thus,

\[
E_{\text{sc}}[n,n_0] = \int U_x[n][r]n_0(r)\,dr + \int \left( U_x'[n'](\epsilon)n'(\epsilon) - U_x'[n'_0](\epsilon)n'_0(\epsilon) \right)\,d\epsilon,
\]

(34)

where \( U_x[n'](\epsilon) \) denotes the exchange energy density for an electron placed at the energy coordinate \( \epsilon \). Here, we introduce a correlation factor \( \alpha(\epsilon) \) that ranges from 0 to 1 quantifying the strength of the SC on each energy coordinate \( \epsilon \). Then, \( E_{\text{sc}} \) can be modified as

\[
E_{\text{sc}}^{\text{gen}}[n,n_0] = \int \left\{ \lambda(\alpha(\epsilon))(\tilde{U}_x[n_0](\epsilon) - U_x'[n'_0](\epsilon))n'_0(\epsilon) + U_x'[n'](\epsilon)n'(\epsilon) \right\}\,d\epsilon,
\]

(35)

where \( \tilde{U}_x[n_0](\epsilon) \) is the exchange energy averaged over the surface with energy coordinate \( \epsilon \) and defined as

\[
\tilde{U}_x[n_0](\epsilon) = \frac{\int U_x[n_0][r]n_0(r)\delta(\epsilon - \epsilon_{\text{diss}}[r])\,dr}{n_0(\epsilon)}.
\]

(36)

In equation (35) \( \lambda \) is some appropriate function which increases monotonically from 0 to 1. It is readily recognized that equation (34) as well as equation (28) corresponds to a special case of equation (35) where \( \alpha(\epsilon) \) is set to 1 for any value of \( \epsilon \). Thus, equation (35) can be regarded as a generalized form of equation (34). Further, equation (35) can be transformed to

\[
E_{\text{sc}}^{\text{gen}}[n,n_0] = \int \left\{ (1 - \lambda(\alpha(\epsilon)))U_x'[n'_0](\epsilon) + \lambda(\alpha(\epsilon))\tilde{U}_x[n_0](\epsilon) \right\}n'_0(\epsilon)\,d\epsilon
\]

\[
+ \int U_x'[n'](\epsilon)n'(\epsilon)\,d\epsilon - U_x'[n'_0](\epsilon)n'_0(\epsilon)\,d\epsilon.
\]

(37)

In equation (37) the factor \( \lambda(\alpha(\epsilon)) \) works as a mixing parameter for the reference energy \( \tilde{U}_x[n_0][r] \) at energy coordinate \( \epsilon \). The last integration in right hand side of equation (37) can also be evaluated variationally by consulting equation (31).
We, thus, obtain a rather simple formulation to improve the functional $E_{xc}$. The remaining problem is how to determine the explicit value of the correlation factor $\alpha(\epsilon)$ in equation (35). A possible prescription is to adopt the non-dynamical (static) correlation factor $f$ introduced by Becke in [3, 11, 32]. The factor $f$ is determined at each reference point from the generalized BR$x$ hole of which population is not being normalized to 1. As required $f$ is designed to vary within the range from 0 to 1 depending on the degree of the delocalization of the exact exchange hole. Then, the explicit form of function $\lambda$ in equation (35) should also be determined, which will involve the optimization of some adjustable parameters. The implementation of the functional equation (35) and the associated benchmark tests will be the issue of our future work.

It is worth discussing here the relation between our approach and other methods [3, 4, 11, 32, 33] which deal with the SC as a major subject. In these developments a device originally proposed by Becke in 2003 [3], referred to as B03 hereafter, plays a central role. The key in B03 is to increase the depth of the exchange hole of a spin at a reference point by fraction $f$ of the exchange hole of the opposite spin. The resultant exchange energy density for electrons with $\alpha$ spin $U_{\alpha\alpha}$ including SC is given by

$$U_{\alpha\alpha} = U_{\alpha0}^{\text{exact}} + fU_{\beta\beta}^{\text{exact}}$$

(38)

as shown in equation (24) in [3]. $U_{\alpha\alpha}^{\text{exact}} (\sigma = \alpha \text{ or } \beta)$ is the exact exchange energy density derived from Kohn–Sham wave functions. When a covalent bond is infinitely stretched we have $f = 1$ for any reference point and consequently $U_{\alpha\alpha}$ in equation (38) is twice the value of $U_{\alpha0}$ as expected. The procedure in B03 to deepen the exchange hole by summing the contribution from the opposite spin fully corresponds to the projection of the density $n_{\sigma}(r)$ onto an energy coordinate $\epsilon$ as depicted in figure 1. Thus, in our theoretical framework the fraction $f$ is implicitly incorporated in the energy distribution and it varies naturally from 0 to 1 according to the extent of the bond stretch. However, at the present applications as revealed in figures 7 and 8, $E_{xc}$ is being overestimated in the middle range of the bond distance. We, thus, introduce in equation (35) the explicit fraction $\alpha(\epsilon)$ to make a correction to $E_{xc}$.

4. Conclusions

We developed a DFT where the energy electron distribution $n^*(\epsilon)$ serves as a fundamental variable. A proof was given for the one-to-one mapping between the subset of the external potentials and that of the $\nu$-rep. energy distributions under a given defining potential $\nu_{\text{def}}$ in the way parallel to the proof for the HK theorem. Further, the Levy’s constraint search and the Kohn–Sham equation are formulated in terms of the density $n^*(\epsilon)$ as a basic variable. We proposed exchange functionals of $n^*(\epsilon)$ by adapting a conventional LDA functional. It turned out that the present approach can realize the potential energy curves of several types of chemical bonds including double and triple bonds in simplest hydrocarbons with comparable accuracies to the original LDA-based functional.

A notable feature of the present theory, which is crucial for the motivation of this work, is that the energy density $n^*(\epsilon)$ is able to incorporate the fragment of an exchange hole locating at a distal atomic site in a stretched molecule. Actually, the projection of the density onto the energy coordinate as written in equation (1) gives a quite favorable result that the density $n_\sigma^\epsilon(\epsilon)$ for spin $\sigma$ of the spin-restricted wave function becomes identical to that of the spin-unrestricted wave function at the bond dissociation limit. By taking advantage of this nature we developed a prototype of a functional $E_{xc}$ that involves the SC $E_{sc}$. It was demonstrated that $E_{xc}$ significantly improves the dissociation curves of the bonds in $H_2$, $C_2H_4$ and $CH_4$. Actually, $E_{sc}$ decreases the dissociation energy $\Delta E_{\text{diss}}$ by ~35 kcal mol$^{-1}$ for the single bonds in $H_2$ and $CH_4$, and by ~50 kcal mol$^{-1}$ for the double bond in $C_2H_4$ as compared to the spin-restricted conventional LDA functional. We note, however, $\Delta E_{\text{diss}}$ are still overestimated due mainly to the erroneous stabilization of $E_{xc}$ in the middle ranges of the bond distances. A method to solve this problem is to attenuate $E_{xc}$ in these regions. Implementation of the method and its applications will be presented in the future publications. As a conclusion, the present approach based on the density $n^*(\epsilon)$ can potentially be a new paradigm in DFT.

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