# Density functional theory for molecules of fractional charge and molecular size consistency

Jing Kong*

Department of Chemistry and Center for Computational and Data Sciences, Middle Tennessee State University, 1301 Main St., Murfreesboro, TN 37130, USA

* Correspondence: jing.kong@mtsu.edu

Abstract

This article concerns the development of density functional theory for electron densities integrated to fractional charges and for molecular fragments separated distantly. We start from a model external potential where a molecule with fractional charge (referred to as fractional molecule) can be defined as part of a single non-fractional molecule. A universal functional of densities of fractional charge, $F_{FC}$, can be derived from this model. The derived functional has the same form as the one from the grand-canonical-ensemble treatment. The Kohn-Sham noninteracting assumption is extendable to densities of fractional charge and the density of a fractional molecule is noninteracting $v$-representable under a nondegeneracy condition. The noninteracting kinetic energy and the exact exchange energy functionals of such a density are well defined and have the same forms as those for nonfractional systems. A correlation functional is defined that pertains to the fractionally occupied highest occupied molecular orbital only. The exact exchange energy is discontinuous as the number of electrons passing through an odd integer but its sum with the new correlation energy is continuous. For a system made of distantly separated densities $\rho^X$ and $\rho^Y$, the corresponding universal functional can be accurately approximated as a sum of local parts $F_{FC}(\rho^X)+F_{FC}(\rho^Y)$, and the size consistency of a molecular system can be satisfied using $F_{FC}$ with a modified outer loop in the two-step constrained search formalism and an appropriate constraint due to the localized external potential. The proposed exchange-correlation functional yields the correct result for a well-designed example in literature.

List of frequently used terms, their indexes of reference, and the page numbers with their explanations.

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## Introduction

Density functional theory (DFT)[1], especially Kohn-Sham (KS) DFT with single determinants (SDs)[2], is the bread-and-butter method for simulating electronic effect in molecules and materials due to its efficiency and accuracy. Contemporary DFT methods, however, are inadequate or even fail for systems with significant nondynamic correlation or charge delocalization. The problem is most pronounced in a system where the local electronic charge (referred to as charge henceforth) or spin become effectively fractional, such as a monomer in an infinitely stretched $H_2^+$ (fractional charge) or $H_2$ (fractional spin)[3, 4]. Both fractional charge and spin can happen simultaneously, such as with the dissociation of a hetero-diatomic molecule[5]. Large fractional charge and fractional spin errors with contemporary functionals are well documented for systems with either fractional charge/spin systems[4] or molecular systems with effective fractional charge/spin[6]. Indeed, functionals that performed well for one type of error were found to do poorly for the other[7]. Efforts have been made in designing methods within the KS framework[8, 9] or in the proximity of it[10, 11] to address effective fractional occupancies in a molecular environment and were shown to make significant improvement over contemporary mainstream functionals.

An early formal treatment of fractional charge (FC) was Janak theorem[12]. It showed that the energy of a Kohn-Sham orbital of a molecule is the derivative of the total energy with respect to the occupancy of that orbital if the latter was allowed to vary continuously. Perdew *et al* later gave a definition of a molecule with a fractional charge as a grand canonical ensemble (GCE) with fluctuating integer charges, and showed that the energy of the system was piecewise linear between integer charges[3]. They also showed, using Janak theorem, that the KS exchange-correlation (XC) potential, the derivative of KS XC energy with respect to the electron density, experienced a constant shift at an integer charge, the well-known derivative discontinuity[3]. The lack of proper derivative discontinuity of contemporary functionals was considered the root cause of their ills in dealing with nondynamic correlation and charge delocalization. Yang *et al* gave an alternative definition of a molecule with fractional charge as the average of an aggregation of many of the same molecule kept far away from each other[13]. The number of identical molecules in the aggregate is determined such way that averaged number of electrons or the total spin on each molecule is the desired fraction. This arrangement achieved the aforementioned piecewise linearity of energy of each molecule via the size-consistency of the ensemble of the many degenerate wavefunctions for the whole aggregate. The energy of each molecule was further assumed to be the functional of only its own density inferred from the size consistency argument. This wavefunction-based definition allowed a general concept of a fractional spin state of a molecule that becomes part of an ensemble of the many degenerate wavefunctions of the aggregate. The energy of this fractional spin state was shown to be a constant, equal to the energy of that molecule with normal integer spin states[14]. The straight-line conditions of fractional charge and fractional spin formed a so-called flat plane condition[6]. In all cases, the fractional charge/spin in a density is represented by the fractional occupancy at the highest occupied molecular orbital(s) (HOMO(s)) of the KS noninteracting solution with orbitals below the HOMO(s) (called subhomo orbitals henceforth) fully occupied, i.e. following the Aufbau rule[12, 15].

Fundamental issues still exist in the DFT treatment of fractional charge, and they were discussed comprehensively in a recent paper by Baerends[5]. It was argued that DFT is based on the wavefunction or the density matrix solution of a single molecule with an integer charge at zero temperature. The system with fractional charge in ref [3] was defined as the statistical ensemble, not a single molecule. An aggregate of many identical molecules in ref[13] could be treated as one supermolecule but the energy of each molecule in the aggregate would be formally a functional of the density of the whole aggregate. The locality of this functional, i.e. being a functional of the density of one molecule only, could not be trivially inferred from the size consistency principle. Without fractional charge being a necessary property of DFT,

the derivative with respect to the charge could not be uniquely defined, and the validity of Janak theorem as an exact condition of the KS solution was questionable. So was the derivative discontinuity as a consequence. Regardless, the ensemble prescription of the fractional charge/spin seems to put SD KS methods off limits formally.

In this article, we attempt to establish a model external potential where a molecule with fractional charge (referred to as *fractional molecule*) can be defined as part of a single non-fractional molecule. A universal functional of densities of fractional charge, $F_{FC}$, can be derived from this model. The derived functional has the same form as the one from the GCE treatment. The derived functional has the same form as the one from the grand-canonical-ensemble treatment. The Kohn-Sham noninteracting assumption is extendable to densities of fractional charge and the density of a fractional molecule is noninteracting $v$-representable under a nondegeneracy condition. The noninteracting kinetic energy and the exact exchange energy functionals of such a density are well defined and have the same forms as those for nonfractional systems. A correlation functional is defined that pertains to the fractionally occupied highest occupied molecular orbital only. The exact exchange energy is discontinuous as the number of electrons passing through an odd integer but its sum with the new correlation energy is continuous. For a system made of distantly separated densities $\rho^X$ and $\rho^Y$, the corresponding universal functional can be accurately approximated as a sum of local parts $F_{FC}(\rho^X)+F_{FC}(\rho^Y)$, and the size consistency of a molecular system can be satisfied using $F_{FC}$ with a modified outer loop in the two-step constrained search formalism and an appropriate constraint due to the localized external potential. The proposed exchange-correlation functional yields the correct result for the flat-plane example[6].

We note that the energy, wavefunction, density and density matrix of a molecule mentioned in this paper are assumed to be of ground states.

## Functional of a density with fractional charge

We start with an isolated (lone in the universe) molecule $M$ with $L$ (a positive integer) number of electrons and denote it as $M_L$. A hydrogen-like atom $A$, a special case of $M$, is placed at a distance from $M$ beyond which the external potential from $M$ to $A$ and vice versa are deemed numerically negligible. This distance is called asymptotically interaction-negligible distance (AIND) [Definition D1], and the corresponding condition is called asymptotically negligible distant interaction (ANDI) [Condition C1]. The nuclear charge of $A$ is set such that $I(A_1)=I(M_L)$, with $I$ standing for ionization potential. This atom is named as *auxiliary atom* [Definition D2]. The combined system $R$ ($R=M..A$) is referred to as *reference molecule* [Definition D3]. $M_L$ and $M_{L-1}$ are further assumed to be nondegenerate and either singlet (even number of electrons) or doublet (odd number of electrons) [Condition C2]. We also use another well-known condition about the convexity of molecular energy, which states the energy of an atom or molecule is convex with respect to the number of electrons [Condition C3], which is considered generally true for electronic systems[3].

The exact ground state of the reference molecule is $M_{L-1}..A_1$. Another state $M_L..A_0$ is asymptotically degenerate with the ground state due to the nondegenerate condition and the convexity of molecular energy conditions of $M$ (C2 and C3), other than trivial degeneracies due to spin directions. The wavefunction of $M_L..A_0$, denoted as $\Psi_{M..A}(L,0)$, is the same as the wavefunction of $M_L$ asymptotically, i.e. $\Psi_{M..A}(L,0)\cong\Psi_M(L)$, because adding $A_0$ to the Hamiltonian of $M_N$ does not change the solution of the Schrödinger equation to any finite numerical accuracy due to the ANDI condition (C1). This results in

$\rho_L^{M_L..A_0} \cong \rho_L^M$ for electron density, and $E_L^{M_L..A_0} \cong E_L^M$ for energy. (The symbol $\cong$ is used to indicate being equal within an arbitrarily small tolerance of error or threshold.) The wavefunction for $M_{L-1}..A_1$ is asymptotically $\Psi_{M..A}(L-1,1) \cong \mathscr{A}[\Psi_M(L-1)\Psi_A(1)]$, the antisymmetric product of the wavefunctions of the isolated $M_{L-1}$ and $A_1$. The electron(s) and external potentials on either side do not affect the solution of the other side numerically due to the ANDI condition, resulting in $\rho_L^{M_{L-1}..A_1} \cong \rho_{L-1}^M + \rho_1^A$ and $E_L^{M_{L-1}..A_1} \cong E_{L-1}^M + E_1^A = E_{L-1}^M - I(M_L) = E_L^M$. This is the same condition underpinning the size consistency principle[16], and is referred to as the size consistency condition [Condition C4 ] in this paper as an alternative to the ANDI condition. An ensemble of these two states, denoted as $R_\delta$, can be made with a weight $\delta$ between 0 and 1 and yields $\rho_L^{R_\delta} = (1-\delta)\rho_L^M + \delta\rho_{L-1}^M + \delta\rho_1^A$ as the density and $E_L^{R_\delta} = (1-\delta)E_L^M + \delta E_{L-1}^M + \delta E_1^A$ as the energy. This system models the ionization of $M_L$ with $\delta$ number of electron transferred to a distant reservoir $A$. Because the density in $R_1$ is well separated between $M$ and $A$ regions, the density for the ensemble has two separated sides too and we find the density on the $M$ side to be well-defined density with a fractional charge:

$$\rho_{L-\delta}^M = (1-\delta)\rho_L^M + \delta\rho_{L-1}^M \tag{1}$$

We refer $\rho_{L-\delta}^M$ as the *fractional density* [Definition D4]. It integrates to a fractional charge $L-\delta$. Likewise, $E(M_{L-\delta})$ is clearly a sum of two sides and it is physically sensible, albeit not imperative, to define the energy on $M$ side, called *fractional energy* henceforth [Definition D5]:

$$E_{L-\delta}^M = (1-\delta)E_L^M + \delta E_{L-1}^M \tag{2}$$

We name $M_N$ as a *fractional molecule* with $\rho_N^M$ and $E_N^M$ as the density and energy with the external potential being the same as that of the molecule $M$ [Definition D6]. $N$ is the number of electrons of the fractional molecule and real and positive. The density and energy of the whole reference molecule are as follows:

$$\rho_{\lceil N \rceil}^{R_\delta} = \rho_N^M + \rho_\delta^A, \quad E_{\lceil N \rceil}^{R_\delta} = E_N^M + E_\delta^A \tag{3}$$

From the above definitions, it seems that $M_N$ may have two reference molecules of different number of electrons when $N$ is an integer: $M_N..A_0$ ($\delta = 0$) and $M_N..A_1$ ($\delta = 1$). However the density on the $M$ side of $M_N..A_1$, unlike $M_N..A_0$, integrates to a number larger than $N$ by an infinitesimal amount because the exact $\rho(A_1)$ permeates the universe (The density of $M_N$ has a smaller presence on the $A$ side because of $I(M_N) > I(A_1)$). It is appropriate to limit the range of $\delta$ to $[0,1)$ such that it can be decided uniquely as $\delta = \lceil N \rceil - N$ and counted as the fraction of electron shifted from $M$ to $A$. Furthermore, the reference molecule can be decided uniquely as $M_N..A_\delta$ for a given $N$ with the number of electrons as $\lceil N \rceil$. $\delta \to 1$ ($\delta = 1 - 0^+$, $0^+$: positive infinitesimal) means that one electron almost completely leaves $M_{\lceil N \rceil}$. $\delta = 0$ ($M_{\lceil N \rceil}...A_0$) corresponds to a normal, non-fractional molecule $M_{\lceil N \rceil}$. We rename the ensemble $R_\delta$ to $R_N$ since $\delta$ is uniquely determined by $N$ that also determines the number of electrons for the reference molecule.

We note that the nondegeneracy condition (C2) of $M_{\lceil N \rceil}$ and $M_{\lfloor N \rfloor}$ ensures a one-to-one mapping between the density and the external potential of a fractional molecule, i.e. $\rho_N^M \Leftrightarrow v_M$. The reason is that this condition leads to a one-to-one mapping between $\rho_{\lceil N \rceil}^M$, $\rho_{\lfloor N \rfloor}^M$, and $v_M$ due to the HK first theorem, and Eq.(1) shows a one-to-one mapping between $\rho_N^M$ and a $\rho_{\lceil N \rceil}^M / \rho_{\lfloor N \rfloor}^M$ set. This nondegeneracy condition also leads to a one-to-one mapping between $\rho_N^M$ and its energy $E_N^M$ for the same set of nuclear charge $M$ per Eq.(2), i.e. $\rho_N^M$ is nondegenerate.

We may extract a functional of a density that integrates to $N$ from the fractional energy $E_N^M$ following Levy's constrained search method[17] for each component of $E_N^M$:

$$\begin{aligned} E_N^M &= (1-\delta)\min_{\rho_{\lceil N \rceil}}(F_{LL}[\lceil N \rceil, \rho_{\lceil N \rceil}] + \int \rho_{\lceil N \rceil} v_M) + \delta \min_{\rho_{\lfloor N \rfloor}}(F_{LL}[\lfloor N \rfloor, \rho_{\lfloor N \rfloor}] + \int \rho_{\lfloor N \rfloor} v_M) \\ &= \min_{\rho_N}(F_{FC}[N, \rho_N] + \int \rho v_M) \\ F_{FC}[N, \rho_N] &\equiv \min_{\delta\rho_{\lceil N \rceil} + (1-\delta)\rho_{\lfloor N \rfloor} = \rho_N} ((1-\delta)F_{LL}[\lceil N \rceil, \rho_{\lceil N \rceil}] + \delta F_{LL}[\lfloor N \rfloor, \rho_{\lfloor N \rfloor}]) \end{aligned} \tag{4}$$

The minimizer of Eq.(4) is $\rho_N^M$.

$F_{FC}[N, \rho_N]$ has the following search space of wavefunction ensembles:

$$(1-\delta)\left|\Psi(\lceil N \rceil)\right\rangle\left\langle\Psi(\lceil N \rceil)\right| + \delta\left|\Psi(\lfloor N \rfloor)\right\rangle\left\langle\Psi(\lfloor N \rfloor)\right| \tag{5}$$

This search space is sufficient because of the assumed convexity of molecular energy with respect to the number of electrons (Condition C3). $F_{FC}$ is a special (two nondegenerate states) case of the universal functional for GCEs[3, 18]. The convexity of the latter has been established recently[18]. It becomes $F_{LL}$ for systems with integer number of electrons, i.e. the case of $\delta = 0$.

To be valid, $F_{FC}$ must be applicable to the reference molecule since the fractional density is defined as part of it. Applying Eq.(4) to the energy of the reference molecule (Eq.(3)) leads to a functional $F_{FC}[N, \rho_N] + F_{FC}[\delta, \rho_\delta]$. Its application requires that the search for $\rho_N^M + \rho_\delta^A$ keeps each component in their own sides, but this functional itself does not contain this constraint because the fractional electron may freely move between the two sides due to the degeneracy of the molecule. Fortunately, such a constraint occurs "naturally" in the Levy-Lieb (LL) constrained search[17, 19] for an isolated molecule (a lone molecule in the universe) in a numerical sense. We observe that the wavefunction of an isolated molecule decays exponentially far away from the molecule, much more rapidly than the external potential from the nuclei[20]. Thus, it is sufficient to constrain the search for its density within a domain limited by the reach of the external potential of the molecule in a two-step constrained search. The energy of a molecule of $N$ electrons with a set of nuclei $X$ then has the following asymptotic solution:

$$E_L^X \cong \min_{\rho_L^{(X)}}(F_{LL}[L, \rho_L^{(X)}] + \int \rho_L^{(X)} v_X), \quad F_{LL}[L, \rho_L] \equiv \min_{\Psi_{\rho_L}} \left\langle \Psi_{\rho_L} \middle| \hat{T} + V_{ee} \middle| \Psi_{\rho_L} \right\rangle \tag{6}$$

where $L$ is the number of electrons (an integer), $X$ a set of nuclear charges and their locations, $v$ the external potential. $F_{LL}$ is the Levy-Lieb (LL) universal functional[19] with a search over wavefunctions $\Psi_\rho$

constrained by the density $\rho$. $\rho_L^{(X)}$ is a trial density constrained to be inside a domain marked by the locale of $X$. This domain is defined as a sphere that encompasses $X$ with the radius further extended by the AIND (D1), subject to a positive threshold. It reads as *interaction-non-negligible domain of the external potential* $v$ made of $X$, and is named $v$-domain [Definition D7] henceforth. Such a limitation on the range of interaction based on the asymptotic behavior of the potential is said to be $v$-local henceforth [Definition D8]. The minimizer of the search for $E_L^X$ is $\rho_L^X$, the density corresponding to $v_X$.

In a reference molecule $M_N..A_\delta$, $M$ and $A$ are in their own $v$-domains. The $v$-locality constraint needs to be applied to the outer loop of the two-step search scheme for the reference molecule because each side of the molecule is assigned to certain number of electrons:

$$\begin{aligned}&\min_{\rho_N^{(M)},\rho_\delta^{(A)}}(F_{FC}[N,\rho_N^{(M)}]+F_{FC}[\delta,\rho_\delta^{(A)}]+\int(\rho_N^{(M)}+\rho_\delta^{(A)})(v_M+v_A))\\&=\min_{\rho_N^{(M)}}(F_{FC}[N,\rho_N^{(M)}]+\int\rho_N^{(M)}v_M)+\min_{\rho_\delta^{(A)}}(F_{FC}[\delta,\rho_\delta^{(A)}]+\int\rho_\delta^{(A)}v_A)=E_N^M+E_\delta^A\end{aligned} \tag{7}$$

The first equality is due to the AIDI condition. Eq.(7) shows the applicability of $F_{FC}$ to the reference molecule. This relation allows the fractional molecule to be treated as if isolated while still being part of a single molecule because an appropriate $v_A$ can always be assumed by definition. It also shows the applicability of the GCE formalism for single molecules.

Several properties of a fractional density and its functional can be observed from the derivation above:

1. The exact value of the AIND is not significant. It is its existence that establishes the arguments here. Indeed, the accuracy of density and energy of an isolated molecule is not affected by the size of the $v$-domain once it is large enough because the wavefunction decays much faster than the external potential away from the molecule. All the integrals for each side are over the whole space.
2. A GCE description of a fractional density is within the realm of the applicability of the HK theorems in the sense that there is a one-to-one correspondence between the density and the external potential. We may also conclude that $F_{FC}[N,\rho_N]$ is piece-wise linear with respect to the fractional charge for a $v$-representable density since the fractional energy (Definition D5) and the electron-nuclear attraction energy are linear.
3. The definition of a fractional molecule $M_N$ is based on the two states of an isolated molecule, $M_{\lceil N\rceil}$ and $M_{\lfloor N\rfloor}$. The isolation allows the placement of the auxiliary atom $A$ outside the $v$-domain of $M$. Indeed, the actual construct of the $A$ side of the reference molecule is inconsequential as long as $I(A_1)=I(M_{\lceil N\rceil})$. Therefore, the properties of a fractional molecule are entirely determined by its external potential and number of electrons, and the fractional molecule should be considered isolated in that sense. We continue to use the auxiliary atom defined in D2 as the $A$ side for convenience.

## Non-interacting kinetic energy functional of fractional density

The density of a reference molecule is (degenerate) interacting wavefunction $v$-representable because the two-state ensemble of the reference molecule, with the nondegeneracy condition of $M$ (C2), can be represented by a complex wavefunction[21]. This density is assumed to be noninteracting wavefunction $v$-representable with the KS assumption[2]. Furthermore, the noninteracting state is

nondegenerate because the KS effective potential would otherwise need to yield the densities of $M_{\lceil N \rceil}$ and $M_{\lfloor N \rfloor}$ for being part of the reference molecule, which is impossible[1]. Thus, *the density of a reference molecule is nondegenerate noninteracting wavefunction $v$-representable with the KS assumption.* This property is commonly referred to as being noninteracting $v$-representable in literature. We also call the fractional density as being noninteracting $v$-representable henceforth [Definition D9] since it is derivable from the nondegenerate noninteracting $v$-representing wavefunction of the reference molecule. This definition extends the concept of noninteracting $v$-representability to densities of fractional charge. The said wavefunction is referred to as *reference SD* henceforth [Definition D10].

A reference SD has a single homo (highest occupied molecular orbital) for a given $N$ due to the one-to-one mapping between the density and ensemble weight $\delta$. We may construct the homo and write the total and the spin first order-density matrices (RDM-1's, symbolized with $\gamma$) for the reference SD with a given $M_N$ as:

$$\begin{aligned}
&\gamma_{subh}^{M_N} = \sum_{i=1}^{K} \varphi_i(\mathbf{r})\varphi_i(\mathbf{r}'),\ \gamma_{\lceil N \rceil,\alpha}^{R_N} = \gamma_{subh}^{M_N} + \varphi_h(\mathbf{r})\varphi_h(\mathbf{r}'),\ \gamma_{\lceil N \rceil,\beta}^{R_N} = \gamma_{subh}^{M_N} + (N_h - 1)\varphi_h(\mathbf{r})\varphi_h(\mathbf{r}'), \\
&\gamma_{\lceil N \rceil}^{R_N} = \gamma_{\lceil N \rceil,\alpha}^{R_N} + \gamma_{\lceil N \rceil,\beta}^{R_N},\ \varphi_h = \sqrt{1 - \frac{\delta}{N_h}}\varphi_h^M + \sqrt{\frac{\delta}{N_h}}\varphi_h^A,\ K = \left\lfloor \frac{\lceil N - 1 \rceil}{2} \right\rfloor,\ N_h = \lceil N \rceil - 2K
\end{aligned} \tag{8}$$

In this equation, $\lceil N \rceil$ is the total number of electrons of the reference molecule, $\varphi$'s are normalized KS orbitals, $\varphi_h$ the homo. The $\delta$ electron on the $A$ side belongs to the homo since the latter has an energy of $-I(M_{\lceil N \rceil})$ [20, 22], causing the homo split between the $M$ and $A$ sides, noted as $\varphi_h^M$ and $\varphi_h^A$, respectively. All the other orbitals (up to $K$) are the subhomo orbitals (denoted as 'subh') per Aufbao rule and are on the $M$ side according to the density distribution. The homo occupancy $N_h$ is either one for odd number of electrons or two for even in the reference molecule due to $2K < N$.

The reference SD (D10) composed of those orbitals is the minimizer of the Lieb kinetic functional of constrained search[19] for the reference molecule. Applying the equivalent density matrix to the kinetic energy formula results in the noninteracting kinetic energy of the reference molecule as a summation of $M$ and $A$ sides:

$$\begin{aligned}
&T_s(R_N) = -\frac{1}{2}Tr(\gamma_N^M \nabla^2) - \frac{1}{2}Tr(\gamma_\delta^A \nabla^2), \\
&\gamma_N^M = 2\gamma_{subh}^{M_N} + (N_h - \delta)\varphi_h^M(\mathbf{r})\varphi_h^M(\mathbf{r}'),\ \gamma_\delta^A = \delta\varphi_h^A(\mathbf{r})\varphi_h^A(\mathbf{r}')
\end{aligned} \tag{9}$$

The derivation of the equation uses the fact $\left\langle \varphi_h^M \middle| \nabla^2 \middle| \varphi_h^A \right\rangle \cong 0$ due to the well-separation between $\varphi_h^M$ and $\varphi_h^A$. We see that it is sufficient to conduct the constrained search of Lieb kinetic energy functional for an RDM-1 in each side separately, leading to the following definition of a noninteracting kinetic energy functional ($T_{NI}$) of a density $\rho_N$ that may be integrated to a positive number (integer or not) ($\gamma$ being a RDM-1):

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[1] The only exception is for $N < 1$, where the wavefunction can be written as $\sqrt{1-\delta}\Psi^M + \sqrt{\delta}\Psi^A$, i.e. a real SD.

$$T_{NI}[\rho_N] \equiv -\frac{1}{2}\min_{\gamma_N \to \rho_N} Tr(\gamma_N \nabla^2) \tag{10}$$

$\rho_N$ is a density integrated to a real number $N$. When $\rho_N$ is $\rho_N^M$, i.e. $v$-representable, the minimizer is $\gamma_N^M$ since $\gamma_N^M$ has the same spatial range as $\rho_N^M$ and the reference SD is the minimizer for the whole molecule. Therefore, this minimizer is derivable from a noninteracting wavefunction and also $N$-representable, with the reference SD being the wavefunction. Equation (10) has the same expression as the more general Lieb kinetic functional for GCEs defined in ref[18], which was shown to be convex. Note that the assumed noninteracting $v$-representability of $\rho_N^M$ implies that a multiplicative potential can be derived from $E_N^M$ for a given $N$ [Condition C5], which is an extension of the original KS assumption based on integer number of electrons.

Eq.(10) is applicable to wavefunction and ensemble, and grand-canonical ensemble $v$-representable densities[18]. We note that it is possible to have an alternative definition of kinetic energy functional as $F_{FC}[\rho]|_{V_{ee}=0}$, i.e. setting $V_{ee}$ to 0 (see Eq.(6)). It corresponds to a GCE of noninteracting Lieb kinetic energy functionals[23]. It is larger than or equal to $T_{NI}$ because an ensemble of RDM-1 remains as an RDM-1. Indeed, the equality only holds for integer number of electrons due to the convexity of $T_{NI}$. This means that $T_{NI}$ is convex with respect to $\delta$. Physically speaking, a GCE of two noninteracting references is not the KS noninteracting solution of the ensemble of the corresponding interacting systems because the electron densities of the two interacting states are not linearly dependent, and thus the corresponding effective KS potentials are different. This means that $\gamma_N^M$ cannot be assumed to be an ensemble of the KS RDM-1's of $M_{\lceil N \rceil}$ and $M_{\lfloor N \rfloor}$ in general.

**Exchange and correlation functionals of fractional density**

The reference SD may be used to define the KS exact exchange for the reference molecule as a major component of the KS XC[24]. We show here that a corresponding exact exchange energy can be defined for a fractional molecule based on the solution of Eq.(10).

$\gamma_N^M$ as an RDM-1 for a noninteracting $v$-representable density is equivalent to a set of orbitals with a fractionally occupied homo[15] and can be constructed from the $M$ side of the KS orbitals of the reference molecule as shown in Eqs.(8) – (10). For a given fractional molecule $M_N$, this occupancy, denoted as $n^M$, can be determined uniquely as the following: $n^M = N - 2K$ and has a range $(0,2]$ due to $2K < N$. When discussions are focused on the homo, $N_h$ and $\delta$ can also be determined uniquely with a given $n$:

$$\forall n^M \in (0,1], \quad N_h = 1; \quad \forall n^M \in (1,2], \quad N_h = 2; \quad \delta = N_h - n^M \tag{11}$$

The thus calculated $\delta$ has the correct range of $[0,1)$.

The fractional occupancy in a homo also leads to fractional spin occupancies. We formally denote them as pairs: $(n_\alpha^M, n_\beta^M)_{N_h}$ and $(n_\alpha^A, n_\beta^A)_{N_h}$ for $M_N$ and $A_\delta$, respectively, with $n_\alpha^M + n_\beta^M = n^M$. When the combination of those homo's forms a SD wavefunction for the reference molecule, the homo spin configurations of $A_\delta$ can be determined by that of $M_N$ based on $N_h$. In particular, $(n_\alpha^M, n_\beta^M)_{N_h}$

corresponding to a reference SD (which is also the KS SD) can be determined based on $n^M$. Those results are summarized as follows:

$$\begin{aligned}&\text{SD:}\quad (n_\alpha^M, n_\beta^M)_1 = (n^M, 0)_1, \quad (n_\alpha^A, n_\beta^A)_1 = (1-n_\alpha^M, 0)_1, \quad (n_\alpha^A, n_\beta^A)_2 = (1-n_\alpha^M, 1-n_\beta^M)_2 \\ &\text{KS SD:}\quad (n_\alpha^M, n_\beta^M)_1 = (n^M, 0)_1, \quad (n_\alpha^M, n_\beta^M)_2 = ({}^{n^M}\!/_2, {}^{n^M}\!/_2)_2\end{aligned} \tag{12}$$

This equation also shows that SD wavefunctions other than the reference SD can be constructed for the reference molecule for $N_h = 2$.

We can now write the nominal RDM-1's per spin $\sigma$ for $M_N$, $A_\delta$ and $R_N$ corresponding to a SD of the reference molecule as follows using the KS orbitals with given homo spin configurations for $M_N$ and $A_\delta$:

$$\begin{aligned}&\gamma_{N,\sigma}^M = \gamma_{subh}^{M_N} + n_\sigma^M \varphi_h^M(\mathbf{r})\varphi_h^M(\mathbf{r}'), \quad \gamma_{\delta,\sigma}^A = n_\sigma^A \varphi_h^A(\mathbf{r})\varphi_h^A(\mathbf{r}') \\ &\gamma_{\lceil N \rceil,\sigma}^{R_N} = \gamma_{N,\sigma}^M + \gamma_{\delta,\sigma}^A + \sqrt{n_\sigma^M n_\sigma^A}(\varphi_h^M(\mathbf{r})\varphi_h^A(\mathbf{r}') + \varphi_h^M(\mathbf{r}')\varphi_h^A(\mathbf{r})),\end{aligned} \tag{13}$$

The exchange energy per spin $\sigma$ of a SD is an explicit functional of RDM-1 of that spin $-\left\langle \gamma_\sigma^2 \right\rangle_{ee}$, where $\left\langle f \right\rangle_{ee}$ stands for $\frac{1}{2}\int f(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1} d\mathbf{r}d\mathbf{r}'$. The square of $\gamma_{\lceil N \rceil,\sigma}^{R_N}$ is as follows because of $\varphi(\mathbf{r})\varphi_h^A(\mathbf{r}) \cong 0$ for any $\varphi(\mathbf{r})$ on the $M$ side:

$$(\gamma_{\lceil N \rceil,\sigma}^{R_N})^2 = (\gamma_{N,\sigma}^M)^2 + (\gamma_{\delta,\sigma}^A)^2 + n_\sigma^M n_\sigma^A (\varphi_h^M(\mathbf{r})\varphi_h^A(\mathbf{r}'))^2 + (\varphi_h^M(\mathbf{r})\varphi_h^A(\mathbf{r}'))^2 \tag{14}$$

The exchange energy of $\gamma_{\lceil N \rceil,\sigma}^{R_N}$ can be shown to be a sum of $M$ and $A$ sides because of $\left\langle (\varphi_h^M \varphi_h^A)^2 \right\rangle_{ee} \cong 0$ due to the ANDI condition, and thus allows the definition of an exchange energy per spin for the fractional molecule $E_{X,\sigma}^M$:

$$E_{X,\sigma}^{R_N}(n_\sigma^M) = -\left\langle (\gamma_{N,\sigma}^M)^2 \right\rangle_{ee} - \left\langle (\gamma_{\delta,\sigma}^A)^2 \right\rangle_{ee} \quad \Rightarrow \quad E_{X,\sigma}^{M_N}(n_\sigma) = -\left\langle (\gamma_{N,\sigma}^M)^2 \right\rangle_{ee} \tag{15}$$

We use $n_\sigma^M$ to index the exchange energy since it determines $n_\sigma^A$ (Eq.(12)) and the subhomo's are always doubly occupied. This leads to the definitions of the nominal total exchange energies for the reference and the fractional molecules:

$$E_X^{R_N}(n_\alpha^M, n_\beta^M) = E_{X,\alpha}^{R_N}(n_\alpha^M) + E_{X,\beta}^{R_N}(n_\beta^M), \quad E_X^{M_N}(n_\alpha^M, n_\beta^M) = E_{X,\alpha}^{M_N}(n_\alpha^M) + E_{X,\beta}^{M_N}(n_\beta^M) \tag{16}$$

We can see that the formula for exchange energies of a fractional molecule is the same as for a non-fractional molecule. The exact exchange (EXX) energies of the fractional molecule and the reference molecule, denoted as $E_{EXX}^M$ and $E_{EXX}^R$, respectively, are the nominal total exchange energies with specific spin occupancies for KS orbitals (Eq.(12)):

$$\begin{aligned}&n \in (0,1]:\ E_{EXX}^{R_N}(n^M) = E_X^{R_N}(n^M, 0), \quad E_{EXX}^{M_N}(n^M) = E_X^{M_N}(n^M, 0); \\ &n \in (1,2]:\ E_{EXX}^{R_N}(n^M) = E_X^{R_N}({}^{n^M}\!/_2, {}^{n^M}\!/_2), \quad E_{EXX}^{M_N}(n^M) = E_X^{M_N}({}^{n^M}\!/_2, {}^{n^M}\!/_2)\end{aligned} \tag{17}$$

$E_{EXX}^{M_N}$ and $E_{EXX}^{R_N}$ are continuous at the boundaries (0 and 2) of $n$. However, they are discontinuous as $n$ increases by an infinitesimal amount from $n=1$. Indeed, $E_X^{M_{\lfloor N \rfloor+0^+}}(\frac{1}{2}(1+0^+),\frac{1}{2}(1+0^+)) \cong E_X^{M_{\lfloor N \rfloor+0^+}}(\frac{1}{2},\frac{1}{2})$ is significantly higher than $E_X^{M_{\lfloor N \rfloor}}(1,0)$ because of the quadratic nature of the exchange energy with respect to the spin occupancies. The jump stems from the change of homo occupancy $N_h$ of the reference molecule from one to two, which leads to the change of the spin occupancies of the homo. This is an effect of electron pairing and needs to be compensated by correlation.

We show that this correlation can be recovered using the SDs of the reference molecule constructed from the KS orbitals of $M_N$ and $A_\delta$ with the relation of the spin configurations in Eq.(12) for $N_h=2$:

$$\lceil N \rceil^{-0.5} \det[\varphi_1^\alpha \varphi_1^\beta ... \varphi_K^\alpha \varphi_K^\beta \varphi_h^\alpha \varphi_h^\beta], \quad \varphi_h^\sigma = \sqrt{n_\sigma^M}\,\varphi_h^M + \sqrt{(1-n_\sigma^M)}\varphi_h^A, \quad n_\alpha^M + n_\beta^M = n^M \tag{18}$$

This set may be indexed by $n_\alpha^M$ for each $n^M$. The expectation value of the universal operator $\hat{T}+V_{ee}$ with such a SD differs from that of the reference SD only in the exchange energy. Because these SDs can be included in the search space of Lieb universal functional as trial interacting wavefunctions, we may define the result of the following search as a part of XC energy of the reference molecule:

$$F_{XC(FC)}^{R_N}[\gamma_{\lceil N \rceil}^{R_N}] = \min_{n^M/2 \le n_\alpha^M \le 1} E_X^{R_N}(n_\alpha^M, n^M - n_\alpha^M) \tag{19}$$

The search space $n^M/2 \le n_\alpha^M \le 1$ is equivalent to the constraint $\tilde{\gamma}_{\lceil N \rceil,\alpha}^{R_N} + \tilde{\gamma}_{\lceil N \rceil,\beta}^{R_N} = \gamma_{\lceil N \rceil}^{R_N}$ ($\tilde{\gamma}$ stands for a spin RDM-1 generally different from the one for the reference SD in Eq.(8)). This leads to a definition of XC energy for the fractional molecule using Eqs.(15) and (16):

$$F_{XC(FC)}^{M_N}[\gamma_N^M] = \min_{n^M/2 \le n_\alpha^M \le 1} E_X^{M_N}(n_\alpha^M, n^M - n_\alpha^M) = E_X^{M_N}(1, n^M - 1) \tag{20}$$

The minimizer $n_\alpha^M = 1$ is derived due to the quadratic nature of $E_X^{M_N}(n_\alpha^M, n_\beta^M)$ with respect to the orbital occupancies such that one fractional occupancy is preferred[15]. The corresponding homo spin configuration for $A_\delta$ is $(0, 2-n^M)_2$ that also minimizes the exchange energy on the $A$ side. We refer the corresponding SD for the reference molecule as V-SD, standing for optimized for $V_{ee}$. It represents the maximum localization of opposite spins with a set of orbitals given by KS orbitals local on each side that makes up the RDM-1 $\gamma_{\lceil N \rceil}^{R_N}$ for the whole reference molecule.

A set of trial interacting wavefunctions indexed by $n_\alpha^M$ for $n^M \in (0,1]$ that yields $\gamma_{\lceil N \rceil}^{R_N}$ can also be constructed:

$$\begin{aligned} &\sqrt{\frac{n_\alpha^M}{n^M}} \lceil N \rceil^{-0.5} \det[\varphi_1^\alpha \varphi_1^\beta ... \varphi_M^\alpha \varphi_M^\beta \varphi_h(\alpha)] + i\sqrt{\frac{n^M - n_\alpha^M}{n^M}} \lceil N \rceil^{-0.5} \det[\varphi_1^\alpha \varphi_1^\beta ... \varphi_M^\alpha \varphi_M^\beta \varphi_h(\beta)] \\ &\varphi_h = \sqrt{n^M}\,\varphi_h^M + \sqrt{1-n^M}\,\varphi_h^A \end{aligned}, \tag{21}$$

The nominal exchange energy due to this wavefunction reaches minimum at $n_\alpha^M = n^M$ due to its quadratic nature, resulting in $F_{XC(FC)}^{R_N}[\gamma_{\lceil N \rceil}^{R_N}] = E_X^{R_N}(n^M, 0)$ and $F_{XC(FC)}^{M_N}[\gamma_N^M] = E_X^M(n^M, 0)$. Those two XC

functionals for the reference and fractional molecules, respectively, are continuous for the whole range of $n$:

$$\begin{aligned} F^{R_N}_{XC(FC)}(n^M) &= E^{R_N}_X(\min(1,n^M), n^M - \min(1,n^M)), \\ F^{M_N}_{XC(FC)}(n^M) &= E^{M_N}_X(\min(1,n^M), n^M - \min(1,n^M)), \quad 0 < n \le 2 \end{aligned} \tag{22}$$

From here, we may define a correlation for those molecules as:

$$\begin{aligned} & E^{R_N}_{C(FC)}(n^M) = F^{R_N}_{XC(FC)}(n^M) - E^{R_N}_{EXX}(n^M), \quad E^{M_N}_{C(FC)}(n^M) = F^{M_N}_{XC(FC)}(n^M) - E^{M_N}_{EXX}(n^M) \\ & \forall n^M \in (0,1], \quad E^{M_N}_{C(FC)} = 0; \quad \forall n^M \in (1,2], \quad E^{M_N}_{C(FC)} = -\frac{(2-n^M)^2}{2}\left\langle (\varphi^M_h(\mathbf{r})\varphi^M_h(\mathbf{r}'))^2 \right\rangle_{ee} \end{aligned} \tag{23}$$

The non-positively defined $E^{M_N}_{C(FC)}$ only pertains to the homo and is nonzero only when $n^M > 1$ and one or both spin occupancies are fractional.

The sudden appearance of $E^{M_N}_{C(FC)}$ as $n$ increases through $n = 1$ reflects the quantum effect of electron pairing of two distant electrons in the context of KS noninteracting reference, as the homo occupancy of the reference molecule changes from 1 to 2. Adding an electron in the homo orbital incurs the Coulomb interaction from the one already there. Indeed one may find with some algebraic manipulation that the derivative of $E^{M_N}_{XC(FC)}$ with respect to $n^M$ upshifts by $\left\langle (\varphi^M_h(\mathbf{r})\varphi^M_h(\mathbf{r}'))^2 \right\rangle_{ee}$, the Coulomb energy between the two electrons, as $n^M$ increases through from $n^M = 1$ by an infinitesimal amount. This observation is consistent with the argument based Perdew et al's analysis based on the GCE treatment that the KS XC potential upshifts as the number of electrons is increased by an infinitesimal amount from an integer[3].

We define the remaining XC energy as dynamic correlation (DC):

$$E^{M_N}_{DC}[\rho^M_N] = F_{FC}[N, \rho^M_N] - T_{NI}[\rho^M_N] - E_J[\rho^M_N] - F^{M_N}_{XC(FC)}, \tag{24}$$

where $E_J$ is the classic Hartree energy. $E^{M_N}_{DC}$ is zero when the fractional molecule has one electron or less because Eq.(21) is the exact solution, e.g. the auxiliary atom in a reference molecule. It is negatively defined otherwise because the search in Eq.(19) is conducted in a (small) subset of all possible density matrices. It persists when both spin occupancies are integer. In that case $E^{M_N}_{DC}$ is generally modeled after dynamic electron-electron cusp conditions in contrast to the strong correlation of electrons in distant pairing.

Several additional properties of the XC functionals defined above can be observed as follows:

1. $E^{M_N}_{C(FC)}$ is smaller than $E^{M_N}_{EXX}$ in absolute value.
2. $E^{R_N}_{EXX}$ and $E^{M_N}_{EXX}$ are calculated with the noninteracting wavefunction whereas $E^{R_N}_{C(FC)}$ and $E^{M_N}_{C(FC)}$ are a result of optimization with respect to $V_{ee}$. These correlation terms can thus be viewed as a recovery of the strong correlation of the pair of electrons in the homo and is due purely to the fractional charge. $E_J[\rho^M_N] + F^{M_N}_{XC(FC)}$ is lower-bounded by Levy's universal functional of RDM-1 for the repulsion energy of the reference molecule[17].

3. Eq.(24) offers an example of formal combination of a noninteracting and a strictly correlation solutions. The V-SD may look like some form of spin polarization but it is not a spin DFT solution where the noninteracting kinetic energy functional is defined for each spin density[25]. Instead, it should be viewed as an interacting mean-field basis for an explicit orbital correlation functional for paired electrons that does not result in additional contribution to the kinetic energy since its RDM-1 is same as the noninteracting one.
4. A well-applied property of a SD is that its exchange hole function at a point in space $\mathbf{r}$ (reference point), defined as $-\rho_\sigma(\mathbf{r})^{-1}\gamma_\sigma^2(\mathbf{r},\mathbf{r}')$, integrates to -1 at any point in space over $\mathbf{r}'$ (or the size of the exchange hole size is said to be 1). This is known as the exchange sum rule. The correlation hole on the other hand integrates to zero. Those sum rules do not apply to a fractional molecule. Indeed, one can easily see that the following expression is non-negative:

$$1-\tilde{\rho}_{N,\sigma}^{M}(\mathbf{r})^{-1}\int(\tilde{\gamma}_{N,\sigma}^{M}(\mathbf{r},\mathbf{r}'))^2\,d\mathbf{r}'=(n_\sigma^M-(n_\sigma^M)^2)(\varphi_h^M(\mathbf{r}))^2\,\tilde{\rho}_{N,\sigma}^{M}(\mathbf{r})^{-1} \quad (25)$$

5. Those sum rules, however, are applicable to the reference molecule, i.e. the EXX hole at any reference point in the reference molecule has a size of 1, and its FC correlation hole has a size of 0. This is a formal difference between the EXX and the FC correlation. It means that the EXX hole of any point in the reference molecule is delocalized to both sides in general, and the delocalized portion (the long-range part) belongs to the homo only as shown in Eq.(13). For $N_h=2$, the FC correlation is calculated with the exchange formula and negative, its hole function with a reference point on the $M$ side must be negative in the $M$ domain (short-range), and positive in the $A$ domain (long-range). In the case of $n^M=1+0^+$, the $F_{XC(FC)}^{M_{\lfloor N\rfloor+0^+}}$ is calculated as $E_X^{M_{\lfloor N\rfloor+0^+}}(1,0^+)$ with a hole normalized to 1 in the short-range, meaning that the EXX hole and the FC correlation hole cancel each other asymptotically in the long-range. This normalization is the basis for Becke'05 (B05)[26] and its derivatives Becke'13 (B13)[8] and Kong-Proynov'16/Becke'13 (KP16/B13)[9] functionals. The latter two were shown to work well for covalent bond dissociations.
6. $E_{C(FC)}^{M_N}$ and $E_{EXX}^{M_N}$ are $v$-local (Definition D8) functionals of $\gamma_N^M$ because of the asymptotic decay of the interelectronic Coulomb operator. They are implicit functional of $\rho_N^M$ that determines $\gamma_N^M$ with Eq.(10). In comparison, the interelectronic interaction considered in a local or semi-local functional has a much shorter effective range that depends on the local behavior of electron density[27]. We call this type of locality $d$-local ($d$ stands for density.) [Definition D11].
7. It has been established that an accurate functional should remain constant with respect to the variation of fractional spin occupancies in the homos[28]. The exact exchange and fractional correlation energies defined here trivially satisfy this condition since they are determined by the total density only.

**General treatment of molecular systems with distantly separated densities**

We have established above a DFT method for treating isolated molecules with fractional homo occupancies. A natural follow-up question is what the relationship is between $F_{FC}$ and the exact functional for a non-fractional molecule. Is the exact functional linearly decomposable as $F_{FC}[N_X,\rho_{N_X}^X]+F_{FC}[N_Y,\rho_{N_Y}^Y]$ in analogy to the energy and density for a non-fractional molecule (denoted as $X...Y$) that has two distantly separated sub-molecules $X$ and $Y$? This assumption was cautioned against in literature as numerical experiments showed global behaviors of the KS potential[5]. One is that the KS potential of $X...Y$ has a step-like shape in-between when $X$ is not the same as $Y$ [29-31]. The other is that the exact KS potential has a non-vanishing barrier in the middle between the two covalently

bonded atoms, $X$ being the same as $Y$ or not [31, 32]. This question is the same as the size consistency issue and the latter has been recognized as a challenge to DFT methods, especially with degeneracy[33]. Here we show that the exact functional can be decomposed as a linear sum of local functionals in an asymptotic sense. The application of such a local functional requires a global search in the outer loop of the two-step constrained search together with the $v$-locality constraint.

We start with two distantly separated densities $\rho_{L_X}^{(X)}$ and $\rho_{L_Y}^{(Y)}$ in two locales $X$ and $Y$ with integer numbers of electrons $L_X$ and $L_Y$. One may carry out a separate LL search for each density, with the search spaces denoted as $\Psi_{\rho_{L_X}^{(X)}}(L_X)$ and $\Psi_{\rho_{L_Y}^{(Y)}}(L_Y)$ with density constraint, respectively. For the total density $\rho_{L_X}^{(X)} + \rho_{L_Y}^{(Y)}$, the search space becomes $\Psi_{X..Y}(L_X, L_Y) \equiv \mathscr{A}[\Psi_{\rho_{L_X}^{(X)}}(L_X)\Psi_{\rho_{L_Y}^{(Y)}}(L_Y)]$ when $\rho_{L_X}^{(X)}$ and $\rho_{L_Y}^{(Y)}$ do not overlap. Assuming $X$ and $Y$ are separated beyond the AIND, the LL search for $\rho_{L_X}^{(X)} + \rho_{L_Y}^{(Y)}$ becomes:

$$\begin{aligned} F_{LL}[L_X + L_Y, \rho_{L_X}^{(X)} + \rho_{L_Y}^{(Y)}] &\equiv \min_{\Psi_{X..Y}(L_X, L_Y) \to \rho_{L_X}^{(X)} + \rho_{L_Y}^{(Y)}} \left\langle \Psi_{X..Y}(L_X, L_Y) \middle| T + V_{ee} \middle| \Psi_{X..Y}(L_X, L_Y) \right\rangle \\ &\cong \min_{\Psi_{\rho_{L_X}^{(X)}}, \Psi_{\rho_{L_Y}^{(Y)}}} \left( \left\langle \Psi_{\rho_{L_X}^{(X)}} \middle| T + V_{ee} \middle| \Psi_{\rho_{L_X}^{(X)}} \right\rangle + \left\langle \Psi_{\rho_{L_Y}^{(Y)}} \middle| T + V_{ee} \middle| \Psi_{\rho_{L_Y}^{(Y)}} \right\rangle \right) = F_{LL}[L_X, \rho_{L_X}^{(X)}] + F_{LL}[L_Y, \rho_{L_Y}^{(Y)}] \end{aligned} \tag{26}$$

The second equality $\cong$ uses the size-consistency condition.

A functional for the molecule $X...Y$ needs to include the case of degeneracy where $\rho^X$ and $\rho^Y$ can be of fractional charge. We have shown such a universal functional of such a density, namely $F_{FC}$, with a search space defined in Eq.(5). We may combine the wavefunctions in the search spaces of $\rho_{N_X}^{(X)}$ and $\rho_{N_Y}^{(Y)}$, $N_X$ and $N_Y$ being positive and real, to construct the search space for $\rho_{N_X}^{(X)} + \rho_{N_Y}^{(Y)}$ as follows ($D_{X..Y}(L_X, L_Y)$ defined as $\left|\Psi_{X..Y}(L_X, L_Y)\right\rangle\left\langle\Psi_{X..Y}(L_X, L_Y)\right|$):

$$\begin{aligned} &(1-\delta_X)(1-\delta_Y) D_{X..Y}(\lceil N_X \rceil, \lceil N_Y \rceil) + (1-\delta_X)\delta_Y D_{X..Y}(\lceil N_X \rceil, \lfloor N_Y \rfloor) + \\ &\delta_X (1-\delta_Y) D_{X..Y}(\lfloor N_X \rfloor, \lceil N_Y \rceil) + \delta_X \delta_Y D_{X..Y}(\lfloor N_X \rfloor, \lfloor N_Y \rfloor) \end{aligned} \tag{27}$$

A universal functional can then be constructed by taking the trace of Eq.(27) with $T + V_{ee}$, resulting in the following expression with the application of the size consistency condition (C4):

$$F_{FC}[N_X, \rho_{N_X}^{(X)}] + F_{FC}[N_Y, \rho_{N_Y}^{(Y)}] \tag{28}$$

We name the sum as $F_{FC}$, i.e. $F_{FC}$ now includes cases where the input density contains distantly separated pieces and each piece integrates to a non-integer. The total number of electrons ($N_X + N_Y$) does not need to be an integer as such a system can always be assumed to be part of a system with integer number of electrons that has distantly separated pieces. $F_{FC}$ becomes $F_{LL}$ (Eq.(26)) when those pieces of density integrate to integers.

When a non-fractional molecule has two locales of nuclei distant from each other, its electron density is distributed around those two locales. $F_{FC}$ can be applied in each locale with the $v$-locality constraint, but the outer loop of the Levy's two-step constrained search needs to be divided into two sub-steps, with

the outer sub-step being the search of the number of electrons, which can be non-integer, at each locale in order to cover all possible densities:

$$\begin{aligned} E_L^{X..Y} &\cong \min_{\rho_{N_X}^{(X)}+\rho_{L-N_X}^{(Y)}} (F_{FC}[L, \rho_{N_X}^{(X)} + \rho_{L-N_X}^{(Y)}] + \int (\rho_{N_X}^{(X)} + \rho_{L-N_X}^{(Y)})(v_X + v_Y)) \\ &= \min_{N_X}(\min_{\rho_{N_X}^{(X)}}(F_{FC}[\rho_{N_X}^{(X)}, N_X] + \int \rho_{N_X}^{(X)} v_X) + \min_{\rho_{N_Y}^{(Y)}}(F_{FC}[\rho_{L-N_X}, L-N_X] + \int \rho_{L-N_X} v_Y)) \\ &= E_{N_X^*}^X + E_{L-N_X^*}^Y \end{aligned} \tag{29}$$

$N_X$ in the equation is real and $N_X^*$ is the minimizer of the outer loop. When $N_X^*$ is found to be in a range between two consecutive non-negative integers, the system is degenerate. Each sub-molecule can be treated as an isolated fractional molecule. The reference molecule of a fractional molecule is a special case of this degeneracy. Another example often discussed in literature is homonuclear diatomic cations $A_2^+$ ($L$ is odd) in the context of charge-delocalization errors[34]. The FC XC ($F_{XC(FC)}$) turns into the EXX and fully accurate for A=Hydrogen with the EXX hole function distributed on both sides.

When $N_X^*$ is found to be an integer only, the following relations hold $I(X_{N_X^*}) > A(Y_{L-N_X^*}), A(X_{N_X^*}) < I(Y_{L-N_X^*})$. When $L$ is odd or both $L$ and $N_X^*$ are even, one or both subsystems are closed-shell and each subsystem can be treated as an ordinary isolated molecule with integer occupancies. When $L$ is even and $N_X^*$ is odd, the bond being stretched is a covalent single bond and the KS homo on each sub-molecule has a spin configuration of $(\uparrow_2, \downarrow_2)_2$ (or more precisely $(\uparrow_2(1+0^+), \downarrow_2(1+0^+))_2$). The EXX hole function at any reference point is distributed on both sides. This type of problem exhibits some of the strongest nondynamic correlation in a molecular system ($E_{C(FC)}^{M_N}$ has the largest absolute value at $n=1$ in Eq.(23)). Application of $F_{XC(FC)}^{M_N}$ treats each dissociated sub-molecule as an isolated doublet system appropriately.

The outer loop over the number of electrons in Eq.(26) does not need to be carried explicitly in practice for the calculation of the total energy of $X..Y$ when $N_X^*$ can be determined otherwise, i.e. with the ionization potential (IP) and electron affinity (EA) data or reasonable estimation of their relative differences. It is however necessary to explain the step-like shape of the KS potential in-between $X$ and $Y$. This is because the variation of the total density $\rho_{N_X}^{(X)} + \rho_{N_Y}^{(Y)}$ involves the variation of $N_X$. The derivative of the energy of each sub-molecule with respect to the variation of its number of electrons determines its IP and EA per Janak theorem[3, 12]. Those quantities of the two sub-molecules together determine the step-like shape of the KS potential. This shows the global nature of the density search of Eq.(26). On the other hand, the variation of $N_X$ does not explain the non-vanishing middle barrier of the exact KS potential between two infinitely separated covalently bonded atoms. This barrier is numerically insignificant but qualitatively represents the entanglement of distant electrons. It is missing from the local treatment prescribed by Eqs.(28) and (29), an accurate asymptotic solution to a molecular system. This solution differs from the exact one in two ways: (a) An exact electron density is above zero everywhere in the universe due to the unique continuation property of an electronic wavefunction[18], i.e. it is not exactly separable; (b) The ANDI condition is an approximation. We note that Eq.(29) can be trivially extended to a system with more than two distantly separated sub-molecules and the total number of electrons being non-integer.

**Consideration of not distantly separated densities**

In practice, the size-consistency condition is often approximately satisfied when the densities are deemed separated subject to a threshold and sub-molecules retain almost all the traits of isolated molecules (This approximation ignores intermolecular electronic effects include static and dynamic polarizations). We symbolize this system as $X.Y$. Such a separation distance is much shorter than the AIND because the density decays much faster than the Coulombic potential, indicating that the $d$-locality (Definition D11) is largely valid. Indeed, the search domain for an isolated molecule in Eq.(6) can be made smaller than the $v$-domain (Definition D7) without losing accuracy by extending the radius of the sphere encompassing the nuclei to where the density vanishes subject to a threshold. (This smaller domain is different from the $d$-domain but the difference is inconsequential to our discussions here and is ignored for now.) It follows that the $F_{FC}$ and $T_{NI}$ can be defined for this smaller domain. On the other hand, the EXX ($E_{EXX}^{M_N}$) and FC correlation ($E_{C(FC)}^{M_N}$) are formally $v$-local. They become $d$-local when $N_X^*$ is found to be integer only and the EXX spin configuration is of integer occupations. Otherwise, they must contain certain cancellation effect for the interelectronic interaction outside of the $d$-local range.

There are two types of cancellation, namely the stretched covalent single bond and the stretched symmetric doublet ($X.X$). In the first case, the doubly occupied KS homo of the system is split between $X$ and $Y$ sides, each with a formal spin configuration of $(½, ½)_2$ in their own homo's, and the total effective FC XC energy calculated as $E_X^{X_{N_X^*}}(1,0) + E_X^{Y_{N_Y^*}}(1,0)$. This means that the hole functions of the EXX and correlation cancel each other in the long-range as analyzed previously and the total FC XC hole is local to each sub-molecule. A numerical example was shown for stretched $H_2$ molecule[35]. In the second case, the KS homo of the system is singly occupied. $F_{XC(FC)}$ is the EXX energy only, and EXX holes are delocalized on both sides. However, the delocalized portion is from the homo only as analyzed earlier and the exchange within the homo is exactly canceled by self-Hartree interaction, i.e. $E_J$ cancels the major part of delocalized EXX. The dominating $d$-local character of $F_{XC(FC)}$ means that the dynamic correlation is largely $d$-local.

**Examples of fractional charge**

The challenge of the fractional charge problem is often illustrated by systems with one and two electrons. One well-designed example[6] is a cluster of eight geometrically equivalent H nuclei placed very far from each other with the number of electrons ranging from 0 to two per H. Full configuration interaction calculations of this system with a minimum basis set showed the energy surface being flat with respect to the variations of number of electrons and their spins, with a straight ridge along the line of eight electrons (one per H). This flat-plane condition is obvious but not satisfied by any approximate functional.

We may treat this cluster as eight equivalent H atoms with each H modeled as $v$-local with $(n_\alpha, n_\beta)$ occupancies, following the size-consistency condition. H and $H^-$ obviously satisfies the nondegeneracy condition (C2). One can see that $E^F_{XC(FC)}$ applied to the so-constructed H atom satisfies this flat-plane condition trivially. The energy surface with respect to $(n_\alpha, n_\beta)$ is flat since the orbital (and thus $\gamma^M$) does not change with the minimum basis and $E^F_{XC(FC)}$ is a function of $n_\alpha + n_\beta$. When $n_\alpha + n_\beta \le 1$, $J + E^M_{XC(FC)} = 0$. When $n_\alpha + n_\beta > 1$, $J + E^F_{XC(FC)}$ becomes the Coulomb energy between one $\alpha$ electron and $(n-1)$ $\beta$ electron, causing a ridge at $n = 1$. This sudden appearance of the Coulomb interaction is the driving force for the derivative discontinuity at $n = 1$ due to the addition of an electron as shown in Eq.(23). (Note that $E_{DC}$ is suppressed since the orbital stays the same for one and two electrons with the minimum basis.) Fig. 1 shows the errors with several contemporary functionals along the line of $(\frac{1}{2}n, \frac{1}{2}n)$, especially with the relatively new KP16/B13[9]. The latter represented an advance in DFT in treating strong correlation because it yielded the exact result for $(\frac{1}{2}, \frac{1}{2})_2$ for a single H, but still fails when $n > 1$ because of the application of the standard exchange-correlation sum rules.

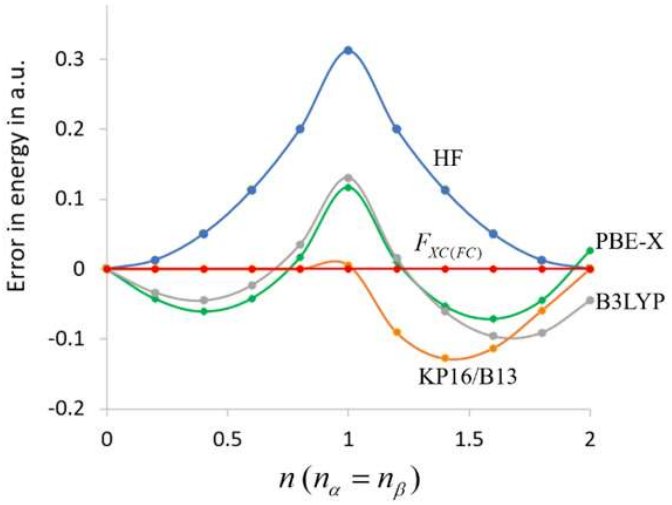


Figure 1. The comparison of various DFT functionals for H atom with fractional occupancies with a minimum basis.

Fig.2 shows the DFT components of the energy with a better approximated fractional density for $1 \le n \le 2$. The system is an ensemble of $He^+$ and He, with the densities of the two states calculated with Hartree-Fock (HF) plus the Becke-Roussel'94 (BR94) correlation functional[36] with a large basis set. The data shown are relative to the straight line between the two end points ($n$ at 1 and 2) for each component. The convexity of the Hartree and kinetic energies and the concavity of the exact exchange and FC correlation energies are to be expected. These two opposite effects largely cancel each other, and their total sum (red line) is somewhat concave, showing that the dynamic correlation needs to be convex to balance it in order to achieve linearity. Just as a reference point, the green line shows the correlation energy calculated with BR94. It has the desired convexity although it does not fully compensate the red line.

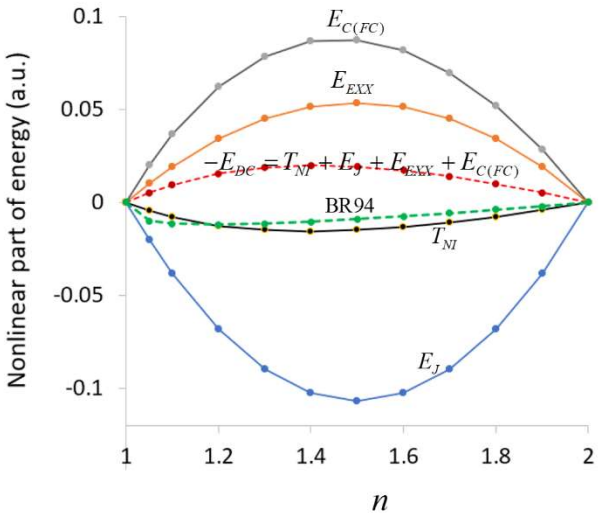


Figure 2. The components of the DFT energy for He atom with fractional occupancy from 1 to 2.

**Conclusions and perspectives**

The main results of the present development are summarized in the introduction. An alternative route of derivation is to start with the size consistency problem and define the fractional molecule as a special case. Either way, three basic assumptions need to be used, namely the non-degeneracy (Condition C2), the convexity of molecular energy (Condition C3) and the extended KS assumption (Condition C5). The latter amounts to an assumption that the KS potential of the reference molecule can be decomposed into the local ones and leads to the definition of EXX and FC correlation for the reference and fractional molecules. The application of the KS assumption to a degenerated system may be questionable in general because the functional derivative with respect to the density becomes problematic[37]. This problem is circumvented for the reference molecule by parameterizing the universal functional with the quantum number for the degeneracy ( $\delta$ ), which ensures the applicability of noninteracting solution for each $\delta$ (Eq.(10)) in principle. A proper solution of Eq.(10) requires another assumption about the continuity of the shape of the KS orbitals as the number of electrons passing through an integer, which admits a constant shift in the XC potential due to the derivative discontiuity.[3, 23] This issue needs further detailed investigations.

The development in this paper focuses on wavefunction-representable densities (Condition C2). It can be applied to more general ensemble-representable densities in principle by replacing the Levy-Lieb functional with Lieb functional[18, 19] for the derivation of $F_{FC}$. The arguments for the $v$ -locality (Eq.(6)) and size-consistency (Eqs.(28) and (29)) still hold. However, such an extension will incur an additional approximation that ignores the possible break of the degeneracy that may exist in a subsystem. An example of such a scenario can be found in ref[38].

Finally, we note that the size-consistency condition for a wavefunction method in analogy to Eq.(29) may be written as:

$$E_L^{X..Y} = \min_{L_X}(E_{L_X}^X + E_{L-L_X}^Y), \tag{30}$$

where $L$ and $L_X$ are integers. Fractional charges in subsystems may occur by state mixing when a degeneracy over $L_X$ happens. A possible alternative route to obtain the universal functional for such a system could be to use the Legendre transform of the RHS of this equation in Lieb's fashion[19] with the $v$ -

locality constraint applied to $\int \rho v$. It is probably sufficient to search all the $v$'s in the two distantly separated locales encompassing the density.

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