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Functional derivative of the universal density functional in Fock space

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Within the framework of zero-temperature Fock-space density-functional theory (DFT), we prove that the Gâteaux functional derivative of the universal density functional, $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_0}$, at ground-state densities with arbitrary normalizations $(\langle\rho_0(\boldsymbol{r})\rangle = n \in \mathcal{R}_+)$ and an electron-electron interaction strength λ, is uniquely defined, but is discontinuous when the number of electrons n becomes an integer, thus providing a mathematically rigorous confirmation for the "derivative discontinuity" initially discovered by Perdew *et al.* [Phys. Rev. Lett. **49**, 1691 (1982)]. However, the functional derivative of the exchange-correlation functional is continuous with respect to the number of electrons in Fock space; i.e., there is no "derivative discontinuity" for the exchange-correlation functional at an integer electron number. For a ground-state density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ of an external potential $v(\boldsymbol{r})$, we show that $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}^{v,\lambda}} = \mu_{\mathrm{SM}}^{n} - v(\boldsymbol{r})$, where the constant μ_{SM}^{n} is given by the following chain of dependences: $\rho_{0,n}^{v,\lambda}(\boldsymbol{r}) \mapsto [v] \mapsto E_0^{v,\lambda}(n) \mapsto \mu_{\mathrm{SM}}^{n} = \partial E_0^{v,\lambda}(k)/\partial k|_{k=n}$. Here $[v]$ is the class of the external potential $v(\boldsymbol{r})$ up to a real constant, and μ_{SM}^{n} is the chemical potential defined according to statistical mechanics. At an integer electron number N, we find that there is no freedom of adding an arbitrary constant to the value of the chemical potential μ_{SM}^{N}, whose exact value is generally not the popular preference of the negative of Mulliken's electronegativity, $-\frac{1}{2}(I+A)$, where I and A are the first ionization potential and the first electron affinity, respectively. In addition, for any external potential converging to the same constant at infinity in all directions, we resolve that $\mu_{\mathrm{SM}}^{N} = -I$. Finally, the equality $\mu_{\mathrm{DFT}} = \mu_{\mathrm{SM}}^{n}$ is rigorously derived via an alternative route, where μ_{DFT} is the Lagrangian multiplier used to constrain the normalization of the density in the traditional DFT approach.

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I. INTRODUCTION

The functional derivative of the universal density functional $F[\rho]$ plays an important role in density-functional theory (DFT) [1–55].

On the one hand, mathematical theorems of the existence of this functional derivative at ensemble v-representable densities of wave functions in an N-particle Hilbert space[1] were proved by Englisch and Englisch [10], by Lieb [11], by van Leeuwen [12], and by Lindgren and Salomonson [13]. An important technical feature in their approaches is the fixed number of electrons [7–13], although the normalization of the density during the variation can vary [10–13]. There is an explicit method for keeping the normalization of the density fixed [7,14], but it has not been extensively used in DFT.

On the other hand, the traditional method of imposing the normalization is a subtle one [7,13]. During the variation of the density-functional energy expression, the normalization of the density $\rho(\boldsymbol{r})$ is allowed to vary, with an additional Lagrangian multiplier term to account for the constraint to an integer electron number N at the final stationary point:

$$F[\rho] + \langle v(\boldsymbol{r})\rho(\boldsymbol{r})\rangle + \mu_{\mathrm{DFT}}\big[\langle\rho(\boldsymbol{r})\rangle - N\big], \tag{1}$$

where $\langle f(\boldsymbol{r})\rangle$ is a shorthand integration notation of a function $f(\boldsymbol{r})$ over the entire space of $\boldsymbol{r}, \int f(\boldsymbol{r})d\tau$. It is tacitly assumed that the functional derivative

$$\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})} \tag{2}$$

exists for the expanded variational domain, while referring to the above-mentioned theorems for a fixed number of electrons in Hilbert space [10–13].

If the Lagarange multiplier method is used, the universal density functional should be defined for densities with an arbitrary normalization, corresponding to wave functions in Fock space, where the above-mentioned theorems of Hilbert space are not directly applicable. Thus, the traditional justification of the Euler-Lagrange equation in DFT is logically inconsistent, because the forms and properties of the various density functionals might be different in Fock and Hilbert spaces.

There are several motivating examples beyond the justification of the Euler-Lagrange equation. A variable normalization of the density reflects a physical situation with a variable number of electrons. In the DFT literature, there are several results related to the notion of functional derivatives that are of questionable validity, from a mathematical point of view: the "exchange-correlation derivative discontinuity" [16–30], the so-called "Janak's theorem" [31–37], the set of homogeneity relations "proved" by Parr and Liu [41,42], and the

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[1] Hereafter for convenience, *Hilbert space* will be used to signify any formulation built upon wave functions of a fixed number of particles, while *Fock space* will be utilized to describe other formalisms constructed from wave functions of a varied number of particles. Technically speaking, the fermionic Fock space $\mathcal{F}_f$ is a fermionic Hilbert space made from the direct sum of antisymmetrized tensor products $\mathcal{H}^N$ of the single-particle Hilbert spaces $\mathcal{H}$ [56]: $\mathcal{F}_f \equiv \oplus_{N=0}^{\infty}\mathcal{H}^N$, with $\mathcal{H}^N \equiv \hat{A}\mathcal{H}^{\otimes N}$ for the antisymmetrizer $\hat{A}$.

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value of the chemical potential [7,12–17,42–48]. Concerns were raised in all of the three cases, but the analysis was perplexed due to the unknown nature of the functional derivative in Fock space [13,37,41].

Particularly, the so-called "exchange-correlation derivative discontinuity" has drawn quite considerable attention recently [16–30]. In the past, there was an earlier attempt to construct a discontinuous functional by Levy and co-workers [16]. Later, an alternative nonvariational approach became popular, in which one would try to directly incorporate the *assumed* discontinuous behavior into the exchange-correlation potential. The major proponents of this later approach are Tozer and co-workers [25], Casida and co-workers [26], and Baerends and co-workers [27]. Although these types of exchange-correlation potential often have empirical parameters, they are of paramount importance in time-dependent DFT, response property, and NMR shielding constant calculations and in obtaining the exchange-correlation potential from the density [25–30]. The works by Tozer and others [25–30] further suggest that the *real* exchange-correlation density energy functionals should be designed such that their approximate exchange-correlation potentials should average between the electron-deficient and electron-abundant limits, in accordance with the very *special* value of the chemical potential as being the negative of Mulliken's electronegativity [7,15–17,36,48,57,58]. Unfortunately, there are already at least six different values for the chemical potential within the present DFT framework [7,12–17,42–48]. Moreover, the backbone of the "exchange-correlation derivative discontinuity" arguments [16–30] relies heavily on the exact value of the chemical potential. Naturally, one would like to ask the following questions: Which one is the exact value for the chemical potential? Does the exact value for the chemical potential differ from the one commonly employed in the theory of the "exchange-correlation derivative discontinuity" [16–30]? What are the consequences if they are indeed distinct?

We set up our goal to resolve all of these issues in this paper. In the following sections, we will adopt the finite-temperature generalization of DFT [4] to fractional electron numbers [18–23,38–40], and based on this, we will extend the results of Englisch and Englisch [10], Lieb [11], van Leeuwen [12], and Lindgren and Salomonson [13] from Hilbert space to Fock space. In the end, our arguments will unambiguously provide a comprehensive, coherent, and consistent understanding of the functional derivative in Fock space, the value of the chemical potential, and the functional derivative discontinuity.

II. TRADITIONAL HILBERT-SPACE DFT

The spinless ensemble density matrix for N electrons is[2]

$$\hat{D}_N = \sum_{\sigma_1,\ldots,\sigma_N} \sum_{p=1}^{\infty} c_p |\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\rangle\langle\Psi_p(\boldsymbol{r}_1'\sigma_1,\ldots,\boldsymbol{r}_N'\sigma_N)|, \tag{3}$$

where $\{\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\}$ are normalized N-electron wave functions with electron i at position $\boldsymbol{r}_i$ with spin σ_i and typically all but a finite number of the coefficients $\{c_p\}$ are zero. In addition,

$$\sum_{p=1}^{\infty} |c_p|^2 = 1. \tag{4}$$

In the following, density matrices are used instead of wave functions to account for possible degeneracies [5,6,11,12]. The kinetic, electron-electron repulsion, and nuclear-electron attraction operators for N electrons are

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N} \boldsymbol{\nabla}_i^2 = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right), \tag{5}$$

$$\hat{V}_{ee} = \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}, \tag{6}$$

and

$$\hat{V}_{ne}^{v} = \sum_{i=1}^{N} v(\boldsymbol{r}_i), \tag{7}$$

respectively. For generality, we will allow the electron-electron interaction to be of an arbitrary strength λ between 0 and 1, and we will only consider those total electronic Hamiltonians

$$\hat{H}^{v,\lambda} = \hat{T} + \lambda\hat{V}_{ee} + \hat{V}_{ne}^{v}, \tag{8}$$

which have eigenvalues bounded from below.

The universal density functional $F^{\lambda}[\rho_N]$ with an electron-electron interaction strength λ is defined by Levy's constrained search method [5,6,11,12] as

$$F^{\lambda}[\rho_N] = \inf_{\hat{D}_N\to\rho_N} F^{\lambda}[\hat{D}_N] = \inf_{\hat{D}_N\to\rho_N} \mathrm{Tr}\Big[\big(\hat{T}+\lambda\hat{V}_{ee}\big)\hat{D}_N\Big], \tag{9}$$

where the universal density-matrix functional $F^{\lambda}[\hat{D}_N]$ with an electron-electron interaction strength λ is defined as

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[2] The Dirac notation will be used wherever possible, unless otherwise noted.

$$\begin{aligned} F^{\lambda}[\hat{D}_N] &= \mathrm{Tr}\Big[\Big(\hat{T}+\lambda\hat{V}_{ee}\Big)\hat{D}_N\Big] \\ &= \sum_{p=1}^{\infty}|c_p|^2\Bigg\{-\frac{1}{2}\sum_{i=1}^{N}\langle\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)|\boldsymbol{\nabla}_i^2|\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\rangle \\ &\quad+\lambda\sum_{i=1}^{N}\sum_{j>i}^{N}\left\langle\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\left|\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\right|\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\right\rangle\Bigg\}. \end{aligned} \tag{10}$$

The expression

$$\hat{D}_N \to \rho_N \tag{11}$$

under the sign of infimization in Eq. (9) means that the search in the density matrices $\hat{D}_N$ is constrained to those yielding a given density $\rho_N(\boldsymbol{r})$:

$$\rho_N(\boldsymbol{r}) = \mathrm{Tr}\Big[\hat{\rho}_N(\boldsymbol{r})\hat{D}_N\Big] = \sum_{p=1}^{\infty}|c_p|^2\left\langle\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\left|\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\right|\Psi_p(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\right\rangle, \tag{12}$$

where $\hat{\rho}_N(\boldsymbol{r})$ is the N-particle density operator, $\Sigma_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{r}_i)$.

Finally, the DFT variational principle gives the ground-state energy for a given external potential $v(\boldsymbol{r})$:

$$E_{0,N}^{v,\lambda} = \min_{\rho_N}\Big\{F^{\lambda}[\rho_N]+V_{ne}^{v}[\rho_N]\Big\} = F^{\lambda}[\rho_{0,N}^{v,\lambda}]+V_{ne}^{v}[\rho_{0,N}^{v,\lambda}], \tag{13}$$

where the nuclear-electron attraction energy density functional is

$$V_{ne}^{v}[\rho_N] = \langle v(\boldsymbol{r})\rho_N(\boldsymbol{r})\rangle, \tag{14}$$

and $\rho_{0,N}^{v,\lambda}(\boldsymbol{r})$ is the ground-state density, which determines the ground-state density matrix $\hat{D}_{0,N}^{v,\lambda}$ through Eq. (9). As shown by Lieb [11] and van Leeuwen [12], one can write the *same* universal density functional in Eq. (9) alternatively as the Legendre transform functional [1,2,11,12]

$$F^{\lambda}[\rho_N] = \sup_{v}\Big\{E_{0,N}^{v,\lambda}-V_{ne}^{v}[\rho_N]\Big\}, \tag{15}$$

where the supremum will become a maximum for a ground-state density $\rho_{0,N}^{v,\lambda}(\boldsymbol{r})$:

$$\begin{aligned} F^{\lambda}[\rho_{0,N}^{v,\lambda}] = F_{\mathrm{HK}}^{\lambda}[\rho_{0,N}^{v,\lambda}] &= \max_{u}\Big\{E_{0,N}^{u,\lambda}-V_{ne}^{u}[\rho_{0,N}^{v,\lambda}]\Big\} \\ &= E_{0,N}^{v,\lambda}-V_{ne}^{v}[\rho_{0,N}^{v,\lambda}]. \end{aligned} \tag{16}$$

Obviously, Eq. (16) is a simple restatement of the DFT variational principle shown in Eq. (13), and the maximum of Eq. (16) is also called as the Hohenberg-Kohn (HK) density functional, $F_{\mathrm{HK}}^{\lambda}[\rho_{0,N}^{v,\lambda}]$, defined only for ground-state densities [1,11,12].

In Refs. [10–13,59], the analytical properties of the density and the external potential used in DFT are carefully evaluated. We will assume the same analytical behavior as in Refs. [10–13,59] and will not go into a detailed consideration of the possible analytical subtleties involved, except to say the following.

For the density $\rho(\boldsymbol{r})$, we will assume that it belongs to the Banach space $\mathcal{Y}\equiv\mathcal{L}^3\cap\mathcal{L}^1$ and, of course, it should be nonnegative. More precisely, we require that the density belongs to $\mathcal{J}\equiv\{\rho(\boldsymbol{r})\,|\,\rho(\boldsymbol{r})\geqslant 0,\rho(\boldsymbol{r})\in\mathcal{L}^1,\text{ and }\boldsymbol{\nabla}\sqrt{\rho(\boldsymbol{r})}\in\mathcal{L}^2\}$, which is a convex subset of $\mathcal{Y}$ [11,12]: $\mathcal{J}\subset\mathcal{Y}$. For the external potential $v(\boldsymbol{r})$, we will assume that it belongs to the dual space of $\mathcal{Y}$, which again is a Banach space $\mathcal{Y}^*\equiv\mathcal{L}^{3/2}+\mathcal{L}^{\infty}$. This means that any external potential could always be partitioned into two parts: $v(\boldsymbol{r})=v_{3/2}(\boldsymbol{r})+v_{\infty}(\boldsymbol{r})$, where the first part belongs to $\mathcal{L}^{3/2}$ and the second part belongs to $\mathcal{L}^{\infty}$. $\mathcal{L}^{b}$ is a Banach space with a norm $\|f\|_b=\langle|f(\boldsymbol{r})|^b\rangle^{1/b}<\infty$. Here, $\mathcal{L}^{\infty}$ is the Banach space of bounded functions, with the norm $\|f\|_{\infty}=\operatorname{ess\,sup}|f(\boldsymbol{r})|<\infty$, where the *essential* supremum is the smallest upper bound of $|f(\boldsymbol{r})|$ *almost everywhere* [60]. In particular, ground-state densities of some external potentials in $\mathcal{Y}^*$ are everywhere positive due to the unique continuation theorem [11,61].

III. ZERO-TEMPERATURE FOCK-SPACE DFT

In the case of a fractional number of electrons[3]—say, $n\in[N,N+1)$—we take the zero-temperature limit of Mermin's finite-temperature DFT [4,17] and define the universal density functional as[4]

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[3] Throughout this entire paper, uppercase italic Roman characters (e.g., N and M) will be used exclusively to represent any nonnegative integers, while lowercase italic Roman characters (e.g., n and m) will be employed to freely denote either fractions or integers. In addition, n and N have the generic relationship: $n\in[N,N+1)$, unless otherwise noted.

[4] The equivalency between these two definitions will be proved in the lemma in Sec. V.

$$F^{\lambda}[\rho_n] = \inf_{(N+1-n)\hat{D}_N+(n-N)\hat{D}_{N+1}\rightarrow\rho_n} \left\{(N+1-n)F^{\lambda}[\hat{D}_N] + (n-N)F^{\lambda}[\hat{D}_{N+1}]\right\} = \inf_{(N+1-n)\rho_N+(n-N)\rho_{N+1}=\rho_n} \left\{(N+1-n)F^{\lambda}[\rho_N] + (n-N)F^{\lambda}[\rho_{N+1}]\right\}, \quad (17)$$

where $\hat{D}_N \rightarrow \rho_N, \hat{D}_{N+1} \rightarrow \rho_{N+1}$, and

$$\hat{D}_n = (N+1-n)\hat{D}_N + (n-N)\hat{D}_{N+1} \rightarrow (N+1-n)\rho_N + (n-N)\rho_{N+1} = \rho_n, \quad (18)$$

respectively.

In general, one should define $F^{\lambda}[\rho_n]$ in Fock space $\mathcal{F}_f$ [56] with all possible linear combinations of density matrices $\{\hat{D}_N | N \in \mathcal{N}\}$ built from antisymmetric wave functions in fermionic Hilbert spaces of an arbitrary integral number of particles $\{\mathcal{H}^N | N \in \mathcal{N}\}$. However, using the same arguments presented by Parr and Yang [7], one can readily show that the infimum of convex sums of all possible Hilbert-space universal density functionals $\{F^{\lambda}[\rho_N] | N \in \mathcal{N}\}$ [similar to the right-hand side (RHS) of Eq. (17)] will only single out the linear combinations of those density matrices constructed from wave functions in the two adjacent Hilbert spaces $\mathcal{H}^N$ and $\mathcal{H}^{N+1}$ for $n \in [N, N+1)$. In the end, the definition of $F^{\lambda}[\rho_n]$ in Eq. (17) is fully equivalent to the more general grand canonical ensemble formulation [5–7,17,18] and the zero-temperature limit of Mermin's finite-temperature DFT [4,17,18]. Hence, we use "zero-temperature Fock-space DFT" interchangeably for any of the above-mentioned three formulations.

In the following, we prove two Hohenberg-Kohn-like theorems within zero-temperature Fock-space DFT.

Theorem 1. For a fixed arbitrary electron-electron interaction strength λ, there is a mapping between an ensemble v-representable density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ and its external potential:

$$\rho_{0,n}^{v,\lambda}(\boldsymbol{r}) = (N+1-n)\rho_{0,N}^{v,\lambda} + (n-N)\rho_{0,N+1}^{v,\lambda} \mapsto [v], \quad (19)$$

where $[v]$ is the class of the external potential $v(\boldsymbol{r})$ up to a real constant $\{u(\boldsymbol{r}) | u(\boldsymbol{r}) = v(\boldsymbol{r}) + C, \text{ and } C \in \mathcal{R}\}$. Moreover, this mapping is continuous with respect to the electron number n.

Proof. First of all, the variational principle in Hilbert space for N and $(N+1)$ electrons dictates

$$\min_{\hat{D}_n=(N+1-n)\hat{D}_N+(n-N)\hat{D}_{N+1}\rightarrow\rho_{0,n}^{v,\lambda}} \left\{(N+1-n)F^{\lambda}[\hat{D}_N] + (n-N)F^{\lambda}[\hat{D}_{N+1}]\right\} + V_{ne}^{v}[\rho_{0,n}^{v,\lambda}] = \left\{(N+1-n)F^{\lambda}[\hat{D}_{0,N}^{v,\lambda}] + (n-N)F^{\lambda}[\hat{D}_{0,N+1}^{v,\lambda}]\right\} + V_{ne}^{v}[\rho_{0,n}^{v,\lambda}] = E_{0,n}^{v,\lambda}, \quad (20)$$

where the minimal energy $E_{0,n}^{v,\lambda}$ is achieved at an ensemble v-representable density matrix $\hat{D}_{0,n}^{v,\lambda} = (N+1-n)\hat{D}_{0,N}^{v,\lambda} + (n-N)\hat{D}_{0,N+1}^{v,\lambda}$, such that both $\hat{D}_{0,N}^{v,\lambda}$ and $\hat{D}_{0,N+1}^{v,\lambda}$ are ground-state density matrices of some external potential $v(\boldsymbol{r})$ with N and $(N+1)$ electrons, respectively. The corresponding ensemble v-representable density is denoted by $\rho_{0,n}^{v,\lambda} = (N+1-n)\rho_{0,N}^{v,\lambda} + (n-N)\rho_{0,N+1}^{v,\lambda}$. There could not be any other alternative solutions and the energy cannot get any lower as it would contradict the minimality of $\hat{D}_{0,N}^{v,\lambda}$ for N electrons and of $\hat{D}_{0,N+1}^{v,\lambda}$ for $(N+1)$ electrons. Equation (20) defines the mapping of the given ensemble v-representable density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ to its ground-state density matrix $\hat{D}_{0,n}^{v,\lambda}$:

$$\rho_{0,n}^{v,\lambda}(\boldsymbol{r}) \mapsto \hat{D}_{0,n}^{v,\lambda}. \quad (21)$$

The next step [49] is to take either of the occupied components of $\hat{D}_{0,n}^{v,\lambda}$—say, the N-electron component $\hat{D}_{0,N}^{v,\lambda}$—and invert the Schrödinger equation,[5]

$$\sum_{i=1}^{N} v(\boldsymbol{r}_i) - E_{0,N}^{v,\lambda} = -\frac{(\hat{T} + \lambda\hat{V}_{ee})\hat{D}_{0,N}^{v,\lambda}}{\hat{D}_{0,N}^{v,\lambda}}, \quad (22)$$

then equate $(N-1)$ of the independent variables to some constants, but such that the potential at these values is nonsingular—say, $\boldsymbol{r}_i = \boldsymbol{r}_{0i}$ $(i = 1, 2, \ldots, N-1)$—and denote the one remaining independent variable as $\boldsymbol{r} = \boldsymbol{r}_N$. The left-hand side (LHS) of Eq. (22) becomes $\{v(\boldsymbol{r}) + C | C \in \mathcal{R}\}$, thus yielding the mapping

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[5] One can also take the *occupied* $(N+1)$-electron component $\hat{D}_{0,N+1}^{v,\lambda}$ of $\hat{D}_{0,n}^{v,\lambda}$ and reach the same conclusion.

$$\hat{D}_{0,n}^{v,\lambda} \mapsto [v]. \tag{23}$$

The combination of mappings in Eqs. (21) and (23) constructs the mapping in Theorem 1. Further, the continuity of Eq. (19) in electron number n can be confirmed from the explicit construction, Eqs. (20) and (22), of the two constituent mappings in Eqs. (21) and (23). ■

Comment. The canonical representative of the class of $[v]$ is simply $v(\boldsymbol{r})-v(\infty)$, where the arbitrary additive constant, $v(\infty)=\lim\inf_{r\to\infty}|v(\boldsymbol{r})|$, is removed, and the continuous mapping becomes unique:

$$\rho_{0,n}^{v,\lambda}(\boldsymbol{r}) \mapsto \{v(\boldsymbol{r})\}_{\text{can}} = v(\boldsymbol{r}) - v(\infty) \in [v]. \tag{24}$$

It is clear that adopting the canonical representative $\{v(\boldsymbol{r})\}_{\text{can}}$ has the similar effect as employing the usual zero-value convention for $v(\boldsymbol{r})$ at infinity, $v(\infty)=0$. ■

Theorem 1 guarantees that the class $[v]$ of the external potential can be recovered from the Fock-space ensemble v-representable density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$, one can then use its ground-state energy $E_{0,n}^{v,\lambda}$ to alternatively define the Fock-space universal density functional in Eq. (17) as the fully equivalent Legendre transform functional in analogy with the traditional Hilbert-space DFT [1,2,11,12] approach,

$$F^{\lambda}[\rho_n] = \sup_{v}\{E_{0,n}^{v,\lambda} - V_{ne}^{v}[\rho_n]\}, \tag{25}$$

where the supremum will become a maximum for a ground-state density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$:

$$\begin{aligned} F^{\lambda}[\rho_{0,n}^{v,\lambda}] = F_{\text{HK}}^{\lambda}[\rho_{0,n}^{v,\lambda}] &= \max_{u}\{E_{0,n}^{u,\lambda} - V_{ne}^{u}[\rho_{0,n}^{v,\lambda}]\} \\ &= E_{0,n}^{v,\lambda} - V_{ne}^{v}[\rho_{0,n}^{v,\lambda}]. \end{aligned} \tag{26}$$

Theorem 2. The variational nature of $(F_{\text{HK}}^{\lambda}[\rho_{0,n}^{u,\lambda}] + V_{ne}^{v}[\rho_{0,n}^{u,\lambda}])$ is

$$F_{\text{HK}}^{\lambda}[\rho_{0,n}^{u,\lambda}] + V_{ne}^{v}[\rho_{0,n}^{u,\lambda}] \geqslant E_{0,n}^{v,\lambda} = F_{\text{HK}}^{\lambda}[\rho_{0,n}^{v,\lambda}] + V_{ne}^{v}[\rho_{0,n}^{v,\lambda}], \tag{27}$$

where the variation is within the set of ensemble v-representable densities. $\rho_{0,n}^{u,\lambda}(\boldsymbol{r})$ is the ground-state density of an external potential $u(\boldsymbol{r})$ that does not necessarily belong to $[v]$ and at $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ the energy expression achieves the minimum.

Proof. It is almost obvious that the definition in Eq. (26) is equivalent to the Levy's constrained search definition in Eq. (17) restricted to ensemble v-representable densities. Theorem 2 is a direct consequence of the variational principle of quantum mechanics as shown in Eq. (20). A very important advantage of the Levy's constrained search definition of the universal density functional in Eq. (17) is that it is valid even if the density is not ensemble v-representable. The variational principle in this case is

$$\begin{aligned} E_{0,n}^{v,\lambda} &= (N+1-n)E_{0,N}^{v,\lambda} + (n-N)E_{0,N+1}^{v,\lambda} \\ &= \min_{\rho_n}\{F^{\lambda}[\rho_n] + V_{ne}^{v}[\rho_n]\}. \end{aligned} \tag{28}$$

Hence, Theorem 2 naturally follows. ■

IV. CONVEXITY OF THE GROUND-STATE ENERGY IN FOCK SPACE

In the following, consider the ground-state energy $E_{0,n}^{v,\lambda}$ as a function of the electron number and denote $E_0^{v,\lambda}(n) \equiv E_{0,n}^{v,\lambda}$ to emphasize the functional dependence on electron number n.

Convexity assumption. Suppose that for every fixed external potential $v(\boldsymbol{r})$, the energy $E_0^{v,\lambda}(n)$ is a convex function with respect to the number of electrons [7,11,50]:

$$\omega_A E_0^{v,\lambda}(n_A) + \omega_B E_0^{v,\lambda}(n_B) \geqslant E_0^{v,\lambda}(n), \tag{29}$$

for any non-negative $\omega_A, \omega_B, n_A, n_B$, and n, such that $\omega_A + \omega_B = 1$ and $n = \omega_A n_A + \omega_B n_B$. ■

Definition. Define lower and upper derivatives of $E_0^{v,\lambda}(n)$:

$$D_L^{v,\lambda}(n) = \lim_{\xi\to 0-} \frac{E_0^{v,\lambda}(n+\xi) - E_0^{v,\lambda}(n)}{\xi} \tag{30}$$

and

$$D_U^{v,\lambda}(n) = \lim_{\xi\to 0+} \frac{E_0^{v,\lambda}(n+\xi) - E_0^{v,\lambda}(n)}{\xi}, \tag{31}$$

respectively. For convex functions [59,62–64],

$$D_L^{v,\lambda}(n) \leqslant D_U^{v,\lambda}(n), \tag{32}$$

where the equality means the differentiability at n. ■

V. GÂTEAUX FUNCTIONAL DERIVATIVE OF THE UNIVERSAL DENSITY FUNCTIONAL IN FOCK SPACE

Lemma. $F^{\lambda}[\rho_n]$ is a convex functional in the following sense. For any non-negative weights ω_p, ω_q, ω_s, and ω_t such that $\omega_p + \omega_q = \omega_s + \omega_t = 1$ and for any densities $\rho_p(\boldsymbol{r})$, $\rho_q(\boldsymbol{r})$, $\rho_s(\boldsymbol{r})$, $\rho_t(\boldsymbol{r})$, and $\rho_n(\boldsymbol{r})$ such that $\omega_p\rho_p(\boldsymbol{r}) + \omega_q\rho_q(\boldsymbol{r}) = \omega_s\rho_s(\boldsymbol{r}) + \omega_t\rho_t(\boldsymbol{r}) = \rho_n(\boldsymbol{r})$,

$$\omega_p F^{\lambda}[\rho_p] + \omega_q F^{\lambda}[\rho_q] \geqslant F^{\lambda}[\rho_n] = \inf_{\omega_s\rho_s + \omega_t\rho_t = \rho_n}\{\omega_s F^{\lambda}[\rho_s] + \omega_t F^{\lambda}[\rho_t]\}. \tag{33}$$

The densities $\rho_p(\boldsymbol{r}), \rho_q(\boldsymbol{r}), \rho_s(\boldsymbol{r}), \rho_t(\boldsymbol{r})$, and $\rho_n(\boldsymbol{r})$ are normalized to some numbers between N and $(N+1)$—i.e., $\{p,q,s,t,n = \omega_p p + \omega_q q = \omega_s s + \omega_t t\} \in [N, N+1)$.

Proof. Using the first definition of $F^{\lambda}[\rho_n]$ in Eq. (17), one has

$$F^{\lambda}[\rho_n] = \inf_{\hat{D}_n=(N+1-n)\hat{D}_N+(n-N)\hat{D}_{N+1}\to\rho_n} \Big\{(N+1-n)F^{\lambda}[\hat{D}_N] + (n-N)F^{\lambda}[\hat{D}_{N+1}]\Big\} \tag{34}$$

and the LHS of Eq. (33) is

$$\begin{aligned}\omega_p F^{\lambda}[\rho_p] + \omega_q F^{\lambda}[\rho_q] &= \omega_p \inf_{\hat{D}_p=(N+1-p)\hat{D}_{p,N}+(p-N)\hat{D}_{p,N+1}\to\rho_p} \Big\{(N+1-p)F^{\lambda}[\hat{D}_{p,N}] + (p-N)F^{\lambda}[\hat{D}_{p,N+1}]\Big\} \\ &\quad + \omega_q \inf_{\hat{D}_q=(N+1-q)\hat{D}_{q,N}+(q-N)\hat{D}_{q,N+1}\to\rho_q} \Big\{(N+1-q)F^{\lambda}[\hat{D}_{q,N}] + (q-N)F^{\lambda}[\hat{D}_{q,N+1}]\Big\} \\ &= \inf_{\substack{\hat{D}=(N+1-n)\hat{D}_N+(n-N)\hat{D}_{N+1}\to\rho_n \\ \{\hat{D}_n=\omega_p\hat{D}_p+\omega_q\hat{D}_q:\hat{D}_p\to\rho_p,\hat{D}_q\to\rho_q\}}} \Big\{(N+1-n)F^{\lambda}[\hat{D}_N] + (n-N)F^{\lambda}[\hat{D}_{N+1}]\Big\},\end{aligned} \tag{35}$$

where, in the last step, one writes

$$p\omega_p\hat{D}_{p,M} + q\omega_q\hat{D}_{q,M} = n\hat{D}_M, \tag{36}$$

where M is either N or $N+1$. The inequality of Eq. (33) is due to the additional constraints in the curly brackets of Eq. (35).

On the other hand, if these additional constraints are released, Eq. (35) becomes a search for the infimum through the entire space of different partitions of the same density via $\{\omega_s\rho_s(\mathbf{r})+\omega_t\rho_t(\mathbf{r})=\rho_n(\mathbf{r})\,|\,\rho_n(\mathbf{r})\equiv\omega_p\rho_p(\mathbf{r})+\omega_q\rho_q(\mathbf{r})\}$. As a result, the first definition of $F^{\lambda}[\rho_n]$ in Eq. (17) will be identical to the infimum of the LHS of Eq. (33), which establishes the equality of Eq. (33). In other words, the equivalency between the two definitions of $F^{\lambda}[\rho_n]$ in Eq. (17) is a special case of Eq. (33). ■

Comment. Lieb, Valone, and van Leeuwen have discussed the convexity of the universal density functional in Hilbert space [6,11,12]. We not only extend their results to an arbitrary number of electrons, but also show the full equivalency between the two definitions of $F^{\lambda}[\rho_n]$ in Eq. (17), which is nontrivial in its own right. Furthermore, using the second definition of $F^{\lambda}[\rho_n]$ in Eq. (17) and following Lieb's and van Leeuwen's arguments [11,12], one can readily prove the full equivalency between the definitions of $F^{\lambda}[\rho_n]$ via Levy's constrained search in Eq. (17) and the Legendre transformation in Eq. (25). ■

Theorem 3. Take an ensemble v-representable density $\rho_{0,n}^{v,\lambda}(\mathbf{r})$. Suppose $\partial E_0^{v,\lambda}(k)/\partial k|_{k=n}$ exists. Then, $F^{\lambda}[\rho]$ has a unique continuous tangential functional at $\rho_{0,n}^{v,\lambda}(\mathbf{r})$ given by

$$L_{\rho_{0,n}^{v,\lambda}}[\rho_n] = \left\langle \left[\left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - v(\mathbf{r}) \right] \rho_n(\mathbf{r}) \right\rangle; \tag{37}$$

i.e., $L_{\rho_{0,n}^{v,\lambda}}[\rho]$ is the unique linear functional such that the inequality,

$$F^{\lambda}[\rho_m] - F^{\lambda}[\rho_{0,n}^{v,\lambda}] \geqslant L_{\rho_{0,n}^{v,\lambda}}[\rho_m - \rho_{0,n}^{v,\lambda}] \tag{38}$$

holds true for an arbitrary density $\rho_m(\mathbf{r})$ with a normalization $\langle\rho_m(\mathbf{r})\rangle=m$.

Proof. $E_{0,n}^{v,\lambda}$ is assumed to be convex in the convexity assumption and it is now assumed to be differentiable at $k=n$; then,

$$E_0^{v,\lambda}(m) - E_0^{v,\lambda}(n) \geqslant (m-n) \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} = \langle\rho_m(\mathbf{r}) - \rho_{0,n}^{v,\lambda}(\mathbf{r})\rangle \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} \tag{39}$$

for any m and an arbitrary density $\rho_m(\mathbf{r})$ with $\langle\rho_m(\mathbf{r})\rangle=m$. Expanding $E_0^{v,\lambda}(m)$ and $E_0^{v,\lambda}(n)$, one further rewrites the above as

$$\big(F^{\lambda}[\rho_{0,m}^{v,\lambda}] + V_{ne}^{v}[\rho_{0,m}^{v,\lambda}]\big) - \big(F^{\lambda}[\rho_{0,n}^{v,\lambda}] + V_{ne}^{v}[\rho_{0,n}^{v,\lambda}]\big) \geqslant \langle\rho_m(\mathbf{r}) - \rho_{0,n}^{v,\lambda}(\mathbf{r})\rangle \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n}. \tag{40}$$

At the same time, for an arbitrary density $\rho_m(\mathbf{r})$ with $\langle\rho_m(\mathbf{r})\rangle=m$,

$$F^{\lambda}[\rho_m] + V_{ne}^{v}[\rho_m] \geqslant F^{\lambda}[\rho_{0,m}^{v,\lambda}] + V_{ne}^{v}[\rho_{0,m}^{v,\lambda}], \tag{41}$$

due to the DFT variational principle. Substituting Eq. (41) into the LHS of Eq. (40) and moving the nuclear-electron attraction energy density functionals to the RHS, one has

$$\begin{aligned} F^{\lambda}[\rho_m]-F^{\lambda}[\rho^{v,\lambda}_{0,n}] &\geqslant \left\langle \rho_m(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right\rangle \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - \left(V^{v}_{ne}[\rho_m]-V^{v}_{ne}[\rho^{v,\lambda}_{0,n}]\right) \\ &= \left\langle \rho_m(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right\rangle \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - \left\langle v(\boldsymbol{r})\left[\rho_m(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right]\right\rangle . \end{aligned} \tag{42}$$

The existence of $L_{\rho^{v,\lambda}_{0,n}}[\rho]$ is proved by combining the two terms of the RHS of Eq. (42) into one:

$$F^{\lambda}[\rho_m]-F^{\lambda}[\rho^{v,\lambda}_{0,n}] \geqslant \left\langle \left[\left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - v(\boldsymbol{r})\right]\left[\rho_m(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right]\right\rangle = L_{\rho^{v,\lambda}_{0,n}}[\rho_m-\rho^{v,\lambda}_{0,n}], \tag{43}$$

which is in the continuous bilinear form $\langle f(\boldsymbol{r})\varrho(\boldsymbol{r})\rangle$ for $f(\boldsymbol{r}) \in \mathcal{Y}^*$ and $\varrho(\boldsymbol{r}) \in \mathcal{Y}$, based on the Riesz's representation theorem [59,62].

The uniqueness of $L_{\rho^{v,\lambda}_{0,n}}[\rho_n]$ has the following origin via *reductio ad absurdum*. Without losing generality, let us suppose that for the same $\rho^{v,\lambda}_{0,n}(\boldsymbol{r})$, there is another continuous linear tangential functional via the Riesz's representation theorem [59,62]:

$$L[\rho_m-\rho^{v,\lambda}_{0,n}] = \left\langle \left[C^{v,\lambda}(n)-u(\boldsymbol{r})\right]\left[\rho_m(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right]\right\rangle, \tag{44}$$

where $u(\boldsymbol{r}) \in \mathcal{Y}^*, u(\boldsymbol{r}) \notin [v]$, and both $C^{v,\lambda}(n)$ and $u(\boldsymbol{r})$ functionally depend on $\rho^{v,\lambda}_{0,n}(\boldsymbol{r})$. Given the ground-state density $\rho^{u,\lambda}_{0,n}(\boldsymbol{r})$ of $u(\boldsymbol{r})$, from the variational principle, we have

$$F^{\lambda}[\rho^{u,\lambda}_{0,n}] + V^{u}_{ne}[\rho^{u,\lambda}_{0,n}] < F^{\lambda}[\rho^{v,\lambda}_{0,n}] + V^{u}_{ne}[\rho^{v,\lambda}_{0,n}] \tag{45}$$

or

$$F^{\lambda}[\rho^{u,\lambda}_{0,n}] - F^{\lambda}[\rho^{v,\lambda}_{0,n}] < -\left(V^{u}_{ne}[\rho^{u,\lambda}_{0,n}] - V^{u}_{ne}[\rho^{v,\lambda}_{0,n}]\right) = \left\langle \left[C^{v,\lambda}(n)-u(\boldsymbol{r})\right]\left[\rho^{u,\lambda}_{0,n}(\boldsymbol{r})-\rho^{v,\lambda}_{0,n}(\boldsymbol{r})\right]\right\rangle . \tag{46}$$

The appearance of $C^{v,\lambda}(n)$ on the RHS of Eq. (46) stems from the possible additive constant in the external potential $u(\boldsymbol{r})$: one can add or subtract a constant to $u(\boldsymbol{r})$ without changing the inequality in Eq. (45). Clearly, Eq. (46) is in contradiction with Eq. (43) for $m=n$. So we know that $u(\boldsymbol{r}) \in [v]$.

Since the external potential $v(\boldsymbol{r})$ is determined by the density $\rho^{v,\lambda}_{0,n}(\boldsymbol{r})$ only up to a constant—say, γ—one then has

$$E_0^{v+\gamma,\lambda}(n) = F^{\lambda}[\rho^{v,\lambda}_{0,n}] + V^{v}_{ne}[\rho^{v,\lambda}_{0,n}] + n \times \gamma = E_0^{v,\lambda}(n) + n \times \gamma, \tag{47}$$

so

$$\frac{E_0^{v+\gamma,\lambda}(m) - E_0^{v+\gamma,\lambda}(n)}{m-n} = \frac{E_0^{v,\lambda}(m) - E_0^{v,\lambda}(n)}{m-n} + \gamma. \tag{48}$$

Further, taking the limit $m \rightarrow n$ on both sides, one has

$$\left.\frac{\partial E_0^{v+\gamma,\lambda}(k)}{\partial k}\right|_{k=n} = \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} + \gamma. \tag{49}$$

Hence, in the final expression the constant γ cancels out[6]:

$$\left.\frac{\partial E_0^{v+\gamma,\lambda}(k)}{\partial k}\right|_{k=n} - [v(\boldsymbol{r})+\gamma] = \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - v(\boldsymbol{r}), \tag{50}$$

which means that $L_{\rho^{v,\lambda}_{0,n}}[\rho]$ is uniquely determined by the density $\rho^{v,\lambda}_{0,n}(\boldsymbol{r})$. ■

Comment. Similarly to the Hilbert-space case [10–12], here too it can be proved that under the assumption of Theorem 3, the tangential functional $L_{\rho_n}[\rho]$ exists if and only if the density $\rho_n(\boldsymbol{r})$ is ensemble v-representable. ■

Corollary 1. Under the assumptions of Theorem 3, the Gâteaux functional derivative or the integral kernel of the Gâteaux functional differential of $F^{\lambda}[\rho_n]$ at $\rho_n(\boldsymbol{r})=\rho^{v,\lambda}_{0,n}(\boldsymbol{r})$ is given by

$$\left.\frac{\delta F^{\lambda}[\rho]}{\delta \rho(\boldsymbol{r})}\right|_{\rho=\rho^{v,\lambda}_{0,n}} = \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} - v(\boldsymbol{r}). \tag{51}$$

Proof. The convexity of $F^{\lambda}[\rho]$ in Fock space has been proved in the lemma. Since in Hilbert space $F^{\lambda}[\rho_N]$ is lower semicontinuous [10–12], $F^{\lambda}[\rho_n]$ defined through linear combinations of $F^{\lambda}[\rho_N]$ and $F^{\lambda}[\rho_{N+1}]$ in Eq. (17) will also be lower semicontinuous (being proved as corollary 1a in the Appendix). For lower semicontinuous convex functionals, it is known that the integral kernel of the tangential functional differential [see Eq. (37)] and the integral kernel of the Gâteaux functional differential coincide whenever one of them

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[6] Consequently, it is meaningful to adopt the canonical representative $\{v(\boldsymbol{r})\}_{\mathrm{can}}$ for $v(\boldsymbol{r})$ hereafter. If necessary, we will drop the subscript {can} for notational simplicity.

exists and is unique [12,63]. ■

Comment. For a fractional electron number $n \notin \mathcal{N}, \partial E_0^{v,\lambda}(k)/\partial k|_{k=n}$ exists and takes unique values for n between any two adjacent integers [7,17,57]:

$$\mu_{\mathrm{SM}}^{n} = \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=n} = \begin{cases} D_L^{v,\lambda}(N) = -I & : n \in (N-1, N), \\ D_U^{v,\lambda}(N) = -A & : n \in (N, N+1), \end{cases} \tag{52}$$

where I and A are the first ionization potential and the first electron affinity, respectively. In statistical mechanics [65], $\partial E_0^{v,\lambda}(k)/\partial k|_{k=n}$ is called the chemical potential μ_{SM}^{n}. ■

Theorem 4. Assume everything from Theorem 3 but $E_0^{v,\lambda}(k)$ being nondifferentiable at the point $k=n$, with a lower derivative $D_L^{v,\lambda}(n)$ and an upper derivative $D_U^{v,\lambda}(n)$. In this case, the tangential functional of $F^{\lambda}[\rho_n]$ at the density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ is not uniquely defined, with an intrinsic arbitrariness specified below:

$$F^{\lambda}[\rho_m] - F^{\lambda}[\rho_{0,n}^{v,\lambda}] \geqslant \left\langle \left[C^{v,\lambda}(n) - v(\boldsymbol{r})\right]\left[\rho_m(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right]\right\rangle \tag{53}$$

holds if and only if

$$D_L^{v,\lambda}(n) \leqslant C^{v,\lambda}(n) \leqslant D_U^{v,\lambda}(n). \tag{54}$$

Proof. From Eq. (32) and the fact $E_0^{v,\lambda}(k)$ is nondifferentiable at $k=n$, we obtain a strict inequality between the lower and upper derivatives:

$$D_L^{v,\lambda}(n) < D_U^{v,\lambda}(n). \tag{55}$$

First consider a variation of the density lowering the number of electrons from n to m:

$$\left\langle \rho_m(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right\rangle = m - n < 0. \tag{56}$$

From the definition of the lower derivative $D_L^{v,\lambda}$ in Eq. (30) and the convexity assumption for $E_0^{v,\lambda}(n)$, it follows that

$$E_0^{v,\lambda}(m) - E_0^{v,\lambda}(n) \geqslant (m-n) D_L^{v,\lambda}(n). \tag{57}$$

Hence, using the same reasoning that leads from Eq. (39) to Eq. (43), one has

$$F^{\lambda}[\rho_m] - F^{\lambda}[\rho_{0,n}^{v,\lambda}] \geqslant -\left\langle v(\boldsymbol{r})\left[\rho_m(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right]\right\rangle + (m-n) D_L^{v,\lambda}(n). \tag{58}$$

For the case of $m \geqslant n$, one can similarly derive

$$\left\langle \rho_m(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right\rangle = m - n \geqslant 0, \tag{59}$$

$$E_0^{v,\lambda}(m) - E_0^{v,\lambda}(n) \geqslant (m-n) D_U^{v,\lambda}(n), \tag{60}$$

and

$$F^{\lambda}[\rho_m] - F^{\lambda}[\rho_{0,n}^{v,\lambda}] \geqslant -\left\langle v(\boldsymbol{r})\left[\rho_m(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right]\right\rangle + (m-n) D_U^{v,\lambda}(n). \tag{61}$$

Equations (58) and (61) indicate that *if* $D_L^{v,\lambda}(n) \leqslant C^{v,\lambda}(n) \leqslant D_U^{v,\lambda}(n)$, Eq. (53) will be true for arbitrary values of m.

Second (the *only if* part), if any other values of $C^{v,\lambda}(n)$ are chosen, Eq. (53) will be violated as shown below. For example, we take $C^{v,\lambda}(n) < D_L^{v,\lambda}(n)$. Due to the convexity assumption for $E_0^{v,\lambda}(n)$,

$$\frac{E_0^{v,\lambda}(m) - E_0^{v,\lambda}(n)}{m-n} > C^{v,\lambda}(n) \tag{62}$$

and

$$F^{\lambda}[\rho_{0,m}^{v,\lambda}] - F^{\lambda}[\rho_{0,n}^{v,\lambda}] < \left\langle \left[C^{v,\lambda}(n) - v(\boldsymbol{r})\right]\left[\rho_{0,m}^{v,\lambda}(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\right]\right\rangle \tag{63}$$

are true for $n > m > m_L$, where m_L is the lower bound of m satisfying Eq. (62). Clearly, Eq. (63) contradicts Eq. (53). Likewise, we can obtain the same contradiction if $C^{v,\lambda}(n) > D_U^{v,\lambda}(n)$, for $m_U > m > n$, where m_U is the upper bound of m satisfying Eq. (62).

Geometrically, Eq. (54) describes any tangential line below the energy $E_0^{v,\lambda}(m)$ curve, while Eq. (62) signifies the portion of the energy $E_0^{v,\lambda}(m)$ curve below a straight line passing through the point $E_0^{v,\lambda}(n)$ with a slope of $C^{v,\lambda}(n)$. ■

Corollary 2. Under the assumptions of Theorem 4, the Gâteaux functional derivative of $F^{\lambda}[\rho_n]$ at $\rho_n(\boldsymbol{r}) = \rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ is not uniquely defined, with an intrinsic arbitrariness specified below:

$$\left.\frac{\delta F^{\lambda}[\rho]}{\delta \rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}^{v,\lambda}} = C^{v,\lambda}(n) - v(\boldsymbol{r}), \tag{64}$$

with a range of possible choices of $C^{v,\lambda}(n)$ characterized by

$$D_L^{v,\lambda}(n) \leqslant C^{v,\lambda}(n) \leqslant D_U^{v,\lambda}(n). \tag{65}$$

Proof. The same as of Corollary 1. ■

Comment. For any integer electron number N [7,17,57],

$$D_L^{v,\lambda}(N) = -I < -A = D_U^{v,\lambda}(N). \tag{66}$$

For later convenience, $C^{v,\lambda}(N)$ can be rewritten as

$$C^{v,\lambda}(N) = \mu_{\mathrm{SM}}^{N} = \left.\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\right|_{k=N}, \tag{67}$$

of course, with the intrinsic arbitrariness

$$-I \leqslant \mu_{\mathrm{SM}}^{N} \leqslant -A. \tag{68}$$

■

Theorem 5. For an arbitrary electron number n (either fractional or integral), $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}^{v,\lambda}}$ is classwise continuous with respect to n: $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}^{v,\lambda}}$ and $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,N}^{v,\lambda}}$ belong to the same class $[-v(\boldsymbol{r})]$.

Proof. Corollaries 1 and 2 prove Theorem 5. ■

VI. “TEMPERATURE REGULARIZATION” OF THE FUNCTIONAL DERIVATIVE AT AN INTEGER NUMBER OF ELECTRONS

In view of the above nonuniqueness, one could be tempted to apply a “temperature regularization” of the type suggested by Perdew *et al.* [17], whose idea goes back to the earlier work by Gyftopoulos and Hatsopoulos [57] (see also Ref. [7], p. 75). The idea is calculating the functional derivative after first promoting the system to some finite low temperature and subsequently taking the zero-temperature limit[7]:

$$\left\{ \left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}} \right\}_{\mathrm{reg}} = \lim_{\beta\to\infty} \left\{ \left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}} \right\}_{\beta}. \tag{69}$$

The result is suggested to be well behaved and expressed as an average of the following two well-defined functional derivatives. From Eqs. (30), (31), and (52), the lower and upper functional derivatives of $F^{\lambda}[\rho]$ can be introduced as [7,17,57]

$$\left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}}^{L} = \lim_{\xi\to 0-} \left.\frac{F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N+\xi}^{v,\lambda}} = D_L^{v,\lambda}(N) - v(\boldsymbol{r}) = -I - v(\boldsymbol{r}) \tag{70}$$

and

$$\left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}}^{U} = \lim_{\xi\to 0+} \left.\frac{F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N+\xi}^{v,\lambda}} = D_U^{v,\lambda}(N) - v(\boldsymbol{r}) = -A - v(\boldsymbol{r}), \tag{71}$$

respectively. The “thermally regularized” functional derivative is stated to be [17]

$$\left\{ \left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}} \right\}_{\mathrm{reg}} = \frac{1}{2}\left(\left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}}^{L} + \left.\frac{\delta F^{\lambda}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}^{v,\lambda}}^{U} \right). \tag{72}$$

This approach to uniquely define the functional derivative at an integer number of electrons is based on the belief that in the zero-temperature limit the chemical potential[8], defined as a derivative of the energy with respect to the electron numbers at a constant entropy [65], would be well defined and equal to the negative of Mulliken’s electronegativity [57,58]:

$$\mu = -\chi = -\frac{I+A}{2}. \tag{73}$$

In contrast, we will show below the ambiguous nature of this “temperature regularization.” More precisely, we will show that any value within the interval $[-I,-A]$, not only $-\frac{1}{2}(I+A)$, can be reached as a value of the chemical potential in the zero-temperature limit.

For our analysis we will use the same three-state model considered before [7,17,57]. In this model system, there are three families of states that are likely to be occupied: a neutral atom with N electrons, energy levels $\{E_k\}$, and degeneracies $\{g_k\}$; its positive ion with $(N-1)$ electrons, energy levels $\{E_j^{+}\}$, corresponding ionization potentials $\{I_j\}$ from E_0, and degeneracies $\{g_j^{+}\}$; and its negative ion with $(N+1)$ electrons, energy levels $\{E_i^{-}\}$, corresponding electron affinities $\{A_i\}$ from E_0, and degeneracies $\{g_i^{-}\}$. In Ref. [7], only the ground states are considered; here, we include excited states as well for generality. With this in mind, the average number of electrons is easily derived from the grand canonical partition function of the system:

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[7] Hereafter, we will use the inverse temperature $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant.

[8] For simplicity of the derivation in this section, the subscript and superscript of the notation for the chemical potential are dropped.

$$\overline{N}(\beta,\mu) = N + \frac{\sum_i g_i^- e^{\beta(A_i+\mu)} - \sum_j g_j^+ e^{-\beta(I_j+\mu)}}{\sum_k g_k e^{-\beta(E_k-E_0)} + \sum_i g_i^- e^{\beta(A_i+\mu)} + \sum_j g_j^+ e^{-\beta(I_j+\mu)}}. \tag{74}$$

Instead of assuming that the average number of electrons and the chemical potential stay fixed while the temperature changes [7,17,57], we adopt a more general and physically more plausible assumption that the average number of electrons $\overline{N}(\beta)$ as a function of the temperature can vary but will approach N in the zero-temperature limit:

$$\lim_{\beta\to\infty}\overline{N}(\beta) = \lim_{\beta\to\infty}\left\{ N + \frac{\sum_i g_i^- e^{\beta[A_i+\mu(\beta)]} - \sum_j g_j^+ e^{-\beta[I_j+\mu(\beta)]}}{\sum_k g_k e^{-\beta(E_k-E_0)} + \sum_i g_i^- e^{\beta[A_i+\mu(\beta)]} + \sum_j g_j^+ e^{-\beta[I_j+\mu(\beta)]}} \right\} = N, \tag{75}$$

where the chemical potential $\mu(\beta)$ naturally becomes a function of temperature itself [65]. As a result, the desire to have a fixed number of electrons at an extremely low temperature [7,17,57],

$$\overline{N}(\beta) = N, \tag{76}$$

is indeed just a special case of our generalization.

In general, the chemical potential $\mu(\beta)$ can vary as a function of the temperature [65]. To every temperature dependence of the chemical potential $\mu(\beta)$, there is a corresponding temperature dependence of the average electron number given by the insertion of this functional form $\mu(\beta)$ into the RHS of Eq. (74). We are interested in those functional forms of $\mu(\beta)$ that satisfy Eq. (75).

Case A. Any choice of a function (can be an arbitrary constant) for the chemical potential within the range $(-I,-A)$ satisfies Eq. (75) since

$$\lim_{\beta\to\infty}\left\{ \frac{\sum_i g_i^- e^{\beta[A_i+\mu(\beta)]} - \sum_j g_j^+ e^{-\beta[I_j+\mu(\beta)]}}{\sum_k g_k e^{-\beta(E_k-E_0)} + \sum_i g_i^- e^{\beta[A_i+\mu(\beta)]} + \sum_j g_j^+ e^{-\beta[I_j+\mu(\beta)]}} \right\} = 0. \tag{77}$$

To derive the above result, note that $-I<\mu(\beta)<-A, A+\mu(\beta)<0$, and $I+\mu(\beta)>0$ by assumption and, at the same time, $A_i<A_0=A$ and $I_j>I_0=I$, due to the order of the energy levels; hence, $A_i+\mu(\beta)<0$ and $I_j+\mu(\beta)>0$.

Case B. For the case of $\mu=-I$ at the zero-temperature limit, the two functional forms $\mu(\beta)=-I+\ln^{-1}\beta$ and $\mu(\beta)=-I+\beta^{-1/2}$ provide two possible solutions. One can easily verify that Eq. (75) and

$$\lim_{\beta\to\infty}\mu(\beta) = -I \tag{78}$$

are concurrently satisfied for both functional forms considered here. In fact, there are infinite solutions of this kind. Any temperature dependence of the type $\mu(\beta)=-I+|\nu(\beta)|$, where $\nu(\beta)$ has the limiting properties $\lim_{\beta\to\infty}\nu(\beta)=\lim_{\beta\to\infty}[\beta\nu(\beta)]^{-1}=0$, provides a possible solution for $\mu(\beta)$ with $-I$ in the zero-temperature limit.

Case C. Similarly to Case B, any temperature dependence of the chemical potential of the type $\mu(\beta)=-A-|\nu(\beta)|$ will result in

$$\lim_{\beta\to\infty}\mu(\beta) = -A, \tag{79}$$

when Eq. (75) is also satisfied.

In conclusion, any values between $-I$ and $-A$ for the chemical potential,

$$-I \leqslant \mu \leqslant -A, \tag{80}$$

are acceptable, provided that Eq. (75) is simultaneously obeyed. Equation (80) is consistent with Eq. (68). Hence, the "temperature regularization" [7,17,57] does not remove the intrinsic arbitrariness for the chemical potential at an integer electron number N.

To further illustrate our arguments succinctly, we have exhibited in Fig. 1 five cases of different temperature-dependent chemical potentials $\mu(\beta)$ and their pertinent temperature-dependent average electron numbers $\overline{N}(\beta,\mu)$, for a model system with $I=1.0$ hartree, $A=0.1$ hartree, and $N=5$. Figure 1 clearly shows that the average electron numbers in these cases with very different functional behaviors for $\mu(\beta)$ all go to the same fixed number in the zero-temperature limit, namely, $\lim_{\beta\to\infty}\overline{N}(\beta,\mu)=N$, but with varied zero-temperature-limit values for the chemical potential between $-I$ and $-A$: $-I\leqslant\lim_{\beta\to\infty}\mu(\beta)\leqslant-A$.

VII. FOCK-SPACE KOHN-SHAM METHOD AND "DERIVATIVE DISCONTINUITY"

For consistency of the notation, let us recall the idea of the Kohn-Sham (KS) system [3,7–9,12,17,25]. At the nonin-

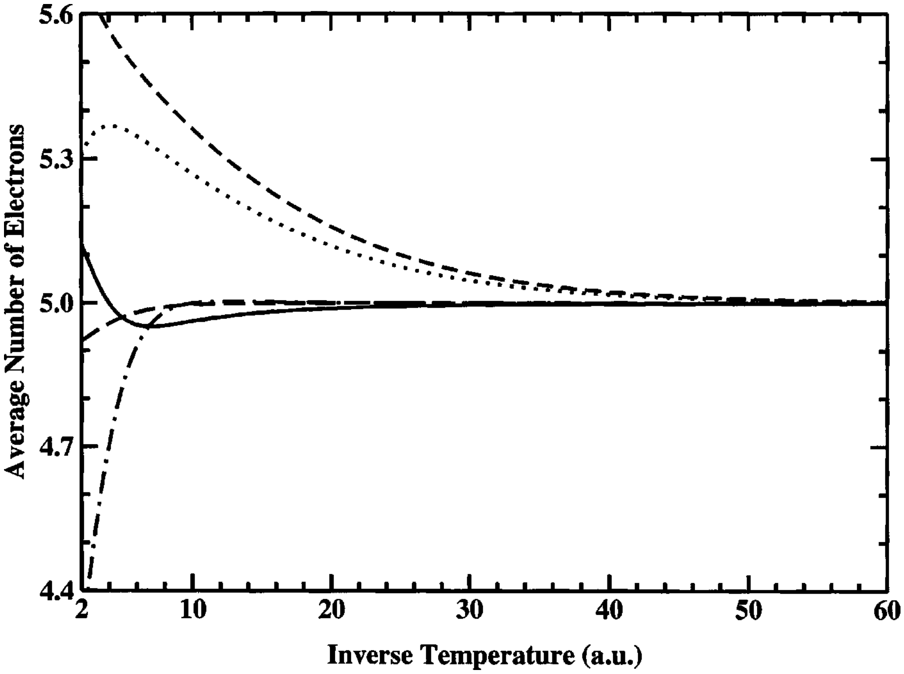

FIG. 1. Comparison of five different temperature-dependent average electron numbers $\overline{N}(\beta,\mu)$, corresponding to different temperature-dependent chemical potentials $\mu(\beta)$, as functions of the inverse temperature β, for a model system with $I=1.0$, $A=0.1$, and $N=5$, respectively. All values are in atomic units. The dotted line is for $\mu(\beta)=-0.2$ and the degeneracy parameters $\{g_0,g_0^-,g_0^+\}=\{1,1,1\}$. The solid line is for $\mu(\beta)=-I+\beta^{-1/2}$ and $\{g_0,g_0^-,g_0^+\}=\{3,2,3\}$. The dot-dashed line is for $\mu(\beta)=-A-\ln^{-1}\beta$ and $\{g_0,g_0^-,g_0^+\}=\{3,2,3\}$. The short-dashed line is for $\mu(\beta)=-(I+A)/2+(\beta\ln\beta)^{-1}$ and $\{g_0,g_0^-,g_0^+\}=\{3,2,3\}$. The long-dashed line is for $\mu(\beta)=-(I+A)/2$ and $\{g_0,g_0^-,g_0^+\}=\{3,2,3\}$.

teracting limit ($\lambda=0$), the original external potential[9] $v(\boldsymbol{r})$ is replaced with an effective potential $v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r})$ in a way to keep the ground-state density identical to the one in the fully interacting limit—namely,

$$\rho_{0,n}^{v,\lambda=1}(\boldsymbol{r}) = \rho_{0,n}^{v_{\rm eff}^{\rm KS},\lambda=0}(\boldsymbol{r}) = \rho_{0,n}(\boldsymbol{r}), \tag{81}$$

where the common density $\rho_{0,n}(\boldsymbol{r})$ is denoted by simply omitting the λ dependence. Also denote $F[\rho_n]=F^{\lambda=1}[\rho_n]$ and $T_S[\rho_n]=F^{\lambda=0}[\rho_n]$, because in the KS limit the universal density functional from Eq. (9) reduces to a pure kinetic form.

The first thing to note is that the specialization to the noninteracting case of the convexity property in Eq. (33) becomes

$$\omega_p T_S[\rho_p] + \omega_q T_S[\rho_q] \geq T_S[\rho_n], \tag{82}$$

using the same assumption for $\omega_p, \omega_q, \rho_p(\boldsymbol{r}), \rho_q(\boldsymbol{r})$, and $\rho_n(\boldsymbol{r})$ as in the lemma. It is a property against which any approximations to $T_S[\rho_n]$ shall be tested.

Case 1. In the following first consider $n\in(N-1,N)$.

Our previous discussion in Eq. (70) was for an arbitrary electron-electron interaction strength λ between 0 and 1, so the functional derivatives for the two limiting cases of $\lambda=1$ and $\lambda=0$ are

$$\left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = E_0^{v,\lambda=1}(N) - E_0^{v,\lambda=1}(N-1) - v(\boldsymbol{r}) = -I - v(\boldsymbol{r}) \tag{83}$$

and

$$\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = E_0^{v_{\rm eff}^{\rm KS},\lambda=0}(N) - E_0^{v_{\rm eff}^{\rm KS},\lambda=0}(N-1) - v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r}) = \epsilon_N^n - v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r}), \tag{84}$$

where the last equality is due to $E_0^{v_{\rm eff}^{\rm KS},\lambda=0}(M)=\Sigma_{i=1}^{M}\epsilon_i^n$ (for positive integer M), and $\{\epsilon_i^n\}$ are the KS orbital energies.

Recall the KS partition of the universal density functional [3,7–9,12,17,25]

$$E_{xc}[\rho_n] = F[\rho_n] - T_S[\rho_n] - \frac{1}{2}\left\langle \frac{\rho_n(\boldsymbol{r})\rho_n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right\rangle, \tag{85}$$

from which one arrives at

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[9] The general KS scheme is not limited to Coulombic external potentials only [12]. The soundness of the KS scheme has been firmly established by van Leeuwen recently [12]. In this section, we will mainly concentrate on those external potentials that converge to the same arbitrary constant at infinity in all directions, which of course, will produce asymptotically exponential-decaying densities for bound ground states [43,66,67]. For later convenience, we will label the set of these "good" external potentials as $\mathcal{V}$ and the set of their corresponding asymptotically exponential-decaying ground-state densities as $\mathcal{D}$.

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = \left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} - \left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} - \int \frac{\rho_{0,n}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' \tag{86}$$

$$= v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r}) - v(\boldsymbol{r}) - \int \frac{\rho_{0,n}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' - \epsilon_N^n - I = v_{xc}^n(\boldsymbol{r}) - \epsilon_N^n - I, \tag{87}$$

where we associate $v_{xc}^n(\boldsymbol{r})$ by a grouping of the following terms [3,7–9,12,17,25]:

$$v_{xc}^n(\boldsymbol{r}) = v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r}) - v(\boldsymbol{r}) - \int \frac{\rho_{0,n}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'. \tag{88}$$

Equation (87) should be interpreted as an actual equality of two previously defined terms rather than as a definition of $v_{xc}^n(\boldsymbol{r})$. Naturally, for exponentially decaying $\rho_{0,n}(\boldsymbol{r})$,

$$\lim_{r\to\infty}\int \frac{\rho_{0,n}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' = 0. \tag{89}$$

On the one hand, for $\lambda=1$, one has

$$\rho_{0,n} = \rho_{0,n}^{v,\lambda=1} = (N-n)\rho_{0,N}^{v,\lambda=1} + (n-N+1)\rho_{0,N-1}^{v,\lambda=1}, \tag{90}$$

with the asymptotic limit [43,66,67]

$$\lim_{r\to\infty}\rho_{0,n} = \lim_{r\to\infty}\rho_{0,n}^{v,\lambda=1} \sim \lim_{r\to\infty}\rho_{0,N}^{v,\lambda=1} \sim e^{-2r\sqrt{2I}}. \tag{91}$$

On the other hand, for $\lambda=0$, one also has

$$\rho_{0,n} = \rho_{0,n}^{v_{\rm eff}^{\rm KS},\lambda=0} = (N-n)\rho_{0,N}^{v_{\rm eff}^{\rm KS},\lambda=0} + (n-N+1)\rho_{0,N-1}^{v_{\rm eff}^{\rm KS},\lambda=0}, \tag{92}$$

with the asymptotic limit [43,66,67]

$$\lim_{r\to\infty}\rho_{0,n} = \lim_{r\to\infty}\rho_{0,n}^{v_{\rm eff}^{\rm KS},\lambda=0} \sim \lim_{r\to\infty}\rho_{0,N}^{v_{\rm eff}^{\rm KS},\lambda=0} \sim e^{-2r\sqrt{2[v_{xc}^n(\infty)-\epsilon_N^n]}}, \tag{93}$$

where the usual zero-value (canonical) convention for $v(\boldsymbol{r})$ at infinity,

$$\lim_{r\to\infty} v(\boldsymbol{r}) = v(\infty) = 0, \tag{94}$$

is used and, consequently,

$$v_{\rm eff}^{\rm KS}[\rho_{0,n}](\infty) = v_{xc}^n(\infty). \tag{95}$$

From the above considerations and after equating the two forms of the asymptotic limit of $\rho_{0,n}$, one gets

$$I = v_{xc}^n(\infty) - \epsilon_N^n. \tag{96}$$

From Eqs. (84) and (87), we finally arrive at

$$\begin{aligned}\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} &= -I + v_{\rm eff}^{\rm KS}[\rho_{0,n}](\infty) - v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r}) \\ &= -I - \left\{v_{\rm eff}^{\rm KS}[\rho_{0,n}](\boldsymbol{r})\right\}_{\rm can}\end{aligned} \tag{97}$$

and

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = v_{xc}^n(\boldsymbol{r}) - v_{xc}^n(\infty) = \left\{v_{xc}^n(\boldsymbol{r})\right\}_{\rm can}. \tag{98}$$

Case 2. Similarly for $m \in (N, N+1)$, one will get

$$A = v_{xc}^m(\infty) - \epsilon_{N+1}^m, \tag{99}$$

$$\begin{aligned}\left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} &= E_0^{v,\lambda=1}(N+1) - E_0^{v,\lambda=1}(N) - v(\boldsymbol{r}) \\ &= -A - v(\boldsymbol{r}),\end{aligned} \tag{100}$$

$$\begin{aligned}\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} &= E_0^{v_{\rm eff}^{\rm KS},\lambda=0}(N+1) - E_0^{v_{\rm eff}^{\rm KS},\lambda=0}(N) - v_{\rm eff}^{\rm KS}[\rho_{0,m}](\boldsymbol{r}) \\ &= \epsilon_{N+1}^m - v_{\rm eff}^{\rm KS}[\rho_{0,m}](\boldsymbol{r}) \\ &= -A + v_{\rm eff}^{\rm KS}[\rho_{0,m}](\infty) - v_{\rm eff}^{\rm KS}[\rho_{0,m}](\boldsymbol{r}) \\ &= -A - \left\{v_{\rm eff}^{\rm KS}[\rho_{0,m}](\boldsymbol{r})\right\}_{\rm can},\end{aligned} \tag{101}$$

and

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} = v_{xc}^m(\boldsymbol{r}) - v_{xc}^m(\infty) = \left\{v_{xc}^m(\boldsymbol{r})\right\}_{\rm can}. \tag{102}$$

The striking observation of Eqs. (98) and (102) is that for an arbitrary n, in general,

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} \neq v_{xc}^n(\boldsymbol{r}), \tag{103}$$

in contradiction to existing practice [7–9,12]. Moreover, from Eqs. (83), (97), (98), (100), (101), and (102), one can clearly identify the following limits at $r\to\infty$:

$$\lim_{r\to\infty}\left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = \lim_{r\to\infty}\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = -I, \tag{104}$$

$$\lim_{r\to\infty}\left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} = \lim_{r\to\infty}\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} = -A, \tag{105}$$

and

$$\lim_{r\to\infty}\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,n}} = \lim_{r\to\infty}\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,m}} = 0, \tag{106}$$

which are true for any values of $n \in (N-1, N)$ and $m \in (N, N+1)$.

In order to understand the "derivative discontinuity" of $F[\rho_N], T_S[\rho_N]$, and $E_{xc}[\rho_N]$ at an integer electron number N, let us use lower and upper functional derivatives of these functionals, defined in close analogy to Eqs. (70) and (71), and take their difference at N:

$$\left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} - \left.\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}} = A - I, \qquad (107)$$

$$\lim_{r\to\infty}\left(\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} - \left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}}\right) = A - I, \qquad (108)$$

and

$$\lim_{r\to\infty}\left(\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} - \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}}\right) = 0. \qquad (109)$$

Clearly, the asymptotic limits of both the lower and upper functional derivatives of the exchange-correlation functional confirm the lack of "derivative discontinuity," due to Eq. (106). Additionally, at the $n\to N$ and $m\to N$ limits,

$$\lim_{\xi\to 0\pm}\{v^{\rm KS}_{\rm eff}[\rho_{0,N+\xi}](\boldsymbol{r})\}_{\rm can} = \{v^{\rm KS}_{\rm eff}[\rho_{0,N}](\boldsymbol{r})\}_{\rm can}, \qquad (110)$$

due to the Hohenberg-Kohn-like theorem in Fock space (see Theorem 1 and its comment).[10] As a result, Eqs. (108) and (109) are true globally, not only at the asymptotic limit:

$$\left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} - \left.\frac{\delta T_S[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}} = A - I, \qquad (111)$$

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} - \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}} = 0. \qquad (112)$$

More interestingly, Eqs. (83) and (100) clearly reconfirm Theorem 5. In the same way, Eqs. (97), (101), and (111) suggest that $\delta T_S[\rho]/\delta\rho(\boldsymbol{r})|^{L}_{\rho=\rho_{0,N}}$ and $\delta T_S[\rho]/\delta\rho(\boldsymbol{r})|^{U}_{\rho=\rho_{0,N}}$ belong to the same class $[-v^{\rm KS}_{\rm eff}[\rho_{0,N}](\boldsymbol{r})]$; Eqs. (98), (102), and (112) indicate that $\delta E_{xc}[\rho]/\delta\rho(\boldsymbol{r})|^{L}_{\rho=\rho_{0,N}}$ and $\delta E_{xc}[\rho]/\delta\rho(\boldsymbol{r})|^{U}_{\rho=\rho_{0,N}}$ coincide with the canonical representative of the class $[v^{N}_{xc}(\boldsymbol{r})]$. More importantly, according to the standard continuity requirement, Eq. (112) further ratifies that the functional derivative of the exchange-correlation functional is continuous with respect to electron number n in Fock space:

$$\left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|_{\rho=\rho_{0,N}} = \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{L}_{\rho=\rho_{0,N}} = \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}\right|^{U}_{\rho=\rho_{0,N}} = \{v^{N}_{xc}(\boldsymbol{r})\}_{\rm can}. \qquad (113)$$

This result will have a profound consequence in resolving the value of the chemical potential at an integer electron number (discussed in the next section).

It should be noticed that Eqs. (107)–(113) are universal statements for general external potentials in $\mathcal{V}$ (including Coulombic potentials) with bound ground states, simple because of Theorem 1 and Corollary 1. Equations (107) and (111)–(113) are our main results regarding the "derivative discontinuity." Once again to emphasize, we find that the exchange-correlation functional does not exhibit a "derivative discontinuity."

VIII. VALUE OF THE CHEMICAL POTENTIAL

Due to the intrinsic arbitrariness in Eq. (68), the value of the chemical potential at an integer electron number is indeed a thorny subject [7,12–17,42–48]. In the present literature, there are at least six different values for $\mu^{N}_{\rm SM}$ [7,12–17,42–48].

The first value is the mean total electronic energy [13,42,46]

$$\mu^{N}_{\rm SM} = \frac{E^{v,\lambda}_0(N)}{N}. \qquad (114)$$

This value of $\mu^{N}_{\rm SM}$ might be inferred from observing the identity in Hilbert space:

$$\begin{aligned}&\langle\Psi(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)|\hat{H}^{v,\lambda}|\Psi(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\rangle - E^{v,\lambda}_0(N)[\langle\Psi(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)|\Psi(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)\rangle - 1]\\ &\equiv F^{\lambda}[\hat{D}_N] + V^{v}_{ne}[\rho_N] - \frac{E^{v,\lambda}_0(N)}{N}[\langle\rho_N(\boldsymbol{r})\rangle - N] \geqslant F^{\lambda}[\rho_N] + V^{v}_{ne}[\rho_N] - \frac{E^{v,\lambda}_0(N)}{N}[\langle\rho_N(\boldsymbol{r})\rangle - N], \qquad (115)\end{aligned}$$

where $\Psi(\boldsymbol{r}_1\sigma_1,\ldots,\boldsymbol{r}_N\sigma_N)$ is any normalized N-electron antisymmetric wave function with density $\rho_N(\boldsymbol{r})$ and density matrix $\hat{D}_N$. The LHS and the central expression of Eq. (115) are the variation functionals employed in the conventional wave function and density matrix approaches [68]. Subtly, the central expression of Eq. (115) looks *similar*, but not *identical*, to the RHS of Eq. (115), which is a special case of the one used in density-functional theory [7,47]:

$$F[\rho] + V^{v}_{ne}[\rho] - \mu_{\rm DFT}[\langle\rho(\boldsymbol{r})\rangle - N]. \qquad (116)$$

A closer scrutiny shows that the variational domain of the RHS of Eq. (115) includes *infimal* normalized wave functions [through $\rho_N(\boldsymbol{r})$], while the variational domains of the LHS and central expression of Eq. (115) only include any arbitrary normalized wave functions and density matrices [with $\rho_N(\boldsymbol{r})$], respectively. Or in other words, in general,

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[10] An earlier account of this continuity for integer electron numbers appeared in Ref. [54].

$$F^{\lambda}[\hat{D}_N] \geqslant F^{\lambda}[\rho_N] = \inf_{\hat{D}_N \to \rho_N} F^{\lambda}[\hat{D}_N], \tag{117}$$

which is a restatement of Eq. (9). Hence, Eq. (114) is generally incorrect [55] and this understanding is a generalization of the arguments by Gál [14]. Furthermore, setting $\lambda=0$ in Eq. (114), one will get the erroneous first-degree homogeneity relation for $T_S[\rho_{0,N}]$ [41,42]. In fact, one can easily derive a similar, more general erroneous first-degree homogeneity relation for $F^{\lambda}[\rho_{0,N}]$ [55],

$$\left\langle \left(\frac{\delta F^{\lambda}[\rho]}{\rho(\boldsymbol{r})} \bigg|_{\rho=\rho_{0,N}} \right) \rho_{0,N}(\boldsymbol{r}) \right\rangle = F^{\lambda}[\rho_{0,N}], \tag{118}$$

based upon the general expression in Eq. (114) [13].

The second one is the highest occupied KS orbital energy ϵ_N^N and is identified to be the negative of the first ionization potential [43]

$$\mu_{\mathrm{SM}}^N = \epsilon_N^N = -I, \tag{119}$$

which is a consequence of assuming $v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\boldsymbol{r})$ to be zero asymptotically [43,51]:

$$\lim_{r\to\infty} v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\boldsymbol{r}) = v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\infty) = 0. \tag{120}$$

This assumption has never been proved to be true in general, nor is consistent with the so-called “derivative discontinuity” argument [16–30], which states that as N passes a fixed integer, $v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\boldsymbol{r})$ will exhibit a finite jump. Of course, with Eq. (120), $v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\boldsymbol{r})$ will definitely not possess any “derivative discontinuity,” but from our discussion in Sec. VII, such an assumption like Eq. (120) is not proved either, because of the finite asymptotic value $v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,N}](\infty)$ in Eqs. (95) and (96). Nonetheless, Eq. (119) is covered within the acceptable range shown in Eqs. (68) and (80).

The third one is “conveniently” linked to the Lagrangian multiplier in DFT [14,15,50,52], which can be shown through the chain rule [14,50,52]

$$\begin{aligned}\mu_{\mathrm{SM}}^N = \frac{\partial E_0^{v,\lambda}(k)}{\partial k}\bigg|_{k=N} &= \left\langle \frac{\delta E_0^{v,\lambda}(k)}{\delta \rho_{0,k}^{v,\lambda}(\boldsymbol{r})} \frac{\partial \rho_{0,k}^{v,\lambda}(\boldsymbol{r})}{\partial k} \right\rangle \bigg|_{k=N} \\ &= \mu_{\mathrm{DFT}} \langle F(\boldsymbol{r}) \rangle = \mu_{\mathrm{DFT}},\end{aligned} \tag{121}$$

where the property of the Fukui function [53] $F(\boldsymbol{r}) = \partial \rho_{0,k}^{v,\lambda}(\boldsymbol{r}) / \partial k|_{k=N}$ has been utilized. Obviously, this approach is basically a Fock-space treatment for both $F(\boldsymbol{r})$ and $\delta E_0^{v,\lambda}(k) / \delta \rho_{0,k}^{v,\lambda}(\boldsymbol{r})$.

Built upon the third one, the fourth one is the negative of Mulliken’s electronegativity [57,58]:

$$\mu_{\mathrm{SM}}^N = -\chi = -\frac{I+A}{2}, \tag{122}$$

which can be derived via the grand canonical ensemble near zero temperature [7,15–17,36,48]. In Sec. VI, we have shown that Eq. (122) is just a particular choice among infinite possible values between $[-I,-A]$.

Same to Eqs. (68) and (80), the fifth one [7,47] is not a fixed number, but between two limits

$$-I \leqslant \mu_{\mathrm{SM}}^N \leqslant -A. \tag{123}$$

Although Eq. (123) covers Eqs. (119), (121), and (122), a considerable difference still exists between Eqs. (119) and (122). Except for $N=1$, Eq. (114) does not satisfy Eq. (123). This offers another evidence for $\mu_{\mathrm{SM}}^N \neq E_0^{v,\lambda}(N)/N$ in general.

The last one is zero [12],

$$\mu_{\mathrm{SM}}^N = 0, \tag{124}$$

which is clearly wrong for general multi-electron systems.

Apart from the question of what is the value of the chemical potential, an important problem stands alone how to actually define the notion itself within the framework of DFT. In the usual DFT practice, the chemical potential μ_{SM}^n is associated with the Lagrangian multiplier μ_{DFT}, for an arbitrary electron number n (either fractional or integral), similar to Eq. (121).

As a complement to this, we will show below that within our approach their equality can be derived alternatively.[11] For this purpose and in order to make a connection with the traditional derivation of the Euler-Lagrange equation in DFT, we vary the energy expression with the Lagrangian normalization term explicitly included, for an arbitrary electron number n (either integral or fractional):

$$\frac{\delta F^{\lambda}[\rho]}{\delta \rho(\boldsymbol{r})}\bigg|_{\rho=\rho_{0,n}^{v,\lambda}} + \frac{\delta\{V_{ne}^{v}[\rho] - \mu_{\mathrm{DFT}}[\langle \rho(\boldsymbol{r})\rangle - n]\}}{\delta \rho(\boldsymbol{r})}\bigg|_{\rho=\rho_{0,n}^{v,\lambda}} = 0. \tag{125}$$

With our expressions of the functional derivative of the universal density functional in Eqs. (51), (64), and (67), Eq. (125) thus becomes

$$\left(\frac{\partial E_0^{v,\lambda}(k)}{\partial k}\bigg|_{k=n} - v(\boldsymbol{r}) \right) + [v(\boldsymbol{r}) - \mu_{\mathrm{DFT}}] = 0 \tag{126}$$

or, just simply,

$$\mu_{\mathrm{DFT}} = \frac{\partial E_0^{v,\lambda}(k)}{\partial k}\bigg|_{k=n} = \mu_{\mathrm{SM}}^n, \tag{127}$$

for an arbitrary electron number n (either integral or fractional). An important feature of our approach is that the above equality is derived without any aid from the Fukui function.

Up to this point, the actual value of μ_{SM}^N remains to be resolved to draw a satisfactory finale. Let us work with the KS method for a fixed integer electron number N with $v(\boldsymbol{r}) \in \mathcal{V}$ and $\rho_{0,N}(\boldsymbol{r}) \in \mathcal{D}$. As usual, with the equality (with $\lambda=1$ and $\lambda=0$ only)

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[11] Although Parr *et al.* [15] took a similar path as outlined below, these authors *assumed* the existence of the functional derivative of $F^{\lambda}[\rho]$ for Fock-space ensemble v-representable densities, while working only with Hilbert-space universal density functionals. Hence, their proof is actually logically inconsistent.

$$\mu_{\rm SM}^{N} \equiv \left. \frac{\partial E_0^{v,\lambda=1}(k)}{\partial k} \right|_{k=N} = \mu_{\rm DFT} \equiv \left. \frac{\delta E_0^{v,\lambda=1}(k)}{\delta \rho_{0,k}(\boldsymbol{r})} \right|_{k=N} = \left. \frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} + v(\boldsymbol{r}) \tag{128}$$

and the KS partition of the universal density functional

$$F[\rho_N] = T_S[\rho_N] + E_{xc}[\rho_N] + \frac{1}{2}\left\langle \frac{\rho_N(\boldsymbol{r})\rho_N(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \right\rangle, \tag{129}$$

one arrives at

$$\left. \frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} = \left. \frac{\delta T_S[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} + \left. \frac{\delta E_{xc}[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} + \int \frac{\rho_{0,N}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' . \tag{130}$$

For any external potential $v(\boldsymbol{r}) \in \mathcal{V}$, Eqs. (106), (109), and (113) guarantee that

$$\lim_{r\to\infty} \left. \frac{\delta E_{xc}[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} = 0, \tag{131}$$

and it has been well established [9,43,66,67] that for $v(\boldsymbol{r}) \in \mathcal{V}$, the corresponding ground-state density will be asymptotically exponential-decaying $\rho_{0,N}(\boldsymbol{r}) \in \mathcal{D}$, such that

$$\lim_{r\to\infty} \left. \frac{\delta T[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} = \lim_{r\to\infty} \left. \frac{\delta T_S[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} = -I, \tag{132}$$

where $T[\rho]$ is the exact kinetic-energy density functional, the kinetic component of $F[\rho]$. With the help of Eq. (89), one derives the asymptotic behavior

$$\lim_{r\to\infty} \left. \frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} = -I. \tag{133}$$

Because $\mu_{\rm SM}^{N}$ is a global constant, one immediately gets

$$\mu_{\rm SM}^{N} = \lim_{r\to\infty}\left(\left. \frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} \right|_{\rho=\rho_{0,N}} + v(\boldsymbol{r}) \right) = -I, \tag{134}$$

from Eqs. (94), (128), and (133). Combining Eqs. (52) and (134), we finalize the value for the chemical potential for an arbitrary electron number n (around an integer N):

$$\mu_{\rm SM}^{n} = \left. \frac{\partial E_0^{v,\lambda}(k)}{\partial k} \right|_{k=n} = \begin{cases} D_L^{v,\lambda}(N) = -I & : n \in (N-1,N], \\ D_U^{v,\lambda}(N) = -A & : n \in (N,N+1]. \end{cases} \tag{135}$$

Moreover, Eq. (135) can be simplified as a single statement below.

Theorem 6. For an arbitrary electron number $n \in (N-1,N]$ with $v(\boldsymbol{r}) \in \mathcal{V}$ and $\rho_{0,n}(\boldsymbol{r}) \in \mathcal{D}$, the chemical potential takes the lower derivative (with respect to the electron number) of the ground-state energy as its value:

$$\mu_{\rm SM}^{n} \equiv \left. \frac{\partial E_0^{v,\lambda}(k)}{\partial k} \right|_{k=n} = D_L^{v,\lambda}(n) = D_L^{v,\lambda}(N) = -I, \tag{136}$$

where N is the nearest integer upper bound of n. For the entire range of $(N-1,N]$, the chemical potential is a constant, hence is continuous with respect to the change of electron number. ■

This is to say that the value of the chemical potential is completely dictated by the asymptotic limit of the functional derivative of the kinetic-energy density functional [see Eqs. (104), (105), (132), and (133)], which in turn is governed solely by the decaying behavior of the least decaying N-electron ground-state density for an n-electron system [see Eqs. (91) and (93)], without any interference from the *unoccupied* $(N+1)$-electron state. Any other definition for $\mu_{\rm SM}^{N}$ not consistent with Eq. (134)—say, the negative of Mulliken's electronegativity in Eq. (122)—will be in direct conflict with the continuity of the functional derivative of the exchange-correlation functional with respect to electron number [see Eq. (113)]. Further, the conclusions of Sec. VII should be true for the extended domains: $n \in (N-1,N]$ and $m \in (N,N+1]$. This result is achieved without any reference whatsoever to the finite asymptotic value $v_{\rm eff}^{\rm KS}[\rho_{0,n}](\infty)$ in Eqs. (95) and (96). Hence, it is a general, universal statement for $v(\boldsymbol{r}) \in \mathcal{V}$ and $\rho_{0,n}(\boldsymbol{r}) \in \mathcal{D}$.

Here, we conclude our investigation into the functional derivative of density functionals and related issues.

IX. SUMMARY

The contributions of our paper to the discussion of the functional derivative in DFT are the following.

(i) It is an old problem but with a renewed interest in recent years [1–55]. There is a lot of confusion accumulated over the years and almost no mathematically rigorous studies except for the papers of Englisch and Englisch [10], Lieb [11], van Leeuwen [12], Lindgren and Salomonson [13], and Gál [14]. Our paper is an additional effort to further strengthen the mathematical foundation of DFT.

(ii) In order to derive the main results, two Hohenberg-Kohn-like theorems for cases of fractional electron numbers are proved.

(iii) We prove that within the zero-temperature Fock-space DFT, the functional derivative $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,N}^{v,\lambda}} = C^{v,\lambda}(N) - v(\boldsymbol{r})$ is not well defined in the case of an integer number of electrons $[\langle\rho(\boldsymbol{r})\rangle = N \in \mathcal{N}_{+}]$, due to the nonuniqueness of $C^{v,\lambda}(N)$, which can be within an entire interval: $D_{L}^{v,\lambda}(N) \leqslant C^{v,\lambda}(N) \leqslant D_{U}^{v,\lambda}(N)$. We further show that the often cited "temperature regularization" [7,17,57] could not fix the uncertainty of $C^{v,\lambda}(N)$ at an integer electron number N.

(iv) We prove that within the zero-temperature Fock-space DFT, the functional derivative $\delta F^{\lambda}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}^{v,\lambda}} = C^{v,\lambda}(n) - v(\boldsymbol{r})$ is well defined as $C^{v,\lambda}(k) = \partial E_{0}^{v,\lambda}(k)/\partial k|_{k=n}$, in the case of a fractional number of electrons $[\langle\rho(\boldsymbol{r})\rangle = n \notin \mathcal{N}_{+}]$.

(v) The above results are proved for an arbitrary electron-electron interaction strength λ between 0 and 1 and are later restricted to the cases $\lambda = 1$ and $\lambda = 0$, thus, for $n \in (N-1, N]$, giving $\delta F[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}} = -I - \{v(\boldsymbol{r})\}_{\mathrm{can}}$, $\delta T_{S}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}} = -I - \{v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{0,n}](\boldsymbol{r})\}_{\mathrm{can}}$, and $\delta E_{xc}[\rho]/\delta\rho(\boldsymbol{r})|_{\rho=\rho_{0,n}} = \{v_{xc}^{n}(\boldsymbol{r})\}_{\mathrm{can}}$. Surprisingly, the canonical representatives of the classes of various potential functions are required to correctly define their corresponding density functional derivatives.

(vi) The functional derivative of the exchange-correlation functional is continuous with respect to the number of electrons in Fock space. Consequently, there is no "derivative discontinuity" for the exchange-correlation functional at an integer electron number.

(vii) The equality $\mu_{\mathrm{DFT}} = \mu_{\mathrm{SM}}^{n}$ is rigorously derived via an alternative route. μ_{DFT} is the Lagrangian multiplier used to constrain the normalization of the density, which in the traditional DFT approach is associated with the chemical potential, $\mu_{\mathrm{SM}}^{n} = \partial E_{0}^{v,\lambda}(k)/\partial k|_{k=n}$, defined according to statistical mechanics.

(viii) Finally, we show that for $v(\boldsymbol{r}) \in \mathcal{V}$, there is no freedom of adding an arbitrary constant to the value of the chemical potential at an integer electron number N and further resolve this intrinsic nonuniqueness by an exact definition: $\mu_{\mathrm{SM}}^{N} = -I$, not the popular preference [7,15–17,36,48,57,58] of the negative of Mulliken's electronegativity, $-\frac{1}{2}(I+A)$.

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APPENDIX

Corollary 1a. $F^{\lambda}[\rho_{n}]$ is lower semicontinuous (l.s.c.) at Fock-space ensemble v-representable densities $\{\rho_{0,n}^{v,\lambda}(\boldsymbol{r})\}$ in $\mathcal{Y}$.

Proof. As shown in Eq. (19), any Fock-space ensemble v-representable density $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ has a unique decomposition into its two adjacent integer N and $(N+1)$ components:

$$\rho_{0,n}^{v,\lambda}(\boldsymbol{r}) = (N+1-n)\rho_{0,N}^{v,\lambda}(\boldsymbol{r}) + (n-N)\rho_{0,N+1}^{v,\lambda}(\boldsymbol{r}). \qquad \text{(A1)}$$

Take a sequence of densities $\rho_{n}^{k}(\boldsymbol{r})$ converging to $\rho_{0,n}^{v,\lambda}(\boldsymbol{r})$ in $\mathcal{Y}$—i.e., $\lim_{k\to\infty}\|\rho_{n}^{k}(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\|_{1} = 0$ and $\lim_{k\to\infty}\|\rho_{n}^{k}(\boldsymbol{r}) - \rho_{0,n}^{v,\lambda}(\boldsymbol{r})\|_{3} = 0$. For the kth element in this converging sequence $\rho_{n}^{k}(\boldsymbol{r})$, consider different splits (labeled with a non-necessarily countable index α) into N and $(N+1)$ components:

$$\rho_{n}^{k}(\boldsymbol{r}) = (N+1-n)\rho_{N}^{\alpha,k}(\boldsymbol{r}) + (n-N)\rho_{N+1}^{\alpha,k}(\boldsymbol{r}), \qquad \text{(A2)}$$

such that $\lim_{k\to\infty}\|\rho_{0,M}^{\alpha,k}(\boldsymbol{r}) - \rho_{0,M}^{v,\lambda}(\boldsymbol{r})\|_{1} = 0$ and $\lim_{k\to\infty}\|\rho_{0,M}^{\alpha,k}(\boldsymbol{r}) - \rho_{0,M}^{v,\lambda}(\boldsymbol{r})\|_{3} = 0$, where M is either N or $(N+1)$. Since it is known [10–12] that $F^{\lambda}[\rho]$ is l.s.c. at Hilbert-space ensemble v-representable densities $\rho_{0,N}^{v,\lambda}(\boldsymbol{r})$ and $\rho_{0,N+1}^{v,\lambda}(\boldsymbol{r})$, for each choice of α, we have

$$F^{\lambda}[\rho_{0,N}^{v,\lambda}] \leqslant \liminf_{k\to\infty} F^{\lambda}[\rho_{N}^{\alpha,k}] \qquad \text{(A3)}$$

and

$$F^{\lambda}[\rho_{0,N+1}^{v,\lambda}] \leqslant \liminf_{k\to\infty} F^{\lambda}[\rho_{N+1}^{\alpha,k}]. \qquad \text{(A4)}$$

A combination of the above two inequalities with Eq. (17) gives

$$\begin{aligned} F^{\lambda}[\rho_{0,n}^{v,\lambda}] &= (N+1-n)F^{\lambda}[\rho_{0,N}^{v,\lambda}] + (n-N)F^{\lambda}[\rho_{0,N+1}^{v,\lambda}] \\ &\leqslant \liminf_{k\to\infty}\left\{(N+1-n)F^{\lambda}[\rho_{N}^{\alpha,k}] + (n-N)F^{\lambda}[\rho_{N+1}^{\alpha,k}]\right\}. \end{aligned} \qquad \text{(A5)}$$

The final step is to observe that the above inequality is preserved after taking the infimum over the set of different density splits $\{\alpha\}$. Once again, using Eq. (17), we obtain the desired result

$$F^{\lambda}[\rho_{0,n}^{v,\lambda}] \leqslant \liminf_{k\to\infty} F^{\lambda}[\rho_{n}^{k}], \qquad \text{(A6)}$$

which says that $F^{\lambda}[\rho_{n}]$ is l.s.c. at Fock-space ensemble v-representable densities $\{\rho_{0,n}^{v,\lambda}(\boldsymbol{r})\}$ in $\mathcal{Y}$. ■

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