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**FULL PAPER**

# ***N*-centered ensemble density-functional theory for open systems**

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**Abstract**

Two (so-called left and right) variants of *N*-centered ensemble density-functional theory (DFT) are presented. Unlike the original formulation of the theory, these variants allow for the description of systems with a fractional electron number. While conventional DFT for open systems uses only the true electron density as basic variable, left/right *N*-centered ensemble DFT relies instead on (a) a fictitious ensemble density that integrates to a central (integral) number *N* of electrons, and (b) a grand canonical ensemble weight  $\alpha$  which is equal to the deviation of the true electron number from *N*. Within such a formalism, the infamous derivative discontinuity that appears when crossing an integral number of electrons is described exactly through the dependence in  $\alpha$  of the left and right *N*-centered ensemble Hartree-exchange-correlation density functionals. Incorporating *N*-centered ensembles into existing density-functional embedding theories is expected to pave the way toward the in-principle-exact description of an open fragment by means of a pure-state *N*-electron many-body wavefunction. Work is currently in progress in this direction.

**KEYWORDS**

embedding, ensemble density-functional theory, fractional electron number, grand canonical energy, open systems

## **1 | INTRODUCTION**

Density-functional theory (DFT) has become over the last two decades the method of choice for performing routine large-scale electronic structure calculations. This success is essentially due to the relatively low computational cost of the method and its (often but not always) good accuracy. In most applications, DFT is applied to closed electronic systems, that is, systems with an integral number *N* of electrons. However, at the formal level, there is no such a restriction. In other words, DFT is in principle able to describe also systems with a fractional electron number, as shown in the pioneering work of Perdew, Parr, Levy, and Balduz (PPLB).<sup>[1]</sup> The extension of DFT to open systems plays a crucial role in the description of charged electronic excitations.<sup>[2]</sup> More recently, it became a key ingredient in the derivation of DFT-based embedding approaches such as partition DFT,<sup>[3–10]</sup> potential-functional embedding theory,<sup>[11]</sup> and frozen density embedding theory for noninteger subsystems' particle numbers.<sup>[12]</sup>

The density  $n(\mathbf{r})$  of an open system integrates to a fractional number  $\mathcal{N}$  of electrons. As shown in Perdew et al.<sup>[1]</sup> and Perdew and Levy,<sup>[2]</sup> the ground-state energy of such a system varies linearly with the deviation  $\alpha = \mathcal{N} - \lfloor \mathcal{N} \rfloor$  of the true electron number from its floor integral value.

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In the language of ensemble DFT,<sup>[6,13]</sup> the density is nothing but a weighted sum of ground-state densities  $n^{N-1}(\mathbf{r})$  and  $n^N(\mathbf{r})$  integrating to  $N-1 = \lfloor \mathcal{N} \rfloor$  and  $N = \lceil \mathcal{N} \rceil$  electrons, respectively:

$$n(\mathbf{r}) = (1-\alpha)n^{N-1}(\mathbf{r}) + \alpha n^N(\mathbf{r}), \quad (1)$$

where, as readily seen, the ensemble weights are  $\alpha$  and  $(1-\alpha)$ , respectively. As shown in Kraisler and Kronik,<sup>[13]</sup> the explicit expression in Equation (1) is convenient for constructing density-functional approximations to the open-system exchange-correlation (xc) energy  $E_{xc}[n]$  as functions of  $\alpha$ .

Quite recently, the authors have proposed an in-principle-exact reformulation of the fundamental gap problem in DFT.<sup>[14]</sup> For that purpose, they introduced the concept of  $N$ -centered ensemble where, unlike in the true physical ensemble described in Equation (1), the ensemble density integrates to an integral number of electrons. The practical advantage of such a reformulation is that the infamous derivative discontinuity contribution to the true gap<sup>[2]</sup> can be expressed as an ensemble Hartree (H) xc energy derivative with respect to the ensemble weight,<sup>[14]</sup> exactly like in DFT for canonical ensembles.<sup>[15]</sup> In the original formulation of the theory,<sup>[14]</sup> the ensemble weights have no physical meaning. They are just auxiliary variables which, through their variations, enable the extraction of quantities of interest like the ionization potential (IP), the electron affinity (EA) or, when a single weight is used, the fundamental gap. In fact,  $N$ -centered ensemble DFT allows for a direct extraction of individual energies for the neutral, anionic and cationic systems,<sup>[14]</sup> which are all closed systems, in a single calculation. In this work, we show how the theory can be adapted to open systems. By considering ionization and affinity processes separately, we obtain two variants (referred to as left and right) of  $N$ -centered ensemble DFT where the ensemble weight is now connected to  $\alpha$  (see Equation 1).

The article is organized as follows. After a brief review on the original formulation of  $N$ -centered ensemble DFT in Section 2.1, the concept of left and right  $N$ -centered ensembles is introduced (Section 2.2). The left/right variants of  $N$ -centered ensemble DFT are then derived in Section 2.3. In this context, we obtain an in-principle-exact reformulation of the IP/EA theorem, as discussed in Section 2.4. An explicit connection (through scaling relations) between left and right ensemble density functionals is then made in Section 2.5. Finally, a brief discussion on density-driven correlation effects, whose importance in canonical ensembles was recently revealed,<sup>[16-18]</sup> is proposed in Section 2.6. As a conclusion to the "Theory" Section 2, we compare left/right  $N$ -centered ensemble DFT with conventional PPLB-DFT for open systems (Section 2.7). A proof of concept study of the Hubbard dimer model is presented in Section 3, with a particular emphasis on the weight-dependence of the Hxc left/right ensemble functionals. Conclusions and perspectives are finally given in Section 4.

## 2 | THEORY

### 2.1 | $N$ -centered ensembles

In a previous work,<sup>[14]</sup> we introduced the concept of  $N$ -centered ensemble for the purpose of calculating fundamental gaps, in principle exactly, within DFT. In standard approaches, the number of electrons is considered to vary continuously between two integers, thus allowing for the description of ionization or affinity processes.<sup>[13,19-40]</sup> The situation is completely different in an  $N$ -centered ensemble where, by construction, the number of electrons (which is obtained by integration of the  $N$ -centered ensemble density) is not affected by the charged excitation. It remains equal to the so-called central number  $N$  of electrons which is an integer. Formally, an  $N$ -centered ensemble is described by the following density matrix operator<sup>[14]</sup>:

$$\hat{\Gamma}^{\{N, \xi_-, \xi_+\}} = \xi_- \hat{\Gamma}^{N-1} + \xi_+ \hat{\Gamma}^{N+1} + \left(1 - \frac{(N-1)\xi_-}{N} - \frac{(N+1)\xi_+}{N}\right) \hat{\Gamma}^N, \quad (2)$$

where  $\xi_-$  and  $\xi_+$  are ensemble weights assigned to the cationic ( $N-1$ )-electron and anionic ( $N+1$ )-electron systems, respectively. Each individual density matrix operator  $\hat{\Gamma}^{N_e}$ , where  $N_e = N, N \pm 1$ , is used to describe an  $N_e$ -electron ground state. If the latter can be described with a pure-state wavefunction  $\Psi^{N_e}$  then  $\hat{\Gamma}^{N_e} \equiv |\Psi^{N_e}\rangle\langle\Psi^{N_e}|$ . In case of degeneracy, it may be written as a convex combination of pure  $N_e$ -electron states  $\hat{\Gamma}^{N_e} \equiv \sum_l \lambda_l |\Psi_l^{N_e}\rangle\langle\Psi_l^{N_e}|$ , where  $\sum_l \lambda_l = 1$ . As readily seen from Equation (2), the number of electrons within the  $N$ -centered ensemble is  $\text{Tr}[\hat{\Gamma}^{\{N, \xi_-, \xi_+\}} \hat{\mathcal{N}}] = N$  where  $\text{Tr}[\dots]$  denotes the trace,  $\hat{\mathcal{N}} = \int d\mathbf{r} \hat{n}(\mathbf{r})$  is the electron counting operator, and  $\hat{n}(\mathbf{r})$  is the density operator at position  $\mathbf{r}$ .

As shown in Senjean and Fromager,<sup>[14]</sup> using two independent weights  $\xi_-$  and  $\xi_+$  allows for a separate extraction of the IP and EA from the  $N$ -centered ensemble energy  $\text{Tr}[\hat{\Gamma}^{\{N, \xi_-, \xi_+\}} \hat{H}]$ , where  $\hat{H}$  is the (second-quantized) Hamiltonian. In the particular case where  $\xi_- = \xi_+ = \xi$ , the  $N$ -centered ensemble density matrix operator simplifies as follows:

$$\hat{\Gamma}^{\{N, \xi\}} = \xi \hat{\Gamma}^{N-1} + \xi \hat{\Gamma}^{N+1} + (1-2\xi) \hat{\Gamma}^N, \quad (3)$$

so that the fundamental gap can be extracted directly by differentiating the corresponding  $N$ -centered ensemble energy  $\text{Tr}[\hat{\Gamma}^{(N,\xi)}\hat{H}]$  with respect to  $\xi$ .<sup>[14]</sup> The potential advantage of such a formalism over conventional approaches is that the infamous derivative discontinuity contribution to the gap can be written as the derivative of the  $N$ -centered ensemble Hxc density functional with respect to the ensemble weight  $\xi$ , exactly like in DFT for canonical ensembles.<sup>[15,41]</sup>

Let us stress that, in the current formulation of  $N$ -centered ensemble DFT, the ensemble weights have no physical meaning. They are just convenient auxiliary variables. Actually, the properties of interest (namely the ground-state energies of the neutral [ $N$ -electron], cationic, and anionic systems) should not depend on the value of the ensemble weights. In the rest of this work, we explore two variants of the theory which are directly applicable to open systems. For such systems, a convenient and physical choice for the ensemble weight value is the deviation of the (fractional) electron number  $\mathcal{N}$  from either its integral floor value  $\lfloor \mathcal{N} \rfloor$  or the ceiling one  $\lceil \mathcal{N} \rceil$ .

## 2.2 | Left and right $N$ -centered ensembles

Starting from Equation (2), we explore in this section different choices of  $N$ -centered ensemble weights  $\xi_-$  and  $\xi_+$  for the purpose of describing an open  $\mathcal{N}$ -electron system. In order to treat both  $\lceil \mathcal{N} \rceil = N$  and  $\lfloor \mathcal{N} \rfloor = N$  scenarios, thus, allowing for the description of fluctuations around the central (integral) number  $N$  of electrons, we introduce what we will refer to as left (subscript “-”) and right (subscript “+”)  $N$ -centered ensemble density matrix operators, respectively:

$$\hat{\Gamma}_-^{(N,\alpha)} = (1-\alpha)\hat{\Gamma}^N + \frac{N\alpha}{N-1}\hat{\Gamma}^{N-1}, \quad (4)$$

$$\hat{\Gamma}_+^{(N,\alpha)} = (1-\alpha)\hat{\Gamma}^N + \frac{N\alpha}{N+1}\hat{\Gamma}^{N+1}, \quad (5)$$

where  $0 \leq \alpha \leq 1$ . Note that, by construction, the number of electrons within these two ensembles is the central number  $N$ :

$$\text{Tr}[\hat{\Gamma}_-^{(N,\alpha)}\hat{\mathcal{N}}] = \text{Tr}[\hat{\Gamma}_+^{(N,\alpha)}\hat{\mathcal{N}}] = N. \quad (6)$$

Moreover, left and right ensembles can be connected to each other as follows:

$$\frac{N}{N-1}\hat{\Gamma}_+^{(N-1,\alpha)} = \hat{\Gamma}_-^{(N,1-\alpha)}. \quad (7)$$

These ensembles are just special cases of the original  $N$ -centered one introduced in Senjean and Fromager.<sup>[14]</sup> Indeed, with the notations of Equation (2), we have

$$\hat{\Gamma}_-^{(N,\alpha)} = \hat{\Gamma}^{(N,\xi_- = \frac{N\alpha}{N-1}, \xi_+ = 0)}, \quad (8)$$

and

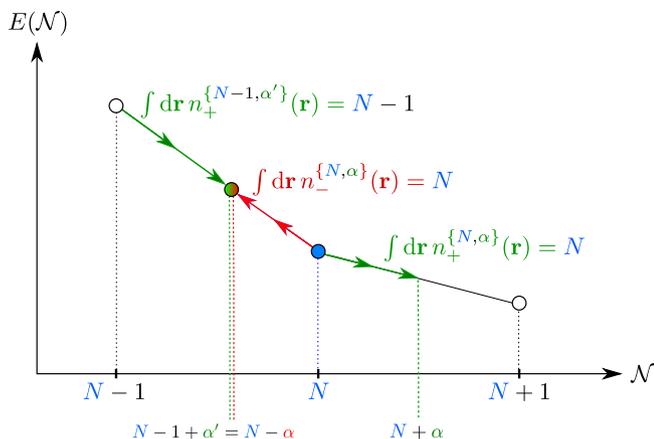
$$\hat{\Gamma}_+^{(N,\alpha)} = \hat{\Gamma}^{(N,\xi_- = 0, \xi_+ = \frac{N\alpha}{N+1})}. \quad (9)$$

The original (two-weight)  $N$ -centered ensemble can actually be recovered from the left and right ones as follows:

$$\hat{\Gamma}^{(N,\xi_-, \xi_+)} = \frac{(N-1)}{2N}\hat{\Gamma}_-^{(N,2\xi_-)} + \frac{(N+1)}{2N}\hat{\Gamma}_+^{(N,2\xi_+)}. \quad (10)$$

Following the standard description of open systems in DFT,<sup>[41]</sup> we propose to use for the value of  $\alpha$  in Equations (4) and (5) the deviation of the true (fractional) electron number  $\mathcal{N}$ , that we assume to vary in the range  $N-1 < \mathcal{N} < N+1$ , from the central number  $N$ , that is,

$$\alpha = |\mathcal{N} - N|. \quad (11)$$



**FIGURE 1** Graphical illustration of left and right  $N$ -centered ensembles. The shorthand notation  $n_{\pm}^{\{N,\alpha\}}(\mathbf{r}) \equiv n_{\Gamma_{\pm}^{\{N,\alpha\}}}(\mathbf{r})$  is used

If  $[\mathcal{N}] = N$ , then  $\alpha = N - \mathcal{N}$  and the open system will be described by the left  $N$ -centered ensemble of Equation (4). If  $[\mathcal{N}] = N$ , then  $\alpha = \mathcal{N} - N$  and the right  $N$ -centered ensemble of Equation (5) will be used instead. This is illustrated graphically in Figure 1.

Let us stress that these ensembles are not the physical ones, which are described by the following density matrix operators<sup>[13]</sup>:

$$\begin{aligned}\hat{\Gamma}(\mathcal{N})^{[\mathcal{N}] = N} &\equiv \hat{\Gamma}(N - \alpha) = (1 - \alpha)\hat{\Gamma}^N + \alpha\hat{\Gamma}^{N-1}, \\ \hat{\Gamma}(\mathcal{N})^{[\mathcal{N}] = N} &\equiv \hat{\Gamma}(N + \alpha) = (1 - \alpha)\hat{\Gamma}^N + \alpha\hat{\Gamma}^{N+1}.\end{aligned}\quad (12)$$

Nevertheless, they can be used as auxiliary ensembles from which the exact properties of the true physical open system can be extracted. Indeed, according to Equations (4) and (5),

$$\hat{\Gamma}^N = \hat{\Gamma}_{\pm}^{\{N,\alpha=0\}} = \hat{\Gamma}_{\pm}^{\{N,\alpha\}} - \alpha \frac{\partial \hat{\Gamma}_{\pm}^{\{N,\alpha\}}}{\partial \alpha} \quad (13)$$

and

$$\begin{aligned}\hat{\Gamma}^{N\pm 1} &= \frac{N \pm 1}{N} \left( \frac{\partial \hat{\Gamma}_{\pm}^{\{N,\alpha\}}}{\partial \alpha} + \hat{\Gamma}^N \right) \\ &= \frac{N \pm 1}{N} \left( \hat{\Gamma}_{\pm}^{\{N,\alpha\}} + (1 - \alpha) \frac{\partial \hat{\Gamma}_{\pm}^{\{N,\alpha\}}}{\partial \alpha} \right),\end{aligned}\quad (14)$$

thus, leading to the final expressions

$$\begin{aligned}\hat{\Gamma}(\mathcal{N})^{[\mathcal{N}] = N} &\equiv \hat{\Gamma}(N - \alpha) \\ &= \left(1 - \frac{\alpha}{N}\right) \hat{\Gamma}_{-}^{\{N,\alpha\}} - \frac{\alpha(1 - \alpha)}{N} \frac{\partial \hat{\Gamma}_{-}^{\{N,\alpha\}}}{\partial \alpha},\end{aligned}\quad (15)$$

and

$$\begin{aligned}\hat{\Gamma}(\mathcal{N})^{[\mathcal{N}] = N} &\equiv \hat{\Gamma}(N + \alpha) \\ &= \left(1 + \frac{\alpha}{N}\right) \hat{\Gamma}_{+}^{\{N,\alpha\}} + \frac{\alpha(1 - \alpha)}{N} \frac{\partial \hat{\Gamma}_{+}^{\{N,\alpha\}}}{\partial \alpha}.\end{aligned}\quad (16)$$

A direct consequence of Equations (15) and (16) is that the physical energy  $E(\mathcal{N}) = \text{Tr}[\hat{\Gamma}(\mathcal{N})\hat{H}]$  of an open system can be extracted from a left or right  $N$ -centered ensemble as follows:

$$\begin{aligned}E(\mathcal{N})^{[\mathcal{N}] = N} &\equiv E(N - \alpha) \\ &= \left(1 - \frac{\alpha}{N}\right) \mathcal{E}_{-}^{\{N,\alpha\}} - \frac{\alpha(1 - \alpha)}{N} \frac{\partial \mathcal{E}_{-}^{\{N,\alpha\}}}{\partial \alpha},\end{aligned}\quad (17)$$

and

$$\begin{aligned}
 E(\mathcal{N}) \stackrel{[\mathcal{N}]=N}{\equiv} E(N+\alpha) \\
 = \left(1 + \frac{\alpha}{N}\right) \mathcal{E}_+^{\{N,\alpha\}} + \frac{\alpha(1-\alpha)}{N} \frac{\partial \mathcal{E}_+^{\{N,\alpha\}}}{\partial \alpha},
 \end{aligned} \tag{18}$$

where  $\mathcal{E}_\pm^{\{N,\alpha\}} = \text{Tr}[\hat{\Gamma}_\pm^{\{N,\alpha\}} \hat{H}]$  are the left/right  $N$ -centered ensemble energies.

Similarly, the true density  $n_{\hat{\Gamma}(\mathcal{N})}(\mathbf{r}) = \text{Tr}[\hat{\Gamma}(\mathcal{N}) \hat{n}(\mathbf{r})]$  can be obtained as follows from the left or right  $N$ -centered ensemble ones  $n_{\hat{\Gamma}_\pm^{\{N,\alpha\}}}(\mathbf{r}) = \text{Tr}[\hat{\Gamma}_\pm^{\{N,\alpha\}} \hat{n}(\mathbf{r})]$ :

$$\begin{aligned}
 n_{\hat{\Gamma}(\mathcal{N})}(\mathbf{r}) \stackrel{[\mathcal{N}]=N}{\equiv} n_{\hat{\Gamma}(N-\alpha)}(\mathbf{r}) \\
 = \left(1 - \frac{\alpha}{N}\right) n_{\hat{\Gamma}_-^{\{N,\alpha\}}}(\mathbf{r}) - \frac{\alpha(1-\alpha)}{N} \frac{\partial n_{\hat{\Gamma}_-^{\{N,\alpha\}}}(\mathbf{r})}{\partial \alpha},
 \end{aligned} \tag{19}$$

and

$$\begin{aligned}
 n_{\hat{\Gamma}(\mathcal{N})}(\mathbf{r}) \stackrel{[\mathcal{N}]=N}{\equiv} n_{\hat{\Gamma}(N+\alpha)}(\mathbf{r}) \\
 = \left(1 + \frac{\alpha}{N}\right) n_{\hat{\Gamma}_+^{\{N,\alpha\}}}(\mathbf{r}) + \frac{\alpha(1-\alpha)}{N} \frac{\partial n_{\hat{\Gamma}_+^{\{N,\alpha\}}}(\mathbf{r})}{\partial \alpha}.
 \end{aligned} \tag{20}$$

Let us finally point out that, according to Equations (13) and (14),

$$\hat{\Gamma}^{N-1} - \hat{\Gamma}^N = -\frac{1}{N} \left( \hat{\Gamma}_-^{\{N,\alpha\}} + (1-\alpha-N) \frac{\partial \hat{\Gamma}_-^{\{N,\alpha\}}}{\partial \alpha} \right), \tag{21}$$

and

$$\hat{\Gamma}^N - \hat{\Gamma}^{N+1} = -\frac{1}{N} \left( \hat{\Gamma}_+^{\{N,\alpha\}} + (1-\alpha+N) \frac{\partial \hat{\Gamma}_+^{\{N,\alpha\}}}{\partial \alpha} \right). \tag{22}$$

Consequently, the IP and EA can be extracted from the left and right  $N$ -centered ensemble energies as follows:

$$\begin{aligned}
 I^N &= \text{Tr} \left[ \left( \hat{\Gamma}^{N-1} - \hat{\Gamma}^N \right) \hat{H} \right] \\
 &= -\frac{1}{N} \left( \mathcal{E}_-^{\{N,\alpha\}} + (1-\alpha-N) \frac{\partial \mathcal{E}_-^{\{N,\alpha\}}}{\partial \alpha} \right),
 \end{aligned} \tag{23}$$

and

$$\begin{aligned}
 A^N &= \text{Tr} \left[ \left( \hat{\Gamma}^N - \hat{\Gamma}^{N+1} \right) \hat{H} \right] \\
 &= -\frac{1}{N} \left( \mathcal{E}_+^{\{N,\alpha\}} + (1-\alpha+N) \frac{\partial \mathcal{E}_+^{\{N,\alpha\}}}{\partial \alpha} \right).
 \end{aligned} \tag{24}$$

As shown in the following, by deriving a DFT for left and right  $N$ -centered ensembles, we obtain from Equations (17)–(20) a novel and in-principle-exact density-functional description of open systems.

### 2.3 | Left/right $N$ -centered ensemble DFT

In this section, we derive a variational Kohn-Sham (KS) DFT expression for the left/right  $N$ -centered ensemble energies. As a result, the open system problem will be mapped (via Equations 17 and 18) onto an auxiliary  $N$ -electron noninteracting ensemble, where the (central) number  $N$  is an integer. The derivation follows<sup>[14]</sup> closely the one presented in Senjean and Fromager<sup>[14]</sup> for two-weight  $N$ -centered ensembles (see Equation 2).

Let us consider the usual ab initio quantum chemical Hamiltonian  $\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{ext}$  where  $\hat{T}$  and  $\hat{W}_{ee}$  are the kinetic energy and two-electron repulsion operators, respectively, and  $\hat{V}_{ext} = \int d\mathbf{r} v_{ext}(\mathbf{r}) \hat{n}(\mathbf{r})$  is the external potential operator. For an isolated molecule, the external local potential  $v_{ext}(\mathbf{r})$  is simply the nuclear potential. If we introduce the analog for left/right  $N$ -centered ensembles of Levy's constrained-search universal functional,

$$\begin{aligned} F_{\pm}^{\{N,\alpha\}}[n] &= \min_{\hat{\gamma}_{\pm}^{\{N,\alpha\}} \rightarrow n} \left\{ \text{Tr} \left[ \hat{\gamma}_{\pm}^{\{N,\alpha\}} \left( \hat{T} + \hat{W}_{ee} \right) \right] \right\} \\ &= \text{Tr} \left[ \hat{\Gamma}_{\pm}^{\{N,\alpha\}}[n] \left( \hat{T} + \hat{W}_{ee} \right) \right], \end{aligned} \quad (25)$$

where the minimization is performed over left/right  $N$ -centered ensemble density matrix operators  $\hat{\gamma}_{\pm}^{\{N,\alpha\}}$  that fulfill the density constraint

$$n_{\hat{\gamma}_{\pm}^{\{N,\alpha\}}}(\mathbf{r}) = \text{Tr} \left[ \hat{\gamma}_{\pm}^{\{N,\alpha\}} \hat{n}(\mathbf{r}) \right] = n(\mathbf{r}), \quad (26)$$

then it becomes possible to express the exact left/right  $N$ -centered ensemble energies variationally as follows:

$$\mathcal{E}_{\pm}^{\{N,\alpha\}} = \min_{n \rightarrow N} \left\{ F_{\pm}^{\{N,\alpha\}}[n] + \int d\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r}) \right\}. \quad (27)$$

The minimum is reached when the density equals the exact left/right  $N$ -centered ensemble one  $n_{\pm}^{\{N,\alpha\}}$ . Note that the true (ie, interacting) density matrix operators  $\hat{\Gamma}_{\pm}^{\{N,\alpha\}}$  in Equations (4) and (5) would be obtained by solving the ground-state Schrödinger equation  $\hat{H}\Psi^{N_e} = E^{N_e}\Psi^{N_e}$  for  $N_e = N$  and  $N_e = N \pm 1$  electrons. Like in regular DFT, we bypass this complicated task by introducing the following KS decomposition,

$$F_{\pm}^{\{N,\alpha\}}[n] = T_{s\pm}^{\{N,\alpha\}}[n] + E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n], \quad (28)$$

where the noninteracting density-functional kinetic energy contribution reads

$$\begin{aligned} T_{s\pm}^{\{N,\alpha\}}[n] &= \min_{\hat{\gamma}_{\pm}^{\{N,\alpha\}} \rightarrow n} \left\{ \text{Tr} \left[ \hat{\gamma}_{\pm}^{\{N,\alpha\}} \hat{T} \right] \right\} \\ &= \text{Tr} \left[ \hat{\gamma}_{s\pm}^{\{N,\alpha\}}[n] \hat{T} \right], \end{aligned} \quad (29)$$

and  $E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n]$  is the left/right  $N$ -centered ensemble Hxc functional. Note that this functional is, for a fixed density  $n$ ,  $\alpha$ -dependent. It differs from the conventional ( $N$ -electron) ground-state Hxc functional  $E_{\text{Hxc}}[n]$ , which is recovered when  $\alpha = 0$ :

$$E_{\text{Hxc}\pm}^{\{N,\alpha=0\}}[n] = E_{\text{Hxc}}[n]. \quad (30)$$

As shown in the following, modeling the dependence in  $\alpha$  of the Hxc functional in this context is analogous to modeling the derivative discontinuity in conventional DFT for open systems. In the light of Gould and Pittalis,<sup>[42]</sup> we define the exact Hx contribution as follows:

$$E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n] = \text{Tr} \left[ \hat{\gamma}_{s\pm}^{\{N,\alpha\}}[n] \hat{W}_{ee} \right], \quad (31)$$

where  $\hat{\gamma}_{s\pm}^{\{N,\alpha\}}[n]$  is the minimizing left/right  $N$ -centered ensemble density matrix operator in Equation (29). According to Equations (25), (28), and (29), the correlation contribution can then be expressed as

$$E_{c\pm}^{\{N,\alpha\}}[n] = \text{Tr} \left[ \hat{\Gamma}_{\pm}^{\{N,\alpha\}}[n] \left( \hat{T} + \hat{W}_{ee} \right) \right] - \text{Tr} \left[ \hat{\gamma}_{s\pm}^{\{N,\alpha\}}[n] \left( \hat{T} + \hat{W}_{ee} \right) \right] < 0. \quad (32)$$

Let us now return to the variational ensemble energy expression of Equation (27). By inserting the exact decomposition of Equation (28), we obtain, according to Equation (29), the final expressions

$$\begin{aligned} \mathcal{E}_{\pm}^{\{N,\alpha\}} &= \min_{\hat{\gamma}_{\pm}^{\{N,\alpha\}}} \left\{ \text{Tr} \left[ \hat{\gamma}_{\pm}^{\{N,\alpha\}} \hat{h} \right] + E_{\text{Hxc}\pm}^{\{N,\alpha\}} \left[ n_{\hat{\gamma}_{\pm}^{\{N,\alpha\}}} \right] \right\} \\ &= \text{Tr} \left[ \hat{\gamma}_{s\pm}^{\{N,\alpha\}} \hat{h} \right] + E_{\text{Hxc}\pm}^{\{N,\alpha\}} \left[ n_{\hat{\gamma}_{s\pm}^{\{N,\alpha\}}} \right], \end{aligned} \quad (33)$$

where  $\hat{h} = \hat{T} + \hat{V}_{\text{ext}}$ . Like in regular ensemble DFTs, the minimizing (noninteracting) density matrix operators  $\hat{\gamma}_{s\pm}^{\{N,\alpha\}}$  in Equation (33) reproduce the exact interacting left/right  $N$ -centered ensemble densities,

$$\begin{aligned} n_{\hat{\gamma}_{s-}^{\{N,\alpha\}}}(\mathbf{r}) &= \left(1 + \frac{\alpha}{N-1}\right) \sum_{i=1}^{N-1} \left| \varphi_{i-}^{\{N,\alpha\}}(\mathbf{r}) \right|^2 + (1-\alpha) \left| \varphi_{N-}^{\{N,\alpha\}}(\mathbf{r}) \right|^2, \\ &= n_{\Gamma_{-}^{\{N,\alpha\}}}(\mathbf{r}), \end{aligned} \quad (34)$$

and

$$\begin{aligned} n_{\hat{\gamma}_{s+}^{\{N,\alpha\}}}(\mathbf{r}) &= \left(1 - \frac{\alpha}{N+1}\right) \sum_{i=1}^N \left| \varphi_{i+}^{\{N,\alpha\}}(\mathbf{r}) \right|^2 + \frac{N\alpha}{N+1} \left| \varphi_{(N+1)+}^{\{N,\alpha\}}(\mathbf{r}) \right|^2, \\ &= n_{\Gamma_{+}^{\{N,\alpha\}}}(\mathbf{r}). \end{aligned} \quad (35)$$

The KS orbitals are obtained by solving the following self-consistent equations,

$$\left( -\frac{\nabla^2}{2} + v_{s\pm}^{\{N,\alpha\}}(\mathbf{r}) \right) \varphi_{i\pm}^{\{N,\alpha\}}(\mathbf{r}) = \varepsilon_{i\pm}^{\{N,\alpha\}} \varphi_{i\pm}^{\{N,\alpha\}}(\mathbf{r}), \quad (36)$$

where the KS potential reads

$$v_{s\pm}^{\{N,\alpha\}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}\pm}^{\{N,\alpha\}} \left[ n_{\hat{\gamma}_{s\pm}^{\{N,\alpha\}}} \right](\mathbf{r}), \quad (37)$$

and

$$v_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}) = \frac{\delta E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n]}{\delta n(\mathbf{r})}. \quad (38)$$

The final step in the formulation of left/right  $N$ -centered ensemble DFT consists in connecting the true energy of the (interacting) open system under study to the KS orbital energies. For convenience, we use the Levy-Zahariev (LZ) shift-in-potential procedure,<sup>[14,43,44]</sup>

$$v_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}) \rightarrow \bar{v}_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}), \quad (39)$$

where

$$\bar{v}_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}) = v_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}) + \frac{E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n] - \int d\mathbf{r} v_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r})n(\mathbf{r})}{\int d\mathbf{r} n(\mathbf{r})}. \quad (40)$$

Note that like in the original version of  $N$ -centered ensemble DFT,<sup>[14]</sup> since

$$E_{\text{Hxc}\pm}^{\{N,\alpha\}}[n] = \int d\mathbf{r} \bar{v}_{\text{Hxc}\pm}^{\{N,\alpha\}}[n](\mathbf{r}) n(\mathbf{r}), \quad (41)$$

the total left/right  $N$ -centered ensemble KS energies match the interacting ones once the LZ shift  $\varepsilon_{i\pm}^{\{N,\alpha\}} \rightarrow \bar{\varepsilon}_{i\pm}^{\{N,\alpha\}}$  has been applied to the orbital energies (see Equations 36 and 37), that is

$$\mathcal{E}_{-}^{\{N,\alpha\}} = \left(1 + \frac{\alpha}{N-1}\right) \sum_{i=1}^{N-1} \bar{\varepsilon}_{i-}^{\{N,\alpha\}} + (1-\alpha) \bar{\varepsilon}_{N-}^{\{N,\alpha\}}, \quad (42)$$

and

$$\mathcal{E}_{+}^{\{N,\alpha\}} = \left(1 - \frac{\alpha}{N+1}\right) \sum_{i=1}^N \bar{\varepsilon}_{i+}^{\{N,\alpha\}} + \frac{N\alpha}{N+1} \bar{\varepsilon}_{(N+1)+}^{\{N,\alpha\}}. \quad (43)$$

Moreover, by applying the Hellmann-Feynman theorem to the variational energy expressions in Equation (33), it comes

$$\begin{aligned} \left. \frac{\partial \mathcal{E}_-^{(N,\alpha)}}{\partial \alpha} - \frac{\partial E_{\text{Hxc-}}^{(N,\alpha)}[n]}{\partial \alpha} \right|_{n=n_{\frac{1}{2}^-}^{(N,\alpha)}} &= \frac{N}{N-1} \sum_{i=1}^{N-1} \varepsilon_{i-}^{(N,\alpha)} - \sum_{i=1}^N \varepsilon_{i-}^{(N,\alpha)} \\ &= \frac{1}{N-1} \sum_{i=1}^{N-1} \left( \varepsilon_{i-}^{(N,\alpha)} - \varepsilon_{N-}^{(N,\alpha)} \right) \\ &= \frac{1}{N-1} \sum_{i=1}^{N-1} \left( \bar{\varepsilon}_{i-}^{(N,\alpha)} - \bar{\varepsilon}_{N-}^{(N,\alpha)} \right), \end{aligned} \quad (44)$$

and, similarly,

$$\left. \frac{\partial \mathcal{E}_+^{(N,\alpha)}}{\partial \alpha} - \frac{\partial E_{\text{Hxc+}}^{(N,\alpha)}[n]}{\partial \alpha} \right|_{n=n_{\frac{1}{2}^+}^{(N,\alpha)}} = -\frac{1}{N+1} \sum_{i=1}^N \left( \varepsilon_{i+}^{(N,\alpha)} - \bar{\varepsilon}_{(N+1)+}^{(N,\alpha)} \right). \quad (45)$$

By combining Equations (17), (18), and (42)-(45) we can finally express the exact open-system energy in terms of the LZ-shifted KS orbital energies as follows:

$$\begin{aligned} E(\mathcal{N}) \stackrel{[\mathcal{N}]=N}{\equiv} E(N-\alpha) \\ = \sum_{i=1}^{N-1} \bar{\varepsilon}_{i-}^{(N,\alpha)} + (1-\alpha) \bar{\varepsilon}_{N-}^{(N,\alpha)} - \frac{\alpha(1-\alpha)}{N} \left. \frac{\partial E_{\text{Hxc-}}^{(N,\alpha)}[n]}{\partial \alpha} \right|_{n=n_{\frac{1}{2}^-}^{(N,\alpha)}}, \end{aligned} \quad (46)$$

and

$$\begin{aligned} E(\mathcal{N}) \stackrel{[\mathcal{N}]=N}{\equiv} E(N+\alpha) \\ = \sum_{i=1}^N \bar{\varepsilon}_{i+}^{(N,\alpha)} + \alpha \bar{\varepsilon}_{(N+1)+}^{(N,\alpha)} + \frac{\alpha(1-\alpha)}{N} \left. \frac{\partial E_{\text{Hxc+}}^{(N,\alpha)}[n]}{\partial \alpha} \right|_{n=n_{\frac{1}{2}^+}^{(N,\alpha)}}. \end{aligned} \quad (47)$$

Equations (46) and (47) are the central result of this work.

As readily seen from these equations, the exact physical energies are recovered by summing up the LZ-shifted occupied KS orbital energies not only in the  $N$ -electron system (ie, when  $\alpha = 0$ ), as expected from Levy and Zahariev,<sup>[43]</sup> but also in the  $(N \pm 1)$ -electron ones (ie, when  $\alpha = 1$ ). This is a nontrivial result since the left/right  $N$ -centered ensemble densities do not reduce exactly to the physical ones when  $\alpha = 1$  (see the pre-factors  $1 \pm (\alpha/N)$  in Equations 19 and 20). In addition, keeping in mind that the physical energies  $E(N \pm \alpha)$  vary linearly with  $\alpha$ , we expect the total LZ-shifted KS energies

$$\sum_{i=1}^{N-1} \bar{\varepsilon}_{i-}^{(N,\alpha)} + (1-\alpha) \bar{\varepsilon}_{N-}^{(N,\alpha)} \quad (48)$$

and

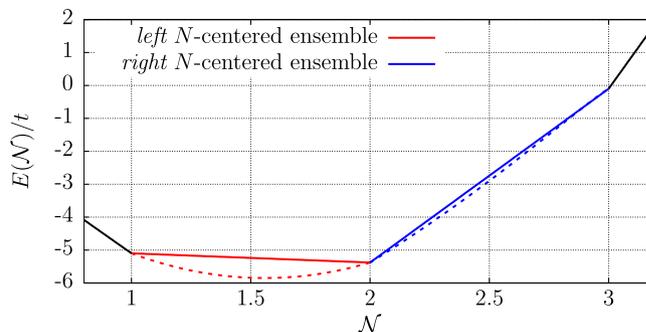
$$\sum_{i=1}^N \bar{\varepsilon}_{i+}^{(N,\alpha)} + \alpha \bar{\varepsilon}_{(N+1)+}^{(N,\alpha)}, \quad (49)$$

for  $N - \alpha$  and  $N + \alpha$  electrons, respectively, to vary (at least) quadratically with  $\alpha$ . Linearity should then be recovered when adding the ensemble Hxc first-order-derivative corrections (third terms on the right-hand side of Equations 46 and 47). This is illustrated in Figure 2 with the Hubbard dimer model (see Section 3 for further details).

## 2.4 | Reformulation of the IP/EA theorem

As shown in Section 2.2, the left/right  $N$ -centered ensemble energies (and their first-order derivatives in  $\alpha$ ) give directly access not only to the physical energy for any fractional electron number  $\mathcal{N}$  (ie, any value of  $\alpha$ ), but also to the IP and the EA (see Equations 23 and 24). From the KS-

**FIGURE 2** Total LZ-shifted KS (dashed lines) and exact (full lines) energies plotted as functions of the electron number for the asymmetric Hubbard dimer with  $\Delta v_{\text{ext}}/t = 10$  and  $U/t = 5$ . Results are shown for the value  $N = 2$  of the central number. See Equations (48) and (49), and the text that follows for further details



DFT expressions in Equations (42)–(45) we obtain the following reformulation of Janak's theorem,<sup>[45]</sup> which holds for any value of  $\mathcal{N}$  or, equivalently, for any value of  $\alpha$  in the range  $0 \leq \alpha \leq 1$ :

$$\begin{aligned} \frac{dE(\mathcal{N})}{d\mathcal{N}} \Big|_{\mathcal{N}=N-\alpha} &= I^N \\ &= \bar{\varepsilon}_{N-}^{\{N,\alpha\}} + \frac{(1-\alpha-N)}{N} \frac{\partial E_{\text{Hxc}}^{\{N,\alpha\}}[n]}{\partial \alpha} \Big|_{n=n_{\pm}^{\{N,\alpha\}}} \end{aligned} \quad (50)$$

and

$$\begin{aligned} \frac{dE(\mathcal{N})}{d\mathcal{N}} \Big|_{\mathcal{N}=N+\alpha} &= A^N \\ &= \bar{\varepsilon}_{(N+1)+}^{\{N,\alpha\}} + \frac{(1-\alpha+N)}{N} \frac{\partial E_{\text{Hxc}}^{\{N,\alpha\}}[n]}{\partial \alpha} \Big|_{n=n_{\pm}^{\{N,\alpha\}}} \end{aligned} \quad (51)$$

This is the second key result of the article.

In the limits  $\mathcal{N} \rightarrow N \pm \eta$  where  $\eta \rightarrow 0^+$ , which consists in taking the  $\alpha = 0$  limit in both left and right  $N$ -centered ensembles, the density becomes simply the conventional  $N$ -electron ground-state density:

$$n_{\pm}^{\{N,\alpha=0\}}(\mathbf{r}) = n_{\pm}^N(\mathbf{r}), \quad (52)$$

and the left/right ensemble Hxc functionals reduce to the conventional ( $N$ -electron) ground-state one (see Equation 30). The KS potential in Equation (36) is unique up to a constant, as we systematically search for the  $N$ - and  $(N \pm 1)$ -electron ground states of a noninteracting system in order to construct left or right  $N$ -centered KS ensembles. As a result,  $\bar{v}_{s-}^{\{N,\alpha=0\}}(\mathbf{r})$  and  $\bar{v}_{s+}^{\{N,\alpha=0\}}(\mathbf{r})$  may differ by a constant. However, once the LZ shift is applied, the potential becomes truly unique (see Equation 40), thus, leading to

$$\bar{v}_{s-}^{\{N,\alpha=0\}}(\mathbf{r}) = \bar{v}_{s+}^{\{N,\alpha=0\}}(\mathbf{r}). \quad (53)$$

Consequently, we have

$$\bar{\varepsilon}_{i-}^{\{N,\alpha=0\}} = \bar{\varepsilon}_{i+}^{\{N,\alpha=0\}}, \quad (54)$$

and, in particular,

$$\begin{aligned} \bar{\varepsilon}_{(N+1)+}^{\{N,\alpha=0\}} - \bar{\varepsilon}_{N-}^{\{N,\alpha=0\}} &= \bar{\varepsilon}_{(N+1)\pm}^{\{N,\alpha=0\}} - \bar{\varepsilon}_{N\pm}^{\{N,\alpha=0\}} \\ &= \varepsilon_{N+1} - \varepsilon_N, \end{aligned} \quad (55)$$

where  $\varepsilon_N$  and  $\varepsilon_{N+1}$  are, respectively, the energies of the HOMO and LUMO obtained from a regular  $N$ -electron KS-DFT calculation. Note that the LZ shift does not affect the HOMO-LUMO gap. Therefore, according to the IP/EA expressions in Equations (50) and (51), the exact fundamental gap can be written as follows:

$$I^N - A^N = \varepsilon_{N+1} - \varepsilon_N + \frac{(N+1)}{N} \frac{\partial E_{\text{Hxc}}^{\{N,\alpha\}}[n_{\Gamma}^N]}{\partial \alpha} \Big|_{\alpha=0} + \frac{(N-1)}{N} \frac{\partial E_{\text{Hxc}}^{\{N,\alpha\}}[n_{\Gamma}^N]}{\partial \alpha} \Big|_{\alpha=0}, \quad (56)$$

where the last two terms on the right-hand side play all together the role of the derivative discontinuity correction to the gap in conventional KS-DFT. Note that, according to Equations (8) and (9), the left and right  $N$ -centered ensemble Hxc functionals are connected to the original  $N$ -centered ensemble functional  $E_{\text{Hxc}}^{\{N, \xi_-, \xi_+\}}[n]$  of Senjean and Fromager<sup>[14]</sup> (the latter describes the Hxc energy of the ensemble defined in Equation (2)) as follows:

$$E_{\text{Hxc}-}^{\{N, \alpha\}}[n] = E_{\text{Hxc}}^{\{N, \xi_- = \frac{N\alpha}{N-1}, \xi_+ = 0\}}[n], \quad (57)$$

and

$$E_{\text{Hxc}+}^{\{N, \alpha\}}[n] = E_{\text{Hxc}}^{\{N, \xi_- = 0, \xi_+ = \frac{N\alpha}{N+1}\}}[n]. \quad (58)$$

Thus, we recover the compact expression:<sup>[14]</sup>

$$I^N - A^N = \varepsilon_{N+1} - \varepsilon_N + \left. \frac{\partial E_{\text{Hxc}}^{\{N, \xi_-, \xi_+\}}[n_{\Gamma^N}]}{\partial \xi} \right|_{\xi=0}. \quad (59)$$

Interestingly, designing density-functional approximations for the original (two-weight)  $N$ -centered ensembles benefits automatically to the left/right variants of the theory through Equations (57) and (58).

## 2.5 | Left or right?

For clarity and convenience, we have derived explicitly both left and right variants of  $N$ -centered ensemble DFT. This is in principle not necessary as we may opt for one of the ensemble (left or right) and simply increment or decrement the central number of electrons. As illustrated in Figure 1, an open  $\mathcal{N}$ -electron system with  $[\mathcal{N}] = N$  can be described either by a left ensemble centered on  $N$  or a right ensemble centered on  $(N-1)$ . In other words, one may express the number of electrons as

$$\mathcal{N} = N - \alpha, \quad (60)$$

or, equivalently,

$$\mathcal{N} = N - 1 + \alpha', \quad (61)$$

where  $\alpha' = 1 - \alpha$ . The two descriptions should of course lead to the same physical density and energy. It is actually quite simple to obtain the left ensemble Hxc density functional from the right one, and vice versa. Indeed, according to Equations (7) and (25),

$$\begin{aligned} F_{-}^{\{N, 1-\alpha\}}[n] &= \frac{N}{N-1} \times \min_{\substack{\tilde{\gamma}_{+}^{\{N-1, \alpha\}} \\ N-1 \rightarrow n}} \left\{ \text{Tr} \left[ \tilde{\gamma}_{+}^{\{N-1, \alpha\}} \left( \hat{T} + \hat{W}_{\text{ee}} \right) \right] \right\} \\ &= \frac{N}{N-1} \min_{\substack{\tilde{\gamma}_{+}^{\{N-1, \alpha\}} \\ (N-1)n \rightarrow N}} \left\{ \text{Tr} \left[ \tilde{\gamma}_{+}^{\{N-1, \alpha\}} \left( \hat{T} + \hat{W}_{\text{ee}} \right) \right] \right\} \\ &= \frac{N}{N-1} F_{+}^{\{N-1, \alpha\}} \left[ \frac{(N-1)n}{N} \right], \end{aligned} \quad (62)$$

where  $n$  is an  $N$ -electron density. Similarly, we can show that, if  $n$  is an  $(N-1)$ -electron density, then

$$F_{+}^{\{N-1, \alpha\}}[n] = \frac{N-1}{N} F_{-}^{\{N, 1-\alpha\}} \left[ \frac{Nn}{(N-1)} \right]. \quad (63)$$

As these scaling relations apply also to the noninteracting kinetic energy, we conclude that

$$E_{\text{Hxc}-}^{\{N, 1-\alpha\}}[n] = \frac{N}{N-1} E_{\text{Hxc}+}^{\{N-1, \alpha\}} \left[ \frac{(N-1)n}{N} \right], \quad (64)$$

and

$$E_{\text{Hxc}^+}^{\{N-1,\alpha\}}[n] = \frac{N-1}{N} E_{\text{Hxc}^-}^{\{N,1-\alpha\}} \left[ \frac{Nn}{(N-1)} \right]. \quad (65)$$

In summary, a single (left or right)  $N$ -centered Hxc functional is needed for describing the variation of the electron number between two integers. One functional is obtained from the other via the scaling relations of Equations (64) and (65).

Note that these relations enable to understand why, in the  $\alpha = 1$  limit of left and right  $N$ -centered ensembles, the sum of the LZ-shifted occupied KS orbital energies matches the physical  $(N - 1)$ - and  $(N + 1)$ -electron energies, respectively (see Equations 38, 40, 46, and 47).

## 2.6 | Density-driven correlations in $N$ -centered ensembles

Very recently, Gould and Pittalis<sup>[16,17]</sup> revealed that direct approximations to Gross-Oliveira-Kohn (GOK) ensemble DFT, where the ensemble consists of  $N$ -electron ground and excited states,<sup>[15]</sup> miss an important correlation effect that they refer to as density-driven correlation. The latter originates from the deviation in density of the individual KS states within the ensemble from the true interacting ones, as shown explicitly by one of the author.<sup>[18]</sup> One may naturally wonder if this kind of correlation exists also in  $N$ -centered ensemble DFT. In the following, we will briefly explain how density-driven correlations can be defined in this context. We leave their detailed study for future work.

Let us follow the derivation of Fromager<sup>[18]</sup> and adapt it to (say left)  $N$ -centered ensembles. We start by extracting the individual  $M$ -electron ( $M = N$  or  $N - 1$ ) total energies  $E(M) = \text{Tr}[\Gamma^M \hat{H}]$ . For that purpose we use Equations (13) and (14), and the variational  $N$ -centered ensemble energy expression of Equation (33), thus, leading to the following (exact) expression:

$$E(M) = \text{Tr} \left[ \hat{\gamma}_{s-M}^{\{N,\alpha\}} \hat{h} \right] + E_{\text{Hxc},M}^{\{N,\alpha\}} \left[ n_{\hat{\gamma}_{s-M}^{\{N,\alpha\}}}, n_{\hat{\gamma}_{s-M}^{\{N,\alpha\}}} \right], \quad (66)$$

where  $\hat{\gamma}_{s-M}^{\{N,\alpha\}}$  is the  $M$ -electron component of the KS  $N$ -centered ensemble density matrix operator:

$$\hat{\gamma}_{s-}^{\{N,\alpha\}} = (1-\alpha) \hat{\gamma}_{s-N}^{\{N,\alpha\}} + \frac{N\alpha}{N-1} \hat{\gamma}_{s-N-1}^{\{N,\alpha\}}. \quad (67)$$

The individual  $N$ - and  $(N - 1)$ -electron Hxc bifunctionals in Equation (66) read

$$E_{\text{Hxc},N}^{\{N,\alpha\}}[n, n^N] = \left( 1 - \alpha \frac{\partial}{\partial \alpha} \right) E_{\text{Hxc}^-}^{\{N,\alpha\}}[n] + \int d\mathbf{r} \frac{\delta E_{\text{Hxc}^-}^{\{N,\alpha\}}[n]}{\delta n(\mathbf{r})} (n^N(\mathbf{r}) - n(\mathbf{r})), \quad (68)$$

and

$$E_{\text{Hxc},N-1}^{\{N,\alpha\}}[n, n^{N-1}] = \frac{N-1}{N} \left( 1 + (1-\alpha) \frac{\partial}{\partial \alpha} \right) E_{\text{Hxc}^-}^{\{N,\alpha\}}[n] + \int d\mathbf{r} \frac{\delta E_{\text{Hxc}^-}^{\{N,\alpha\}}[n]}{\delta n(\mathbf{r})} \left( n^{N-1}(\mathbf{r}) - \frac{(N-1)}{N} n(\mathbf{r}) \right), \quad (69)$$

respectively. One should then realize that the density constraint in Equation (29) does not necessarily imply that the individual KS densities match the true interacting ones:

$$n_{\hat{\gamma}_{s-M}^{\{N,\alpha\}}} \neq n_{\Gamma^M}. \quad (70)$$

This can be illustrated easily with the asymmetric Hubbard dimer model, which will be studied in detail in Section 3. In this model, the one-electron ground-state density (which is an atomic site occupation) reads

$$n^{M=1} = \frac{1}{2} + \frac{\Delta v}{2\sqrt{4t^2 + \Delta v^2}}, \quad (71)$$

where  $t$  is the strength of the kinetic energy and  $\Delta v$  is the analog of the local potential (here it is just a number that controls the asymmetry in the dimer). When the dimer is asymmetric (ie,  $\Delta v \neq 0$ ), the Hxc potential (which is the difference in potential between the KS noninteracting

$N$ -centered ensemble and the interacting one) is nonzero. In the weakly correlated regime, this can be readily seen from Equation (79). Therefore, according to Equation (71), the true and KS one-electron states (each of them being a component of a [left]  $N$ -centered ensemble with  $N = 2$ ) do not have the same density. If we now return to the general case, it is then relevant to decompose each individual correlation energy into state-driven (SD) and density-driven (DD) contributions, by analogy with GOK ensembles:<sup>[18]</sup>

$$E_{c,M}^{\{N,\alpha\}} \left[ n_{\gamma_s^{\{N,\alpha\}}}, n_{\gamma_{s=M}^{\{N,\alpha\}}} \right] \equiv E_{c,M}^{\{N,\alpha\}SD} + E_{c,M}^{\{N,\alpha\}DD}, \quad (72)$$

where

$$E_{c,M}^{\{N,\alpha\}SD} := E_{c,M}^{\{N,\alpha\}} \left[ n_{\gamma_s^{\{N,\alpha\}}}, n_{\Gamma^M} \right]. \quad (73)$$

While we do not expect the conventional ground-state functional  $E_{\text{Hxc}}[n]$  to be a good approximation to (neutrally) excited-state Hxc energies, one may wonder how good the approximation  $E_{\text{Hxc},M}^{\{N,\alpha\}}[n, n^M] \approx E_{\text{Hxc}}[n^M]$  is since an  $N$ -centered ensemble consists of ground states only. Answering this question is expected to pave the way toward the rationalization and development of density-functional approximations that incorporate derivative discontinuity corrections. Work is currently in progress in this direction.

## 2.7 | Comparison with conventional DFT for open systems

In standard PPLB-DFT for open systems,<sup>[1]</sup> the density  $n$  of the true physical open system is used as basic variable. It gives, by integration, the total (fractional) number  $\mathcal{N}$  of electrons:

$$\mathcal{N} = \int d\mathbf{r} n(\mathbf{r}). \quad (74)$$

The Hxc energy is then obtained from the universal ground-state functional  $E_{\text{Hxc}}[n]$  which is defined over the domain of densities that can integrate to any integral or fractional number of electrons. Despite its formal beauty, this grand canonical formulation of DFT is not necessarily the most appealing one when it comes to perform practical calculations. Indeed, modeling  $E_{\text{Hxc}}[n]$  accurately for any number of electrons (including fractional ones) is not straightforward. Most importantly, the model should be able to reproduce the derivative discontinuity that the functional is expected to exhibit when crossing an integer.<sup>[2]</sup> Note that, for open systems, the KS potential is truly unique (not up to a constant anymore). Indeed, the chemical potential has to be adjusted such that the grand canonical ground-state energies of the  $(N-1)$ - and  $N$ -electron systems (we assume that  $N-1 < \mathcal{N} < N$ ) are equal.

The situation is completely different in (say) left  $N$ -centered ensemble DFT, where we use two variables instead. The first one is the left  $N$ -centered ensemble density that integrates to the so-called central number  $N = \lceil \mathcal{N} \rceil$  of electrons. The second variable  $\alpha = N - \mathcal{N}$  is the deviation of the central number from the true electron number  $\mathcal{N}$ . Even though alternative ensemble DFT approaches<sup>[13,36]</sup> do not rely on a centered density, they use information about the  $(N-1)$  and  $N$ -electron systems (ie, systems with an integral number of electrons) as  $N$ -centered ensemble DFT does. They are similar from this point of view.

Since a density  $n$  that integrates to  $N$  can be reproduced by either a pure  $N$ -electron ground state or a left  $N$ -centered ensemble, it is essential to construct a functional  $E_{\text{Hxc}}^{\{N,\alpha\}}[n]$  that is both density- and  $\alpha$ -dependent. At first sight, this version of DFT for open systems looks much more complicated than the PPLB one. What makes the  $N$ -centered formulation appealing is that the infamous derivative discontinuity is now obtained through the derivative in  $\alpha$  of the  $N$ -centered ensemble density-functional Hxc energy. As a result, if one can model the dependence in  $\alpha$  of the latter functional, one can in principle solve the derivative discontinuity problem.

## 3 | APPLICATION TO THE HUBBARD DIMER

### 3.1 | Hamiltonian and density functionals

A proof of concept study of the (not necessarily symmetric) Hubbard dimer is presented in this section. This is one of the simplest solvable models exhibiting a nontrivial interplay between electron-electron interaction and inhomogeneity. It is often used as a lab for testing new ideas in DFT, gaining more insight into those and their approximate formulations.<sup>[14,44,46-53]</sup> In this model, the ab initio Hamiltonian  $\hat{H}$  is simplified as follows:

$$\hat{T} \rightarrow -t \sum_{\sigma=\uparrow\downarrow} \left( \hat{c}_{0\sigma}^\dagger \hat{c}_{1\sigma} + \hat{c}_{1\sigma}^\dagger \hat{c}_{0\sigma} \right), \hat{W}_{ee} \rightarrow U \sum_{i=0}^1 \hat{n}_i \hat{n}_{i+1}, \hat{V}_{\text{ext}} \rightarrow \Delta v_{\text{ext}} (\hat{n}_1 - \hat{n}_0) / 2, \hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}, \quad (75)$$

where  $\hat{n}_i = \sum_{\sigma=\uparrow\downarrow} \hat{n}_{i\sigma}$  is the density operator on site  $i$  ( $i = 0, 1$ ). Note that the external potential reduces to a single number  $\Delta v_{\text{ext}}$  which controls the asymmetry of the dimer. The density also reduces to a single number  $n = n_0$  which is the occupation of site 0 given that  $n_1 = N - n$  for an  $N$ -centered ensemble. In the following, the central number of electrons will be fixed to  $N = 2$  and the hopping parameter will be set to  $t = 1$ . All density functionals can be derived analytically except the correlation ones that can be computed to arbitrary accuracy via Lieb maximizations.<sup>[14,44,48]</sup>

As shown in Appendix A, within left/right  $N$ -centered ensemble DFT, the exact ground-state energy of an open system with  $\mathcal{N}_\pm = 2 \pm \alpha$  electrons reads

$$E(\mathcal{N}_\pm) \equiv \left[ \frac{2 \pm \alpha}{2} \left( T_{s_\pm}^{(N=2,\alpha)}(n) + E_{\text{Hxc}\pm}^{(N=2,\alpha)}(n) + \Delta v_{\text{ext}} \times (1-n) \right) \pm \frac{\alpha(1-\alpha)}{2} \frac{\partial T_{s_\pm}^{(N=2,\alpha)}(n)}{\partial \alpha} \pm \frac{\alpha(1-\alpha)}{2} \frac{\partial E_{\text{Hxc}\pm}^{(N=2,\alpha)}(n)}{\partial \alpha} \right]_{n=n_\pm^{(N=2,\alpha)}(\Delta v_{\text{ext}})}. \quad (76)$$

According to Equations (8), (9), (29), and (31), the expressions for the left/right  $N$ -centered ensemble noninteracting kinetic and Hx energy functionals can be obtained from the two-weight  $N$ -centered ensemble functionals of our previous work.<sup>[14]</sup> Indeed, the left functionals correspond to  $\xi_- = \frac{N\alpha}{N-1}$  and  $\xi_+ = 0$ , thus, leading to

$$T_{s_-}^{(N=2,\alpha)}(n) = -2t \sqrt{1 - (n-1)^2} = T_s^{N=2}(n), \quad (77)$$

$$\Delta v_{\text{KS}-}^{(N=2,\alpha)}(n) = \frac{2t(n-1)}{\sqrt{1 - (n-1)^2}}, \quad (78)$$

where  $\Delta v_{\text{KS}-}^{(N=2,\alpha)}(n) = \partial T_{s_-}^{(N=2,\alpha)}(n) / \partial n$  is the KS potential for the left ensemble, and

$$E_{\text{Hx}-}^{(N=2,\alpha)}(n) = \frac{U(1-\alpha)}{2} \left( 1 + (n-1)^2 \right). \quad (79)$$

Similarly for the right functionals, we have  $\xi_- = 0$  and  $\xi_+ = \frac{N\alpha}{N+1}$ , thus, leading to

$$T_{s_+}^{(N=2,\alpha)}(n) = -2t \sqrt{\left( \frac{2\alpha}{3} - 1 \right)^2 - (n-1)^2}, \quad (80)$$

$$\Delta v_{\text{KS}+}^{(N=2,\alpha)}(n) = \frac{2t(n-1)}{\sqrt{\left( \frac{2\alpha}{3} - 1 \right)^2 - (n-1)^2}}, \quad (81)$$

and

$$E_{\text{Hx}+}^{(N=2,\alpha)}(n) = \frac{U}{2} \left[ 1 + \frac{\alpha}{3} + \frac{9(1-\alpha)}{(2\alpha-3)^2} (n-1)^2 \right]. \quad (82)$$

As readily seen from Equation (81), the noninteracting  $v$ -representability condition for the right  $N$ -centered ensemble is  $\alpha$ -dependent:

$$\frac{2\alpha}{3} < n < 2 - \frac{2\alpha}{3}. \quad (83)$$

Various density-functional approximations are tested in the following. For simplicity, we will restrict our study to functional-driven errors<sup>[54]</sup> which means that all density-functional energies will be computed with the exact  $N$ -centered ensemble densities. The investigation of density-driven errors<sup>[54]</sup> is left for future work. Let us start with two approximations that would be applicable also to ab initio problems. The simplest one consists in neglecting correlation effects and using a regular ( $\alpha$ -independent) Ground-State exchange functional. In this model, we simply have to consider the  $\alpha = 0$  limit of Equations (79) and (82). The approximation will be referred to as GS-Hx. A conventional ( $\alpha$ -independent) Ground-State correlation functional might then be added, thus, leading to a second approximation referred to as GS-Hxc. In this context, we use the correlation

functional of Carrascal et al.<sup>[47]</sup> which has been parameterized on the two-electron Hubbard dimer. Finally, in order to investigate the importance of the  $\alpha$ -dependence in both exchange and correlation ensemble energies, we consider two additional approximations. In the first one, which is referred to as ensemble exact exchange (EEXX), Equations (79) and (82) are employed, and correlation effects are neglected. Adding the Ground-State correlation functional of Carrascal et al.<sup>[47]</sup> leads to our last (so-called GS-c) approximation. The four approximations are summarized in Table 1.

### 3.2 | Influence of the ensemble derivative-in- $\alpha$ Hxc density functional

As shown in Equations (46) and (47), the true physical energy of an open system cannot be expressed solely as a function of the shifted KS orbital energies. An additional ensemble Hxc first-order-derivative correction has to be accounted for as soon as the true number of electrons deviates from an integer. In Figure 2, we plot the exact expressions for the true physical energy using the left and right ( $N = 2$ )-centered ensembles, with and without the ensemble derivative-in- $\alpha$  Hxc corrections. As expected, the exact energy is a piecewise linear function of the electron number. Removing the derivative-in- $\alpha$  correction induces curvature. Hence, in the language of left/right  $N$ -centered ensemble DFT, describing the piecewise linearity of the energy consists in modeling the dependence in  $\alpha$  of the ensemble Hxc density functional. As clearly shown in Figure 2, no derivative-in- $\alpha$  correction is needed when the number of electrons is an integer. This is a direct consequence of the scaling relations in Equations (64) and (65), and the fact that, by construction, summing up the LZ-shifted occupied KS orbital energies gives the exact energy for an integral number of electrons.<sup>[43]</sup>

### 3.3 | Symmetric case

In this section, we investigate the performance of the various approximations (see Table 1) in the symmetric dimer ( $\Delta v_{\text{ext}}/t = 0$ ) for different values of  $U/t$ , as shown in Figure 3. As expected, the GS-Hxc energy is always below the GS-Hx one, because the correlation energy functional is always negative (and there is no additional derivative-in- $\alpha$  correction). This statement also holds when comparing GS-c with EEXX. Since we use the highly accurate parametrization of Carrascal et al.<sup>[47]</sup> for the two-electron GS correlation energy functional, the GS-Hxc and GS-c approximations are on top of the exact curve for  $\mathcal{N} = 2$ . This is definitely not the case for the GS-Hx approximation which describes neither the correlation effects nor the  $\alpha$ -dependence. This is the reason why GS-Hx performs so poorly for any  $\mathcal{N}$  value, especially when  $U/t$  is large. Note that it also gives a wrong energy for  $\mathcal{N} = 1$ . Indeed, even if there is only one electron (and therefore no correlation), the Hx part of the functional is still  $\alpha$ -independent within GS-Hx, and therefore only meaningful when  $\mathcal{N} = 2$  (ie,  $\alpha = 0$ ).

Returning to the GS-Hxc and GS-c approximations, they are both exact for  $\mathcal{N} = 2$ . When deviating from this central electron number, the  $\alpha$ -independent correlation functional of Carrascal et al. becomes an approximation, as one cannot expect the correlation energy to be the same for systems with different numbers of electrons. In contrast, EEXX is exact for  $\mathcal{N} = 1$ , by construction. It is also exact for  $\mathcal{N} = 3$ , which is due to the particle-hole symmetry of the model. In the range  $1 < \mathcal{N} < 3$ , EEXX is not exact anymore due to the lack of the  $\alpha$ -dependent correlation functional. The effect of the latter on the true physical energy can be directly evaluated by comparing EEXX to the exact curve.

Interestingly, all the approximations give physical energies that vary linearly with  $\mathcal{N}$  (or  $\alpha$ ). As shown in Appendix B, this is due to the fact that, in the symmetric dimer, the left and right ( $N = 2$ )-centered ensemble densities are equal to  $n = 1$ .

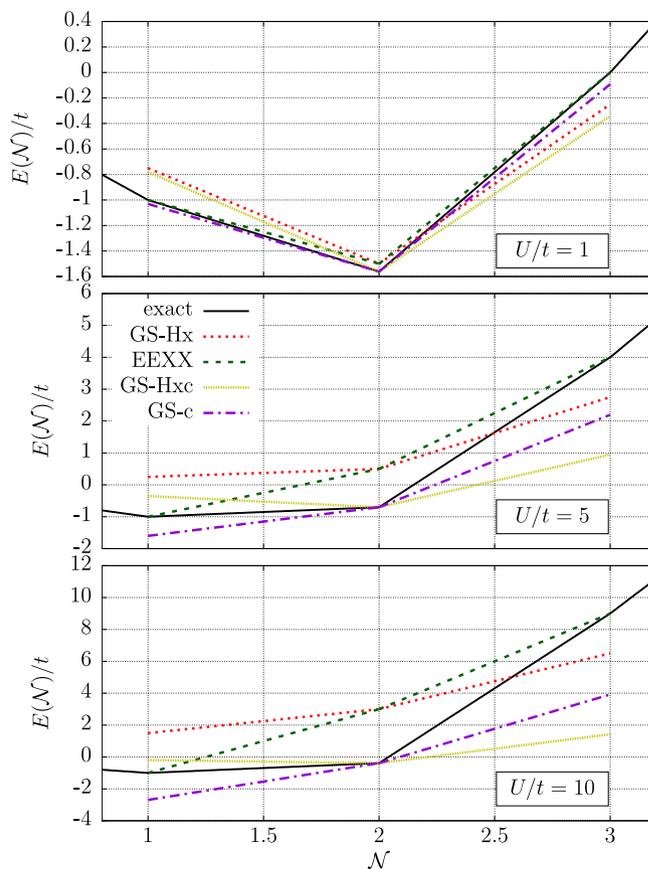
### 3.4 | Asymmetric case

Let us now investigate the asymmetric case (we choose  $\Delta v_{\text{ext}}/t = 5$ ) for different values of  $U/t$ . As shown in Figure 4, unlike in the symmetric case, approximate energies exhibit curvature in  $\mathcal{N}$ . In the particular case of GS-Hx and GS-Hxc (which are  $\alpha$ -independent functionals), the curvature is due to the  $\alpha$ -dependence in both the noninteracting kinetic energy density functional and the interacting  $N$ -centered ensemble density. In the weakly correlated regime ( $U/t = 1$  and  $U/\Delta v_{\text{ext}} = 1/5$ ) one cannot distinguish the exact curve from the EEXX one, showing that the ensemble

Acronym	$E_{\text{Hxc}\pm}^{(N=2,\alpha)}(n) \approx$	References
GS-Hx	$E_{\text{Hx}}(n)$	Equation (79) with $\alpha = 0$
GS-Hxc	$E_{\text{Hx}}(n) + E_c(n)$	Carrascal et al <sup>[47]</sup>
EEXX	$E_{\text{Hxc}\pm}^{(N=2,\alpha)}(n)$	Equations (79) and (82)
GS-c	$E_{\text{Hxc}\pm}^{(N=2,\alpha)}(n) + E_c(n)$	Equations (79) and (82), Carrascal et al <sup>[47]</sup>

**TABLE 1** Density-functional approximations tested in this work

**FIGURE 3** Exact and approximate energies of the symmetric ( $\Delta v_{\text{ext}}/t = 0$ ) Hubbard dimer plotted as functions of the electron number  $\mathcal{N}$  (or, equivalently, as functions of  $\alpha$ ). The central number of electrons is  $N = 2$ . Results are shown for  $U/t = 1, 5$ , and 10. Approximations are detailed in Table 1



( $\alpha$ -dependent) correlation density functional is equal to 0 in this regime, for any  $\alpha$ . This is due to the fact that the ensemble densities reach the border of their noninteracting  $v$ -representability domain when  $|\Delta v_{\text{ext}}| \gg U$  and  $|\Delta v_{\text{ext}}| \gg t$ . For this particular value of the ensemble density, the ensemble correlation density functional vanishes. Note that the same behavior occurred in the original  $N$ -centered ensemble DFT, for which the explanation can be found in appendix C.3 of our previous work.<sup>[14]</sup> Because the  $v$ -representability domain of the left  $N$ -centered ensemble density is  $\alpha$ -independent, the two-electron ( $\alpha = 0$ ) correlation density functional is also very close to 0 in between  $1 \leq \mathcal{N} \leq 2$ , such that GS-c is now on top of the exact curve just like EEXX. It also explains why GS-Hxc and GS-Hx give the same true physical energy here but, in contrast to EEXX and GS-c, they are not exact, thus, highlighting the importance of the ( $\alpha$ -dependent) ensemble Hx functional in this regime. For  $2 \leq \mathcal{N} \leq 3$ , the two-electron correlation energy is not equal to zero such that EEXX and GS-Hx differ slightly from GS-c and GS-Hxc, respectively. Hence, GS-c is not exact anymore, in contrast to EEXX.

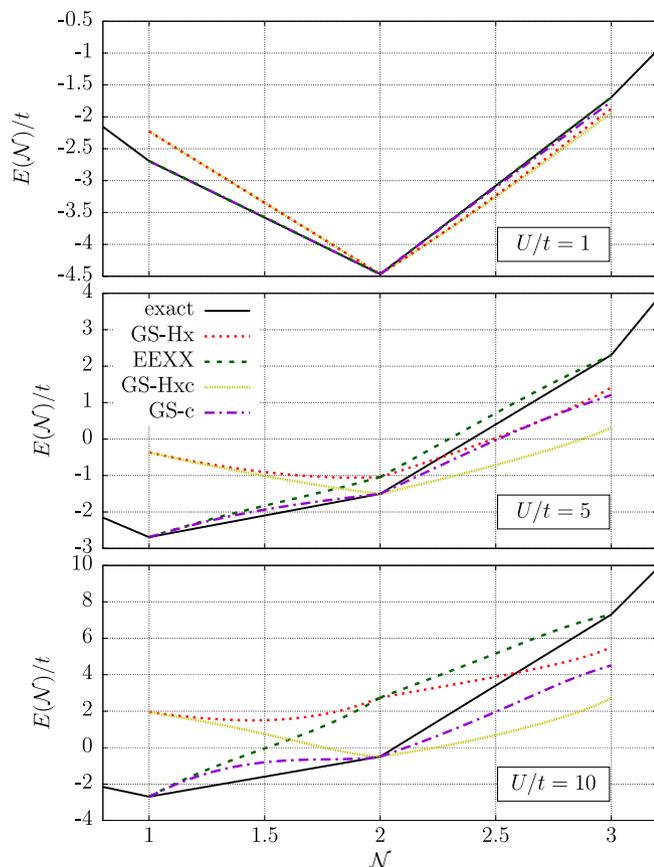
As shown in the lower panels of Figure 4, the curvature of the approximate energies becomes more pronounced as  $U/t$  increases. As expected, EEXX is not accurate anymore, especially around  $\mathcal{N} = 2$ , where the correlation energy becomes important. Unlike in the strongly correlated symmetric case, GS-c reproduces essentially the exact energy when  $\mathcal{N} = 1$  (ie,  $\alpha = 1$ ). In this case, the left  $N$ -centered ensemble density is actually equal to  $n_{-}^{(N=2, \alpha=1)} = 1 + \Delta v_{\text{ext}} / \sqrt{4t^2 + \Delta v_{\text{ext}}^2}$  (see Equation A11), thus, leading to

$$n_{-}^{\{N=2, \alpha=1\}} \xrightarrow{|\Delta v_{\text{ext}}|/t \rightarrow +\infty} 2. \quad (84)$$

Similarly, it can be shown that, for  $\alpha = 1$ , the right  $N$ -centered ensemble density reads  $n_{+}^{(N=2, \alpha=1)} = 1 + \Delta v_{\text{ext}} / \left(3\sqrt{4t^2 + \Delta v_{\text{ext}}^2}\right)$  such that

$$n_{+}^{\{N=2, \alpha=1\}} \xrightarrow{|\Delta v_{\text{ext}}|/t \rightarrow +\infty} 2 - \frac{2}{3}. \quad (85)$$

Thus, we conclude that, for large  $\Delta v_{\text{ext}}/t$  values, the two ensemble densities reach the border of their noninteracting  $v$ -representability domains (see Equations 78 and 81), such that the exact ( $\alpha$ -dependent) ensemble density-functional correlation energy becomes zero. For the left ensemble, it is clear that the  $\alpha$ -independent correlation energy used in the GS-c approximation is also equal to zero, as the border of the  $v$ -representability domain does not depend on  $\alpha$ . Therefore, both GS-c and EEXX become exact when  $\mathcal{N} = 1$ . However, when  $\mathcal{N} = 3$ , GS-c introduces a spurious correlation energy contribution obtained by inserting the right ensemble density value  $n = 2 - 2/3$  into the two-electron ( $\alpha = 0$ ) ground-state correlation functional.



**FIGURE 4** Exact and approximate energies of the asymmetric ( $\Delta v_{\text{ext}}/t = 5$ ) Hubbard dimer plotted as functions of the electron number  $\mathcal{N}$  (or, equivalently, as functions of  $\alpha$ ). The central number of electrons is  $N = 2$ . Results are shown for  $U/t = 1, 5$ , and  $10$ . Approximations are detailed in Table 1

## 4 | CONCLUSIONS AND PERSPECTIVES

So-called left and right variants of  $N$ -centered ensemble DFT have been explored. Unlike in the original formulation of the theory,<sup>[14]</sup> both open and closed electronic systems can be described. In left/right  $N$ -centered ensemble DFT, the key variables are the left/right ensemble density, which integrates to the central integral number  $N$  of electrons, and the (absolute) deviation  $\alpha$  of the true electron number from  $N$ . Within such a formalism, the infamous derivative discontinuity is taken care of by the  $\alpha$ -dependent  $N$ -centered ensemble Hxc functional. Its  $\alpha$ -dependence plays also a key role in reproducing the correct piecewise linearity of the energy, as illustrated in this work with the Hubbard dimer model. What we learn from this model is that conventional ( $\alpha$ -independent) xc functionals are not sufficient for describing open systems in the context of  $N$ -centered ensemble DFT. Developing ab initio  $\alpha$ -dependent density-functional approximations is a challenging but necessary task. As a starting point, a (semi-)local approximation could be obtained, for example, by applying the theory to finite uniform electron gases.<sup>[55]</sup> Work is currently in progress in this direction.

Various applications of left/right  $N$ -centered ensemble DFT can already be foreseen. Regarding density-functional embedding techniques, it could be used in place of conventional DFT for grand canonical ensembles when describing open fragments. The practical advantage would come from the explicit description of derivative discontinuity contributions to the energy through the dependence in  $\alpha$  of the Hxc functional. Another even more appealing feature of the  $N$ -centered formalism is the possibility to use a (pure-state)  $N$ -electron many-body wavefunction for describing an open fragment. Even though such an idea seems counterintuitive and difficult to implement, it can be made formally exact if appropriate density-functional corrections are introduced. The basic idea is to consider the following decomposition:

$$F_{\pm}^{[N,\alpha]} \left[ n_{\Gamma_{\pm}^{[N,\alpha]}} \right] = F \left[ n_{\Gamma_{\pm}^{[N,\alpha]}} \right] + \Delta F_{\pm}^{[N,\alpha]} \left[ n_{\Gamma_{\pm}^{[N,\alpha]}} \right], \quad (86)$$

where  $n_{\Gamma_{\pm}^{[N,\alpha]}}$  is the left/right  $N$ -centered ensemble density (from which the density of the open system can be extracted, according to Equations 19 and 20), and

$$\Delta F_{\pm}^{[N,\alpha]} [n] = F_{\pm}^{[N,\alpha]} [n] - F_{\pm}^{[N,\alpha=0]} [n]. \quad (87)$$

Since  $F[n] = F_{\pm}^{(N,\alpha=0)}[n]$  is the standard Levy's constrained-search functional, the first term on the right-hand side of Equation (86) can be rewritten as

$$\begin{aligned}
 F[n_{\pm}^{(N,\alpha)}] &= \min_{\Psi \rightarrow n_{\pm}^{(N,\alpha)}} \langle \Psi | \hat{T} + \hat{W}_{ee} | \Psi \rangle \\
 &= \langle \Psi_{\pm}^{(N,\alpha)} | \hat{T} + \hat{W}_{ee} | \Psi_{\pm}^{(N,\alpha)} \rangle,
 \end{aligned}
 \tag{88}$$

where  $\Psi_{\pm}^{(N,\alpha)}$  is an auxiliary many-body wavefunction with density  $n_{\pm}^{(N,\alpha)}$ . Combining Equations (27), (86), and (88) leads to the following hybrid wavefunction/DFT  $N$ -centered ensemble energy expression,

$$\mathcal{E}_{\pm}^{(N,\alpha)} = \langle \Psi_{\pm}^{(N,\alpha)} | \hat{T} + \hat{W}_{ee} + \hat{V}_{\text{ext}} | \Psi_{\pm}^{(N,\alpha)} \rangle + \Delta F_{\pm}^{(N,\alpha)}[n_{\Psi_{\pm}^{(N,\alpha)}}],
 \tag{89}$$

from which the energy of an open fragment can be extracted, in principle exactly (see Equations 17 and 18). Further exploration of this formalism is left for future work.

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## AUTHOR CONTRIBUTIONS

**Bruno Senjean:** Conceptualization; data curation; formal analysis; investigation; methodology; writing-original draft. **Emmanuel Fromager:** Conceptualization; data curation; formal analysis; investigation; methodology; supervision; validation; writing-original draft.

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## APPENDIX A: EXACT ANALYTICAL EXPRESSIONS FOR THE HUBBARD DIMER

In the following, the central number of electrons will be set to  $N = 2$ . The ensemble energies read

$$\mathcal{E}_{\pm}^{\{N=2,\alpha\}}(\Delta v_{\text{ext}}) = \min_n \{ T_{s_{\pm}}^{\{N=2,\alpha\}}(n) + E_{\text{Hxc}\pm}^{\{N=2,\alpha\}}(n) + \Delta v_{\text{ext}} \times (1-n) \}, \quad (\text{A1})$$

where the minimizing densities are  $n_{\pm}^{\{N=2,\alpha\}}(\Delta v_{\text{ext}})$ . Note that

$$\frac{\partial}{\partial \alpha} \mathcal{E}_{\pm}^{\{N=2,\alpha\}}(\Delta v_{\text{ext}}) = \left[ \frac{\partial T_{s_{\pm}}^{\{N=2,\alpha\}}(n)}{\partial \alpha} + \frac{\partial E_{\text{Hxc}\pm}^{\{N=2,\alpha\}}(n)}{\partial \alpha} \right]_{n=n_{\pm}^{\{N=2,\alpha\}}(\Delta v_{\text{ext}})}, \quad (\text{A2})$$

where the Hx and the noninteracting kinetic density functionals are given in Equations (77), (79), (80) and (82), such that

$$\frac{\partial T_{s^-}^{\{N=2,\alpha\}}(n)}{\partial \alpha} = 0, \quad (\text{A3})$$

$$\frac{\partial E_{\text{Hxc}^-}^{\{N=2,\alpha\}}(n)}{\partial \alpha} = -\frac{U}{2} (1 + (1-n)^2), \quad (\text{A4})$$

$$\frac{\partial T_{s^+}^{\{N=2,\alpha\}}(n)}{\partial \alpha} = -\frac{4t}{9} \frac{(2\alpha-3)}{\sqrt{(\frac{2\alpha}{3}-1)^2 - (n-1)^2}}, \quad (\text{A5})$$

and

$$\frac{\partial E_{\text{HX}^+}^{(N=2,\alpha)}(n)}{\partial \alpha} = \frac{U}{2} \left[ \frac{1}{3} + \frac{9(2\alpha-1)(n-1)^2}{(2\alpha-3)^3} \right]. \quad (\text{A6})$$

Plugging Equations (A1) and (A2) into Equations (17) and (18), one recovers the exact analytical expression for the true physical energies in Equation (76). In this article, we choose to focus on the functional-driven errors only, such that the exact left and right  $N$ -centered ensemble densities are used. The latter are obtained by differentiating the left and right  $N$ -centered ensemble energies,

$$\mathcal{E}_{-}^{(N=2,\alpha)}(\Delta v_{\text{ext}}) = (1-\alpha)E^{N=2}(\Delta v_{\text{ext}}) + 2\alpha\varepsilon_{\text{H}}(\Delta v_{\text{ext}}) \quad (\text{A7})$$

and

$$\mathcal{E}_{+}^{(N=2,\alpha)}(\Delta v_{\text{ext}}) = (1-\alpha)E^{N=2}(\Delta v_{\text{ext}}) + \frac{2\alpha}{3}(\varepsilon_{\text{H}}(\Delta v_{\text{ext}}) + U), \quad (\text{A8})$$

with respect to  $\Delta v_{\text{ext}}$ , where  $\varepsilon_{\text{H}}(\Delta v_{\text{ext}}) = -(1/2)\sqrt{4t^2 + \Delta v_{\text{ext}}^2}$  is the HOMO energy. According to the Hellmann-Feynman theorem,

$$\begin{aligned} \frac{\partial \mathcal{E}_{\pm}^{(N=2,\alpha)}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}} &= \frac{1}{2} \text{Tr} \left[ \hat{\Gamma}_{\pm}^{(N=2,\alpha)}(\hat{n}_1 - \hat{n}_0) \right] \\ &= \frac{1}{2} \text{Tr} \left[ \hat{\Gamma}_{\pm}^{(N=2,\alpha)}(\hat{N} - 2\hat{n}_0) \right] \\ &= \frac{N}{2} - n_{\pm}^{(N=2,\alpha)}(\Delta v_{\text{ext}}), \end{aligned} \quad (\text{A9})$$

thus, leading to the following expressions for the left and right  $N$ -centered densities:

$$n_{\pm}^{(N=2,\alpha)}(\Delta v_{\text{ext}}) = 1 - \frac{\partial \mathcal{E}_{\pm}^{(N=2,\alpha)}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}}. \quad (\text{A10})$$

Inserting Equations (A7) and (A8) into the latter expression leads to

$$n_{-}^{(N=2,\alpha)}(\Delta v_{\text{ext}}) = 1 - 2\alpha \frac{\partial \varepsilon_{\text{H}}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}} - (1-\alpha) \frac{\partial E^{N=2}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}}, \quad (\text{A11})$$

and

$$n_{+}^{(N=2,\alpha)}(\Delta v_{\text{ext}}) = 1 - \frac{2\alpha}{3} \frac{\partial \varepsilon_{\text{H}}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}} - (1-\alpha) \frac{\partial E^{N=2}(\Delta v_{\text{ext}})}{\partial \Delta v_{\text{ext}}}, \quad (\text{A12})$$

where

$$\frac{\partial \varepsilon_{\text{H}}(\Delta v)}{\partial \Delta v} = -\frac{\Delta v}{2\sqrt{4t^2 + \Delta v^2}}, \quad (\text{A13})$$

The expressions for the ground-state energy of the two-electron Hubbard dimer and its derivatives are given in the appendix of Deur et al.<sup>[48]</sup>

## APPENDIX B: PIECEWISE LINEARITY IN THE SYMMETRIC CASE

In this appendix, we derive the analytical formulas for the approximate grand canonical energies in the symmetric case ( $\Delta v = 0$ ). Let us start from the expressions of the left and right ensemble energies

$$\mathcal{E}_{-}^{\{N=2,\alpha\}}(\Delta v) = (1-\alpha)E^{N=2}(\Delta v) + 2\alpha E^{N=1}(\Delta v) \quad (\text{B1})$$

$$\mathcal{E}_{+}^{\{N=2,\alpha\}}(\Delta v) = (1-\alpha)E^{N=2}(\Delta v) + \frac{2\alpha}{3}E^{N=3}(\Delta v), \quad (\text{B2})$$

where  $E^{N=1}(\Delta v = 0) = -t$ ,  $E^{N=3}(\Delta v = 0) = U - t$  and

$$E^{N=2}(\Delta v = 0) = \frac{1}{2}\left(U - \sqrt{U^2 + 16t^2}\right). \quad (\text{B3})$$

Note that  $\mathcal{E}_{\pm}^{\{N,\alpha\}}(\Delta v = 0) = F_{\pm}^{\{N,\alpha\}}(n = 1)$ , thus, leading to,

$$F_{-}^{\{N=2,\alpha\}}(n = 1) = \frac{1-\alpha}{2}\left(U - \sqrt{U^2 + 16t^2}\right) - 2\alpha t, \quad (\text{B4})$$

$$F_{+}^{\{N=2,\alpha\}}(n = 1) = \frac{1-\alpha}{2}\left(U - \sqrt{U^2 + 16t^2}\right) + \frac{2\alpha}{3}(U - t). \quad (\text{B5})$$

As the noninteracting kinetic energy functionals read

$$T_{s-}^{\{N=2,\alpha\}}(n = 1) = -2t, \quad (\text{B6})$$

$$T_{s+}^{\{N=2,\alpha\}}(n = 1) = -2t\left(1 - \frac{2\alpha}{3}\right), \quad (\text{B7})$$

one obtains the following expression for the left and right Hxc energy functionals:

$$E_{\text{Hxc-}}^{\{N=2,\alpha\}}(n = 1) = \frac{1-\alpha}{2}\left(U - \sqrt{U^2 + 16t^2} + 4t\right), \quad (\text{B8})$$

$$E_{\text{Hxc+}}^{\{N=2,\alpha\}}(n = 1) = \frac{2}{3}\alpha U + E_{\text{Hxc-}}^{\{N=2,\alpha\}}(n = 1). \quad (\text{B9})$$

The grand canonical energies are then given by

$$E(\mathcal{N} = 2 - \alpha) = \frac{(2-\alpha)}{2}\left(E_{\text{Hxc-}}^{\{N,\alpha\}}(n = 1) - 2t\right) - \frac{\alpha(1-\alpha)}{2}\frac{\partial E_{\text{Hxc-}}^{\{N,\alpha\}}(n = 1)}{\partial \alpha} \quad (\text{B10})$$

$$E(\mathcal{N} = 2 + \alpha) = -2t\left(1 - \frac{\alpha}{2}\right) + \left(1 + \frac{\alpha}{2}\right)E_{\text{Hxc+}}^{\{N,\alpha\}}(n = 1) + \frac{\alpha(1-\alpha)}{2}\frac{\partial E_{\text{Hxc+}}^{\{N,\alpha\}}(n = 1)}{\partial \alpha} \quad (\text{B11})$$

By realizing that

$$E_{\text{Hxc-}}^{\{N=2,\alpha\}}(n = 1) = (\alpha - 1)\frac{\partial E_{\text{Hxc-}}^{\{N=2,\alpha\}}(n = 1)}{\partial \alpha}, \quad (\text{B12})$$

$$E_{\text{Hxc+}}^{\{N=2,\alpha\}}(n = 1) = (\alpha - 1)\frac{\partial E_{\text{Hxc+}}^{\{N=2,\alpha\}}(n = 1)}{\partial \alpha} + \frac{2}{3}U, \quad (\text{B13})$$

where  $\partial E_{\text{Hxc}\pm}^{\{N=2,\alpha\}}(n = 1)/\partial \alpha$  is constant ( $\alpha$ -independent), it is straightforward to see that all quadratic terms (with respect to  $\alpha$ ) in Equations (B10) and (B11) cancel out as expected. The slopes of the true physical energies are, according to Equations (12) and (B3),

$$\frac{\partial E(\mathcal{N} = 2 \pm \alpha)}{\partial \alpha} = \frac{1}{2}\left(\pm U - 2t + \sqrt{U^2 + 16t^2}\right). \quad (\text{B14})$$

Turning to the different approximations considered in Section 3 of this article, we follow the same reasoning and end up with the following constant slopes for  $\Delta v = 0$  for GS-Hx,

$$\frac{\partial E(\mathcal{N} = 2 \pm \alpha)}{\partial \alpha} = t \pm \frac{U}{4}, \quad (\text{B15})$$

for EEXX,

$$\frac{\partial E(\mathcal{N} = 2 \pm \alpha)}{\partial \alpha} = t \pm \frac{U}{2}, \quad (\text{B16})$$

for GS-Hxc,

$$\frac{\partial E(\mathcal{N} = 2 - \alpha)}{\partial \alpha} = -\frac{1}{4} \left( U - \sqrt{U^2 + 16t^2} \right), \quad (\text{B17})$$

$$\frac{\partial E(\mathcal{N} = 2 + \alpha)}{\partial \alpha} = 2t + \frac{1}{4} \left( U - \sqrt{U^2 + 16t^2} \right), \quad (\text{B18})$$

and finally for GS-c,

$$\frac{\partial E(\mathcal{N} = 2 - \alpha)}{\partial \alpha} = -\frac{U}{2} + \frac{1}{4} \sqrt{U^2 + 16t^2}, \quad (\text{B19})$$

$$\frac{\partial E(\mathcal{N} = 2 + \alpha)}{\partial \alpha} = 2t + \frac{U}{2} - \frac{1}{4} \sqrt{U^2 + 16t^2}. \quad (\text{B20})$$

Note that in the case  $\mathcal{N} = 2 - \alpha$ , the slope with respect to  $\mathcal{N}$  in Figures 3 and 4 are the same as the above but with opposite sign. As readily seen from Equations (B14) and (B17) in the atomic limit  $t \rightarrow 0$ , the energy of the open system within GS-Hxc has the same slope (equal to zero) as the exact one for  $1 \leq \mathcal{N} \leq 2$ . As GS-Hxc is exact at  $\mathcal{N} = 2$ , GS-Hxc is also exact in the range  $1 \leq \mathcal{N} \leq 2$  in the atomic limit. Another interesting behavior, in the symmetric case and in the atomic limit, is that none of the approximations considered in this article can describe the derivative discontinuity of the grand canonical energy when crossing  $\mathcal{N} = N = 2$ . Indeed, all the approximations feature a constant slope in between  $1 \leq \mathcal{N} \leq 3$ , making no difference between the ionization potential and the electronic affinity, and thus, no fundamental gap. This is obviously not correct, as the exact fundamental gap is equal to  $U$  in this limit. Therefore, in order to reproduce the correct behavior, weight-dependent correlation functionals are required. Such developments are left for future work.