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Neutral electronic excitations and derivative discontinuities: An extended N-centered ensemble density functional theory perspective

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This work merges two different types of many-electron ensembles, namely, the Theophilou-Gross-Oliveira-Kohn ensembles of ground and neutrally excited states, and the more recent N-centered ensembles of neutral and charged ground states. On that basis, an in-principle exact and general, so-called extended N-centered, ensemble density functional theory of charged and neutral electronic excitations is derived. We revisit in this context the concept of density functional derivative discontinuity for neutral excitations, without ever invoking nor using the asymptotic behavior of the ensemble electronic density. The present mathematical construction fully relies on the weight dependence of the ensemble Hartree-exchange-correlation density functional energy, which makes the theory applicable to lattice models and opens new perspectives for the description of gaps in mesoscopic systems.

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I. INTRODUCTION

Kohn-Sham density functional theory (KS-DFT) [1] is prominently used nowadays to obtain approximate but reliable ground-state electronic energies around the equilibrium geometries of large systems with up to thousands of electrons. To go beyond ground-state properties, time-dependent extensions have been proposed, such as linear response time-dependent DFT (TD-DFT), where the first-order KS response function and the Hartree-exchange-correlation (Hxc) density functional kernel allow for the extraction of excited-state energies [2], or real-time (or propagation) TD-DFT that relies on the numerical propagation of the electronic equations of motion and is not limited in principle to perturbations falling into the linear regime [3]. Alternatively, and popularized in condensed matter physics, the more involved many-body perturbation theory [4,5] within *GW* [6–8] together with the Bethe-Salpeter equation, which relies on the two-particle (frequency-dependent) Green's function, can be used [9–11]. All the aforementioned methods are computationally more demanding than KS-DFT. Even more problematic, linear response TD-DFT does not generally give an accurate description of charge transfer excitations [12], and multiple excitations are even absent from the spectra [13], when the popular semilocal adiabatic approximation is employed [2,14].

During the last decade, increasing attention has been paid to time-independent ensemble extensions of DFT (ensemble DFT) [15–37], from which in-principle exact excitation energies can be inferred with the same computational cost as regular (ground-state) KS-DFT. Such an extension was originally proposed by Theophilou [38,39], Gross, Oliveira, and Kohn [40] for *neutral* excitation energies (i.e., difference of energy between states of a system with N electrons) and is referred to as TGOK-DFT, following the name of the authors. The use of TGOK ensembles in other settings than DFT, both for the description of electronic and bosonic low-lying excited states, has also become increasingly appealing [41–45].

Quite recently, the concept of N-centered ensemble [46,47] has been introduced by analogy with TGOK-DFT to evaluate, in principle exactly, *charged* excitation energies (i.e., excitation energies between ground states corresponding to different electron numbers). Importantly, N-centered ensemble DFT shed a new light on the concept of density functional derivative discontinuity for charged excitations, which emerged from the seminal work of Perdew, Parr, Levy, and Balduz (PPLB) in the context of DFT for fractional particle number [48,49]. Within the formulation of PPLB, it is in principle sufficient to extend the domain of definition of the Hxc density functional to fractional electron numbers in order to account for derivative discontinuities. However, it has been argued that invoking a fractional number of electrons is maybe not the correct route to pursue [50–54]. This debate aligns with the approach taken in N-centered ensemble DFT, where the derivative discontinuity is alternatively described through weight derivatives of the ensemble density functional Hxc energy at *fixed* ensemble density. Such derivatives are well defined in the N-centered formalism since, by construction, the ensemble density always integrates to the fixed and central (integer) number of electrons N, hence the name of the theory. Extensive discussions about the equivalence between weight derivatives and derivative discontinuities for ground states can be found in Ref. [37].

While a regular (so-called *left* in Ref. [47]) N-centered ensemble consists of $(N-1)$- and N-electron ground states, we propose in this work to incorporate neutrally excited (i.e., N-electron excited) states into the ensemble, thus allowing, for example, to decompose neutral excitation processes into separate ionization ones, as originally suggested by Levy [55].

On that basis, exactifying KS orbital energies in the description of neutral excitations consists in exactifying both ground- and excited-state KS ionization potentials, a procedure from which derivative discontinuities emerge [55]. As mentioned previously, in N-centered ensemble DFT, the description of derivative discontinuities (that connect to the piecewise-linear behavior of the ground-state energy [48,49,56]) is recast into the modeling of weight dependencies in the ensemble Hxc density functional [37,57]. Even though its practical advantage still needs to be assessed, in particular because the incorporation of weight dependencies into regular density functional approximations is not straightforward when the ensemble energy is evaluated variationally [32,37], the N-centered strategy offers a mathematically elegant and simplified alternative in describing how KS orbital energies are affected by charged excitation processes. Our motivation is to extend this strategy to neutral excitations. Even though we do not exploit in this work the following possibility, the formalism is flexible enough to include anionic states. The resulting combined TGOK/N-centered ensemble formalism, that we refer to as *extended N* centered, lays the foundations of a unified and general ensemble density functional theory of charged and neutral electronic excitations. Most importantly, as shown in the following, this formalism sheds a different light on the concept of derivative discontinuity for *neutral* excitations [18,35,55,58], which is much less discussed in the literature than for charged excitations.

The paper is organized as follows. After motivating in Sec. II the decomposition of a neutral excitation process into two ionization processes, and reviewing briefly TGOK-DFT in Sec. III, we introduce the extended N-centered ensemble density functional formalism in Sec. IV. On that basis, the concept of derivative discontinuity in the context of neutral excitation processes is revisited in Sec. V. The theory is then applied to the two-electron Hubbard dimer, as a proof of concept. The exact derivations and numerical tests are presented in Sec. VI. Conclusions and outlook are finally given in Sec. VII.

II. PROBLEMATICS: ON THE EXACTIFICATION OF KOHN-SHAM ORBITAL ENERGIES

The occupied and virtual orbital energies $\{\varepsilon_i\}_{i=1,2,...}$ generated from a regular N-electron ground-state KS-DFT calculation can be used to compute total ground- and excited-state N-electron KS energies,

$$\mathcal{E}_\nu^N = \sum_i n_\nu^i \varepsilon_i, \tag{1}$$

where $n_\nu^i \in \{0, 1, 2\}$ denotes the integer occupation of the ith KS orbital in the νth KS state ($\nu \geqslant 0$) and $\sum_i n_\nu^i = N$. It is well known that when it comes to describing neutral excitation processes, the bare KS excitation energies and the true interacting ones $\{\omega_\nu\}_{\nu>0}$ do not match:

$$\omega_\nu \equiv E_\nu^N - E_0^N \neq \mathcal{E}_\nu^N - \mathcal{E}_0^N. \tag{2}$$

In the context of linear response TD-DFT, these two quantities are connected through the Hxc kernel, i.e., the density functional derivative of the (time-dependent) Hxc potential. We focus in the following on in-principle exact time-independent density functional approaches to neutral electronic excitations and, more specifically, to ensemble ones. At this point we should stress that, unlike in charged processes, any constant shift in the Hxc potential and therefore in the orbital energies,

$$\varepsilon_i \rightarrow \varepsilon_i + c, \tag{3}$$

leaves neutral KS excitation energies unchanged:

$$\mathcal{E}_\nu^N - \mathcal{E}_0^N \rightarrow \left(\mathcal{E}_\nu^N + Nc\right) - \left(\mathcal{E}_0^N + Nc\right) = \mathcal{E}_\nu^N - \mathcal{E}_0^N. \tag{4}$$

From this standpoint, it seems impossible to exactify the KS orbital energies in the description of neutrally excited states. Nevertheless, as recalled in Sec. III, it is possible to describe exactly the deviation of the physical excitation energy from the KS one by means of an ensemble-weight-dependent Hxc density functional. A subtle but crucial point, which has not been taken into account in Eq. (4), is the fact that the KS orbital energies of the reference N-electron ground-state KS-DFT calculation are not those that describe the (even infinitesimally) excited system [58]. Interestingly, a similar issue has already been discussed for the fundamental gap problem in the context of N-centered ensemble DFT [57] where, by construction, the ensemble Hxc potential is also defined up to a constant, unlike in the more conventional DFT for fractional electron numbers [37]. In fact, within N-centered ensemble DFT, the fundamental and optical gap problems have the exact same mathematical formulation [46]. What Ref. [57] revealed [in one dimension (1D)] is that, if the N-centered ensemble Hxc potential is (arbitrarily) adjusted such that it asymptotically approaches zero infinitely far from the center of the system under study, by plotting the difference in Hxc potentials between, on the one hand, the ensemble that contains both ground N-electron and $(N+1)$-electron (with weight ξ_+) states, and, on the other hand, the regular pure N-electron ground state ($\xi_+ = 0$ in this case), one can see a plateau in the central region of the system that grows in length as $\xi_+ \rightarrow 0^+$. Ultimately, it looks as if the regular Hxc potential for N electrons in the ground state had been shifted, thus ensuring, in the present case, the exactification of the KS electron affinity when $\xi_+ \rightarrow 0^+$ (and of the KS ionization potential when $\xi_+ = 0$). In summary, the KS orbital energies are affected by the (even infinitesimal) occupation of higher-energy orbitals and this is reflected by a shift in the Hxc potential. A similar analysis has been performed by Kraisler *et al.* [58] for neutral excitations, which is our main focus.

In this work, we follow a connected but slightly different path. We propose to achieve a description of neutral excitations through an exactification of the KS orbital energies that exclusively relies on an appropriate (so-called extended N-centered) ensemble weight-dependent Hxc density functional, by analogy with the N-centered ensemble dealing with the fundamental gap [37,57]. Based on the observation made in Eq. (4) and the seminal work of Levy [55], the key idea consists in evaluating a neutral excitation energy *via* two different *charged* processes, namely, the ionization of the ground ($\nu = 0$) and the targeted excited ($\nu > 0$) N-electron states, i.e.,

$$E_\nu^N - E_0^N = I_0^N - I_\nu^N, \tag{5}$$

where

$$\left\{I_\nu^N = E_0^{N-1} - E_\nu^N\right\}_{\nu\geqslant 0} \tag{6}$$

will be referred to as ground- and excited-state ionization potentials (IPs).

Turning to the KS system, for each ionization process, a specific shift can be applied to the Hxc potential (which is unique up to a constant, as long as the number of electrons is fixed to the integer N) in order to *enforce* the KS IPs to match the true interacting ones, i.e.,

$$\begin{aligned} &\varepsilon_i \rightarrow \varepsilon_i + c_1 = \overline{\varepsilon}_i, \\ &\mathcal{E}_0^{N-1} - \mathcal{E}_0^N \rightarrow \mathcal{E}_0^{N-1} - \mathcal{E}_0^N - c_1 \overset{!}{=} I_0^N, \end{aligned} \tag{7}$$

and

$$\begin{aligned} &\varepsilon_i \rightarrow \varepsilon_i + c_2 = \tilde{\varepsilon}_i, \\ &\mathcal{E}_0^{N-1} - \mathcal{E}_\nu^N \rightarrow \mathcal{E}_0^{N-1} - \mathcal{E}_\nu^N - c_2 \overset{!}{=} I_\nu^N. \end{aligned} \tag{8}$$

If, for example, the excited state of interest ν is described by a single-electron excitation (one hole, one particle) from the highest occupied molecular orbital (HOMO) $i = N$ to a virtual one $i(\nu) > N$, then we automatically obtain from Eqs. (5), (7), and (8) what we consider as the exactification of the KS orbital energies for neutral excitations, i.e.,

$$E_\nu^N - E_0^N = \tilde{\varepsilon}_{i(\nu)} - \overline{\varepsilon}_N. \tag{9}$$

The question that is addressed in the rest of this work is how such a construction can be derived, in principle exactly (and with no need to invoke the asymptotic behavior of the ensemble density infinitely far from the center of the system under study, as will be discussed later), from a unified and general ensemble density functional formalism in which both charged and neutral excitation processes can be described simultaneously.

III. BRIEF REVIEW OF REGULAR TGOK ENSEMBLE DFT

TGOK-DFT is a time-independent ensemble extension of standard ground-state DFT to neutral excited states where the ground-state energy is replaced by the so-called ensemble energy, which is a convex combination of (N-electron) ground- and excited-state energies,

$$E^{\boldsymbol{\xi}} \overset{\text{TGOK}}{:=} \left(1 - \sum_{\nu>0} \xi_\nu^N\right) E_0^N + \sum_{\nu>0} \xi_\nu^N E_\nu^N, \tag{10}$$

where

$$\boldsymbol{\xi} \overset{\text{TGOK}}{\equiv} \left\{\xi_\nu^N\right\}_{\nu>0} \tag{11}$$

is the collection of positive and *independent* ensemble weight values that are assigned to the ordered-in-energy N-electron excited states $\{\Psi_\nu^N\}_{\nu>0}$, i.e.,

$$E_\nu^N = \left\langle \Psi_\nu^N \middle| \hat{H} \middle| \Psi_\nu^N \right\rangle < E_{\nu+1}^N. \tag{12}$$

The electronic Hamiltonian operator $\hat{H}$ of the system under study reads as

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ext}}, \tag{13}$$

where $\hat{T}$ describes the kinetic energy, $\hat{W}_{\text{ee}}$ is the two-electron repulsion operator, $\hat{V}_{\text{ext}} = \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\hat{n}(\mathbf{r})$ is the external local potential operator, and $\hat{n}(\mathbf{r})$ denotes the density operator at position $\mathbf{r}$. Note that the weight ξ_0^N assigned to the ground-state energy E_0^N in Eq. (10) is such that the collection of weights (including the ground-state one) is normalized:

$$\xi_0^N + \sum_{\nu>0} \xi_\nu^N \overset{\text{TGOK}}{=} 1. \tag{14}$$

This constraint, where ξ_0^N is an affine function of the independent excited-state ensemble weights [59], ensures that the total number of electrons is preserved when deviating from the ground-state $\boldsymbol{\xi} = 0$ limit of the theory, i.e.,

$$\int d\mathbf{r}\, n^{\boldsymbol{\xi}}(\mathbf{r}) = N, \quad \forall\, \boldsymbol{\xi} \tag{15}$$

where

$$n^{\boldsymbol{\xi}}(\mathbf{r}) \overset{\text{TGOK}}{:=} \left(1 - \sum_{\nu>0} \xi_\nu^N\right) n_{\Psi_0^N}(\mathbf{r}) + \sum_{\nu>0} \xi_\nu^N n_{\Psi_\nu^N}(\mathbf{r}) \tag{16}$$

is the ensemble density, $\{n_{\Psi_\nu^N}(\mathbf{r})\}_{\nu\geqslant 0}$ being the individual N-electron ground- and excited-state densities. In the following, we use the more compact notation

$$n^{\boldsymbol{\xi}}(\mathbf{r}) = \text{Tr}[\hat{\Gamma}^{\boldsymbol{\xi}}\hat{n}(\mathbf{r})], \tag{17}$$

where

$$\hat{\Gamma}^{\boldsymbol{\xi}} \overset{\text{TGOK}}{=} \left(1 - \sum_{\nu>0} \xi_\nu^N\right) \left|\Psi_0^N\right\rangle\!\left\langle\Psi_0^N\right| + \sum_{\nu>0} \xi_\nu^N \left|\Psi_\nu^N\right\rangle\!\left\langle\Psi_\nu^N\right| \tag{18}$$

is the ensemble density matrix operator and Tr denotes the trace. Note that we have assumed, for simplicity, that both ground and excited states are not degenerate but the formalism can be extended straightforwardly to ensembles of multiplets [40].

The TGOK ensemble energy, as defined in Eqs. (10) and (12), can be determined variationally, i.e.,

$$E^{\boldsymbol{\xi}} = \min_{\hat{\gamma}^{\boldsymbol{\xi}}} \text{Tr}[\hat{\gamma}^{\boldsymbol{\xi}}\hat{H}] = \text{Tr}[\hat{\Gamma}^{\boldsymbol{\xi}}\hat{H}], \tag{19}$$

where $\hat{\gamma}^{\boldsymbol{\xi}}$ is a trial ensemble density matrix operator, provided that the ensemble weights are collected in decreasing order [60]:

$$\xi_\nu^N \geqslant \xi_{\nu+1}^N, \quad \nu \geqslant 0. \tag{20}$$

On that basis, an ensemble KS-DFT of neutral excited states can be derived [40], where the ensemble Hxc density functional is defined exactly, as follows:

$$\begin{aligned} E_{\text{Hxc}}^{\boldsymbol{\xi}}[n] &= \min_{\hat{\gamma}^{\boldsymbol{\xi}}\rightarrow n} \text{Tr}[\hat{\gamma}^{\boldsymbol{\xi}}(\hat{T} + \hat{W}_{\text{ee}})] - \min_{\hat{\gamma}^{\boldsymbol{\xi}}\rightarrow n} \text{Tr}[\hat{\gamma}^{\boldsymbol{\xi}}\hat{T}] \\ &:= F^{\boldsymbol{\xi}}[n] - T_{\text{s}}^{\boldsymbol{\xi}}[n], \end{aligned} \tag{21}$$

where $F^{\boldsymbol{\xi}}[n]$ (and its noninteracting analog $T_{\text{s}}^{\boldsymbol{\xi}}[n]$) is simply the extension to ensembles (with given fixed ensemble weight values $\boldsymbol{\xi}$) of the Levy-Lieb functional [61,62]. The density constraint used in both minimizations reads as $n_{\hat{\gamma}^{\boldsymbol{\xi}}}(\mathbf{r}) = \text{Tr}[\hat{\gamma}^{\boldsymbol{\xi}}\hat{n}(\mathbf{r})] = n(\mathbf{r})$.

Note that the ensemble Hxc functional is both a functional of the density n *and* a function of the ensemble weights $\boldsymbol{\xi}$.

The reason is that, unlike in ground-state DFT of open electronic systems, where the ensemble weight is deduced from the fractional number of electrons, a TGOK ensemble cannot be identified solely from its density. Indeed, a density n that integrates to a given *integer* number N of electrons may be both pure-ground-state and ensemble v representable at the same time [see Eq. (37) in Ref. [63] and the discussion that follows]. Without additional information about the ensemble (namely, the ensemble weight values), the functional would not "know" if it has to compute the Hxc energy of a pure ground state ($\boldsymbol{\xi} = 0$) or that of an ensemble ($\boldsymbol{\xi} > 0$).

Finally, like in ground-state KS-DFT, the ensemble density functional Hxc energy can be decomposed into (weight-dependent) Hx and correlation contributions, which read as [24]

$$\begin{aligned} E^{\boldsymbol{\xi}}_{\rm Hx}[n] &= \lim_{\alpha\to 0^+} \frac{F^{\boldsymbol{\xi},\alpha}[n] - F^{\boldsymbol{\xi},\alpha=0}[n]}{\alpha} \\ &= \left.\frac{\partial F^{\boldsymbol{\xi},\alpha}[n]}{\partial \alpha}\right|_{\alpha=0^+} \end{aligned} \tag{22}$$

and

$$E^{\boldsymbol{\xi}}_{\rm c}[n] = E^{\boldsymbol{\xi}}_{\rm Hxc}[n] - E^{\boldsymbol{\xi}}_{\rm Hx}[n], \tag{23}$$

respectively, where

$$F^{\boldsymbol{\xi},\alpha}[n] = \min_{\hat{\gamma}^{\boldsymbol{\xi}}\to n} {\rm Tr}[\hat{\gamma}^{\boldsymbol{\xi}}(\hat{T} + \alpha \hat{W}_{\rm ee})] \tag{24}$$

is the analog for electrons that partially interact (through the positive scaling α of the electronic repulsion) of the TGOK Levy-Lieb functional $F^{\boldsymbol{\xi}}[n]$ introduced in Eq. (21). Note that $F^{\boldsymbol{\xi},\alpha=1}[n] = F^{\boldsymbol{\xi}}[n]$ and $F^{\boldsymbol{\xi},\alpha=0}[n] = T^{\boldsymbol{\xi}}_{\rm s}[n]$. It is important to stress that, unlike in regular pure ground-state KS-DFT, neither the definition of the Hx energy nor its separation into Hartree and exchange contributions are straightforward in the context of ensemble DFT [16,29,32,37,64]. The latter point will be discussed a bit further after Eq. (62).

In the context of TGOK-DFT, the variational ensemble energy expression of Eq. (19) can be recast into a minimization over noninteracting ensemble density matrix operators

$$E^{\boldsymbol{\xi}} = \min_{\hat{\gamma}^{\boldsymbol{\xi}}} \{ {\rm Tr}[\hat{\gamma}^{\boldsymbol{\xi}}(\hat{T} + \hat{V}_{\rm ext})] + E^{\boldsymbol{\xi}}_{\rm Hxc}[n_{\hat{\gamma}^{\boldsymbol{\xi}}}]\}, \tag{25}$$

where the (weight-dependent [37]) minimizing KS wave functions $\{\Phi^{\boldsymbol{\xi}}_\nu\}_{\nu\geqslant 0}$ fulfill the following self-consistent noninteracting Schrödinger equation

$$\left[\hat{T} + \hat{V}_{\rm ext} + \int d\mathbf{r}\, v^{\boldsymbol{\xi}}_{\rm Hxc}(\mathbf{r})\hat{n}(\mathbf{r})\right]\left|\Phi^{\boldsymbol{\xi}}_\nu\right\rangle = \mathcal{E}^{\boldsymbol{\xi}}_\nu\left|\Phi^{\boldsymbol{\xi}}_\nu\right\rangle, \tag{26}$$

$v^{\boldsymbol{\xi}}_{\rm Hxc}(\mathbf{r}) = \delta E^{\boldsymbol{\xi}}_{\rm Hxc}[n]/\delta n(\mathbf{r})|_{n=n^{\boldsymbol{\xi}}}$ being the weight-dependent Hxc potential. Equivalently, the orbitals from which the KS ensemble is constructed fulfill the following ensemble KS equations:

$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2} + v_{\rm ext}(\mathbf{r}) + v^{\boldsymbol{\xi}}_{\rm Hxc}(\mathbf{r})\right]\varphi^{\boldsymbol{\xi}}_i(\mathbf{r}) = \varepsilon^{\boldsymbol{\xi}}_i \varphi^{\boldsymbol{\xi}}_i(\mathbf{r}). \tag{27}$$

The latter differ from regular (ground-state) KS equations by (i) the weight dependence of the Hxc potential, and (ii) the fact that the KS orbitals, which reproduce the exact ensemble density $n^{\boldsymbol{\xi}}(\mathbf{r})$, are fractionally occupied, i.e.,

$$n^{\boldsymbol{\xi}}(\mathbf{r}) = \sum_{\nu\geqslant 0} \xi_\nu n_{\Phi^{\boldsymbol{\xi}}_\nu}(\mathbf{r}) = \sum_i \left(\sum_{\nu\geqslant 0}\xi_\nu n^i_\nu\right)\left|\varphi^{\boldsymbol{\xi}}_i(\mathbf{r})\right|^2, \tag{28}$$

where n^i_ν is the occupation of the KS orbital $\varphi^{\boldsymbol{\xi}}_i$ in the KS analog $\Phi^{\boldsymbol{\xi}}_\nu$ of the pure state ν. Note that the (weight-dependent) total KS energies simply read as

$$\mathcal{E}^{\boldsymbol{\xi}}_\nu = \sum_i n^i_\nu \varepsilon^{\boldsymbol{\xi}}_i. \tag{29}$$

Turning to the problematic raised in Sec. II, we should first recall that the exact deviation of the true interacting excitation energies from the KS ones is given by the derivative with respect to the ensemble weights (at fixed ensemble density) of the ensemble Hxc density functional energy [40,59]:

$$E^N_\nu - E^N_0 - \left(\mathcal{E}^{\boldsymbol{\xi}}_\nu - \mathcal{E}^{\boldsymbol{\xi}}_0\right) = \left.\frac{\partial E^{\boldsymbol{\xi}}_{\rm Hxc}[n]}{\partial \xi^N_\nu}\right|_{n=n^{\boldsymbol{\xi}}}. \tag{30}$$

Therefore, within regular TGOK-DFT, the exactification of the ensemble KS orbital energies occurs only when the above ensemble weight derivative vanishes, which may happen for very specific (*a priori* unknown) weight values [18,22]. In other words, such an exactification cannot, in general, be achieved, unless we introduce intermediate ionization processes, as suggested in Sec. II. The main challenge in this case lies in the design of a unified ensemble density functional formalism where both neutral and charged excitations can be described. A solution to this problem is proposed in Sec. IV.

As a side comment, which aims at preventing confusions later on, we want to stress that, in principle, the Hxc ensemble weight derivative [i.e., the KS excitation energy correction on the right-hand side of Eq. (30)] and the Hxc density functional derivative discontinuity [18,35,58] are two distinct concepts. The latter, which affects the energy of the KS acceptor orbital $i(\nu)$ introduced in Eq. (9), appears in the $\boldsymbol{\xi} \to \mathbf{0}^+$ limit of the theory, when comparison is made with regular N-electron ground-state KS-DFT (where $\boldsymbol{\xi} = \mathbf{0}$) from which the energy of the HOMO is evaluated. The two concepts become equivalent in this special case, as it will become clear from the upcoming Eqs. (60) and (61), once the extended N-centered ensemble DFT formalism has been introduced. This is the purpose of Sec. IV.

IV. EXTENDED *N*-CENTERED ENSEMBLE DFT

Senjean and Fromager [46] introduced some years ago the so-called N-centered ensemble DFT formalism where the fundamental gap of N-electron ground states is described with the exact same mathematical language as in TGOK-DFT. The approach also allows for a separate description of ionization and affinity processes [37,46,47,57], which is essential in the present context. The close resemblance of N-centered ensemble DFT with TGOK-DFT is exploited in the following in order to provide an in-principle exact ensemble density functional description of ionized excited states. The resulting ensemble formalism, where neutral excited states are incorporated into a regular (ground-state) N-centered ensemble, will be referred to as *extended* N-centered ensemble formalism.

A. Combining TGOK with N-centered ensembles

By analogy with regular N-centered ensemble DFT, where the ensemble weights assigned to the $(N-1)$- and $(N+1)$-electron ground states are allowed to vary independently [46], we propose to combine TGOK and N-centered (Nc) ensembles as follows:

$$\hat{\Gamma}^{\boldsymbol{\xi}} \overset{\text{TGOK}+N\text{c}}{=} \left(1-\sum_{\nu>0}\frac{N_\nu}{N}\xi_\nu\right)|\Psi_0\rangle\langle\Psi_0| + \sum_{\nu>0}\xi_\nu|\Psi_\nu\rangle\langle\Psi_\nu|, \tag{31}$$

where $\Psi_0 \equiv \Psi_0^N$ is the reference N-electron ground state to which all possible excitation processes (neutral and charged, including multiple-electron excitations) can be applied. In other words, the integer number of electrons $N_\nu = \int d\mathbf{r}\, n_{\Psi_\nu}(\mathbf{r})$ that is described by the excited-state wave function Ψ_ν $(\nu > 0)$ is not necessarily equal to the (integer) number of electrons in the ground state,

$$N_0 = N, \tag{32}$$

that is referred to as the central number of electrons. However, by construction, the ensemble density still integrates to N, like in TGOK-DFT [see Eqs. (15) and (17)].

As further discussed in Sec. V, the fact that the net number of electrons in the ensemble does *not* vary with the ensemble weights, unlike in the traditional PPLB-DFT of fractional electron numbers [48], plays a central role in the exact description of derivative discontinuities in terms of ensemble weight derivatives [37,57]. More precisely, the key feature of N-centered ensemble DFT is the fact that ensemble weights can vary while holding the ensemble density fixed [46]. In PPLB-DFT, the Hxc functional has no weight dependence (i.e., it is solely a functional of the density) simply because the ensemble weight is itself a functional of the density [37] which can be defined, for example, as the deviation of the (fractional) electron number from its floor value. Hence, in PPLB-DFT, any variation in weight automatically induces a change in density.

Turning back to the extended N-centered ensemble of Eq. (31), we point out that the ensemble weights assigned to the ground and excited states are positive,

$$\xi_0 = 1-\sum_{\nu>0}\frac{N_\nu}{N}\xi_\nu \geqslant 0, \tag{33a}$$

$$\xi_\nu \geqslant 0, \quad \forall\, \nu > 0 \tag{33b}$$

and, most importantly, unlike in conventional TGOK or PPLB ensembles, they do *not* sum up to 1, in general:

$$\sum_{\nu\geqslant 0}\xi_\nu = 1 + \sum_{\nu>0}\frac{(N-N_\nu)}{N}\xi_\nu. \tag{34}$$

In addition, within each subensemble containing all the states with the same number $N \pm p$ $(p = 0, 1, 2, \ldots, N)$ of electrons, we impose the following weight ordering constraints [see Eq. (20)]:

$$\xi_\nu \overset{N_\nu=N_{\nu+1}=N\pm p}{\geqslant} \xi_{\nu+1}, \tag{35}$$

in order to be able to exploit, if necessary, the TGOK variational principle within each $(N \pm p)$-electron sector of the Fock space. This simply ensures that the fully extended N-centered ensemble of interest can be determined variationally, thus allowing for an in-principle-exact density functional description of its energy. Note that, in this work, the constraint of Eq. (35) will be used only for N-electron states (i.e., $p = 0$) while the $(N-1)$ sector will be reduced to ground states. The $(N+1)$ sector will not be used. These choices are motivated by the problem raised in Sec. II and are by no means a limitation of the present ensemble formalism, which is very general.

Let us finally turn to the extended N-centered ensemble energy,

$$E^{\boldsymbol{\xi}} \overset{\text{TGOK}+N\text{c}}{=} \left(1-\sum_{\nu>0}\frac{N_\nu}{N}\xi_\nu\right)E_0 + \sum_{\nu>0}\xi_\nu E_\nu, \tag{36}$$

where $E_0 = E_0^N$ is the reference N-electron ground-state energy and E_ν is an N_ν-electron eigenvalue of the electronic Hamiltonian, i.e.,

$$\hat{H}|\Psi_\nu\rangle = E_\nu|\Psi_\nu\rangle, \quad \nu \geqslant 0 \tag{37}$$

with $N_\nu \in \{N, N\pm 1, N\pm 2, \ldots\}$. Like in TGOK-DFT [59], the linearity of the ensemble energy in the ensemble weights,

$$\boldsymbol{\xi} \overset{\text{TGOK}+N\text{c}}{\equiv} \{\xi_\nu\}_{\nu>0}, \tag{38}$$

allows for a straightforward extraction of individual energy levels (and, therefore, of the excitation energies) through first-order differentiations. Indeed, since both ground-state $(\nu = 0)$ [see Eq. (32)] and excited-state $(\nu > 0)$ energies can be expressed as

$$E_\nu \underset{\nu\geqslant 0}{=} \frac{N_\nu}{N}E_0 + \sum_{\lambda>0}\delta_{\lambda\nu}\left(E_\lambda - \frac{N_\lambda}{N}E_0\right), \tag{39}$$

where, according to Eq. (36),

$$\frac{\partial E^{\boldsymbol{\xi}}}{\partial \xi_\lambda} = E_\lambda - \frac{N_\lambda}{N}E_0 \tag{40}$$

and

$$E_0 = E^{\boldsymbol{\xi}} - \sum_{\lambda>0}\xi_\lambda\frac{\partial E^{\boldsymbol{\xi}}}{\partial \xi_\lambda}, \tag{41}$$

we immediately obtain the following compact expression in terms of the ensemble energy (and its first-order derivatives):

$$E_\nu \underset{\nu\geqslant 0}{=} \frac{N_\nu}{N}E^{\boldsymbol{\xi}} + \sum_{\lambda>0}\left(\delta_{\lambda\nu} - \frac{N_\nu}{N}\xi_\lambda\right)\frac{\partial E^{\boldsymbol{\xi}}}{\partial \xi_\lambda}. \tag{42}$$

Note that Eq. (42) generalizes expressions that have been derived previously and separately in regular TGOK [59] (for neutral excited states) and N-centered [37,46] (for charged excited states) ensemble theories. As shown in the following section, once a KS density functional description of the extended N-centered ensemble energy $E^{\boldsymbol{\xi}}$ is established, it becomes possible to relate formally any charged or neutral KS excitation energy to the true physical one.

B. Density functionalization of the approach

According to both regular (ground-state) Rayleigh-Ritz and TGOK [38,60] variational principles, the extended

N-centered ensemble energy of Eq. (36) can be determined variationally, thus allowing for its in-principle-exact ensemble density functional description. The exact same formalism as in TGOK-DFT can actually be used [see Eqs. (25)–(29)]. The only difference is that we are now allowed to consider occupations in the KS wave functions [see Eq. (29)] that do not necessarily sum up to N:

$$\sum_i n_\nu^i = N_\nu. \tag{43}$$

By rewriting the ensemble energy as [see Eqs. (25), (26), and (28)]

$$E^{\boldsymbol{\xi}} = \sum_{\nu\geqslant 0} \xi_\nu \mathcal{E}_\nu^{\boldsymbol{\xi}} + E_{\text{Hxc}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi}}] - \int d\mathbf{r}\, v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) n^{\boldsymbol{\xi}}(\mathbf{r}), \tag{44}$$

and applying the Hellmann-Feynman theorem to its variational expression in Eq. (25), which leads to

$$\frac{\partial E^{\boldsymbol{\xi}}}{\partial \xi_\lambda} = \mathcal{E}_\lambda^{\boldsymbol{\xi}} - \frac{N_\lambda}{N}\mathcal{E}_0^{\boldsymbol{\xi}} + \left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n]}{\partial \xi_\lambda}\right|_{n=n^{\boldsymbol{\xi}}}, \tag{45}$$

we deduce from Eq. (42) the following exact expression for any individual energy level included into the ensemble:

$$\begin{aligned} E_\nu \underset{\nu\geqslant 0}{=} \mathcal{E}_\nu^{\boldsymbol{\xi}} &+ \frac{N_\nu}{N}\left(E_{\text{Hxc}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi}}] - \int d\mathbf{r}\, v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) n^{\boldsymbol{\xi}}(\mathbf{r})\right) \\ &+ \sum_{\lambda>0}\left(\delta_{\lambda\nu} - \frac{N_\nu}{N}\xi_\lambda\right)\left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n]}{\partial \xi_\lambda}\right|_{n=n^{\boldsymbol{\xi}}}, \end{aligned} \tag{46}$$

where, in the second term on the right-hand side, we recognize the analog for ensembles of the Levy-Zahariev shift in potential [46,59,65]. Note in passing that a similar shift was actually recovered in an earlier work by Kraisler and Kronik [56] where the authors described the piecewise-linear behavior of the ground-state energy within ensemble DFT for fractional electron numbers. At this point we should make an important observation that will be exploited later on, namely, that the above expression is invariant under constant shifts in the ensemble Hxc potential $v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) \rightarrow v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) + c$, since [see Eqs. (15), (29), and (43)]

$$\begin{aligned} &\mathcal{E}_\nu^{\boldsymbol{\xi}} - \frac{N_\nu}{N}\int d\mathbf{r}\, v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) n^{\boldsymbol{\xi}}(\mathbf{r}) \\ &\quad = \left(\mathcal{E}_\nu^{\boldsymbol{\xi}} + N_\nu c\right) - \frac{N_\nu}{N}\int d\mathbf{r}\, \left(v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) + c\right) n^{\boldsymbol{\xi}}(\mathbf{r}), \end{aligned} \tag{47}$$

even though the ensemble may contain states that describe different numbers of electrons. This major difference between (extended or not) N-centered ensemble DFT and the conventional DFT for fractional electron numbers originates from the fact that, in the former theory, the number of electrons is artificially held constant and equal to the integer N [see Eq. (15)]. This flexibility allows us to recover, in the N-electron ground-state limit of the theory [in this case, the ensemble weights are set to $\boldsymbol{\xi} = 0$ in Eq. (46)], the Hxc potential of regular N-electron ground-state KS-DFT, which is also uniquely defined up to a constant. This point is more thoroughly discussed for the fundamental gap problem in Refs. [57] and [37]. It is also important to note that setting $\boldsymbol{\xi} = 0$ in Eq. (46) consists in fact in taking the limit $\boldsymbol{\xi} \rightarrow 0^+$ of extended N-centered ensemble KS-DFT because infinitesimal deviations from the zero weight limit $\boldsymbol{\xi} = 0$ [which does correspond to regular N-electron ground-state KS-DFT, according to Eqs. (25), (36), and (38)] are needed to evaluate weight derivatives of the ensemble Hxc density functional [second line of Eq. (46)]. This is how any (charged or neutral) excited-state energy level can be described, in principle exactly, through the extended N-centered ensemble formalism (i.e., by considering the $\boldsymbol{\xi} \rightarrow 0^+$ limit), on the basis of regular DFT ($\boldsymbol{\xi} = 0$), which provides a variational description of the N-electron ground-state energy only.

We finally conclude from Eq. (46) that the energy associated to any (charged or neutral) excitation $\nu \rightarrow \kappa$ can be expressed exactly in terms of its KS analog as follows:

$$\begin{aligned} E_\kappa - E_\nu = \mathcal{E}_\kappa^{\boldsymbol{\xi}} - \mathcal{E}_\nu^{\boldsymbol{\xi}} &+ \frac{(N_\kappa - N_\nu)}{N}\left(E_{\text{Hxc}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi}}] - \int d\mathbf{r}\, v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) n^{\boldsymbol{\xi}}(\mathbf{r})\right) \\ &+ \sum_{\lambda>0}\left(\delta_{\lambda\kappa} - \delta_{\lambda\nu} - \frac{(N_\kappa - N_\nu)}{N}\xi_\lambda\right)\left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n]}{\partial \xi_\lambda}\right|_{n=n^{\boldsymbol{\xi}}}. \end{aligned} \tag{48}$$

Equation (48) is our first key result. It generalizes the neutral excitation energy expression of TGOK-DFT [40,59] that was recalled in Eq. (30).

V. REVISITING DENSITY FUNCTIONAL DERIVATIVE DISCONTINUITIES INDUCED BY NEUTRAL EXCITATIONS

In order to achieve an exactification of the KS orbital energies along the lines of Sec. II, we apply the general formalism of Sec. IV to a particular type of extended N-centered ensemble which includes only the neutrally excited N-electron states, with weights $\{\xi_\lambda^N\}_{\lambda>0}$, *and* the ionized $(N-1)$-electron ground state, with weight $\xi_- := \xi_0^{N-1}$. Therefore, in this special case, the collection of ensemble weights reduces to

$$\boldsymbol{\xi} \equiv (\{\xi_\lambda^N\}_{\lambda>0}, \xi_-), \tag{49}$$

and Eq. (48), where the summation in $\lambda > 0$ (last term on the right-hand side) runs over both the neutral excited states Ψ_λ^N (to which the weights ξ_λ^N are assigned) and the ground ionized state Ψ_0^{N-1} simply labeled as "$\lambda = -$" (to which the weight ξ_- is assigned), becomes

$$\begin{aligned} E_\kappa - E_\nu = \mathcal{E}_\kappa^{\boldsymbol{\xi}} - \mathcal{E}_\nu^{\boldsymbol{\xi}} &+ \frac{(N_\kappa - N_\nu)}{N}\left(E_{\text{Hxc}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi}}] - \int d\mathbf{r}\, v_{\text{Hxc}}^{\boldsymbol{\xi}}(\mathbf{r}) n^{\boldsymbol{\xi}}(\mathbf{r})\right) \\ &+ \sum_{\lambda>0}\left(\delta_{\lambda\kappa} - \delta_{\lambda\nu} - \frac{(N_\kappa - N_\nu)}{N}\xi_\lambda^N\right)\left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n]}{\partial \xi_\lambda^N}\right|_{n=n^{\boldsymbol{\xi}}} \\ &+ \left(\delta_{-\kappa} - \delta_{-\nu} - \frac{(N_\kappa - N_\nu)}{N}\xi_-\right)\left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n]}{\partial \xi_-}\right|_{n=n^{\boldsymbol{\xi}}}. \end{aligned} \tag{50}$$

If, in the above expression, we choose for κ the ground ionized state (i.e., $\delta_{\lambda\kappa} = 0$ in the third line, $\delta_{-\kappa} = 1$ in the fourth line, $N_\kappa = N - 1$, $E_\kappa = E_0^{N-1}$, and $\mathcal{E}^{\xi}_{\kappa} = \sum_{i=1}^{N-1} \varepsilon_i^{\xi}$), and for $\nu \geqslant 0$, any ground or excited N-electron state (i.e., $\delta_{-\nu} = 0$ in the fourth line, $N_\nu = N$, and $E_\nu = E_\nu^N$), then we can express any ground- or excited-state IP as $I_\nu^N = E_\kappa - E_\nu$ [see Eq. (6)]. This gives the following more explicit exact expression

$$
\begin{aligned}
I_\nu^N \underset{\nu\geqslant 0}{=} & \sum_{i=1}^{N-1} \varepsilon_i^{\xi} - \mathcal{E}_\nu^{\xi} - \frac{1}{N}\left(E^{\xi}_{\rm Hxc}[n^{\xi}] - \int d\mathbf{r}\, v^{\xi}_{\rm Hxc}(\mathbf{r}) n^{\xi}(\mathbf{r})\right) \\
& + \sum_{\lambda>0}\left(-\delta_{\lambda\nu} + \frac{\xi_\lambda^N}{N}\right) \left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_\lambda^N}\right|_{n=n^{\xi}} \\
& + \left(1 + \frac{\xi_-}{N}\right)\left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_-}\right|_{n=n^{\xi}},
\end{aligned}
\tag{51}
$$

thus leading to

$$
\begin{aligned}
I_\nu^N \underset{\nu\geqslant 0}{=} & -\varepsilon^{\xi}_{i(\nu)} - \frac{1}{N}\left(E^{\xi}_{\rm Hxc}[n^{\xi}] - \int d\mathbf{r}\, v^{\xi}_{\rm Hxc}(\mathbf{r}) n^{\xi}(\mathbf{r})\right) \\
& + \left(1 + \frac{\xi_-}{N}\right)\left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_-}\right|_{n=n^{\xi}} \\
& + \sum_{\lambda>0}\left(\frac{\xi_\lambda^N}{N} - \delta_{\lambda\nu}\right) \left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_\lambda^N}\right|_{n=n^{\xi}},
\end{aligned}
\tag{52}
$$

where, along the lines of Sec. II, we assumed, for simplicity and clarity, that within the KS ensemble, the neutral excited states $\nu > 0$ of interest are described by a single-electron excitation from the HOMO $\varphi_N^{\xi} =: \varphi^{\xi}_{i(0)}$ to a higher-energy orbital that we denote $\varphi^{\xi}_{i(\nu)}$ [where the index $i(\nu) > N$ of the acceptor orbital depends on the excited state of interest $\nu > 0$], i.e., its energy reads as follows in terms of the KS orbital energies, $\mathcal{E}_\nu^{\xi} = \sum_{i=1}^{N-1} \varepsilon_i^{\xi} + \varepsilon^{\xi}_{i(\nu)}$, the HOMO energy being $\varepsilon_N^{\xi} =: \varepsilon^{\xi}_{i(0)}$.

The description of both single excitations from lower-energy orbitals and double excitations [36,66,67] within the present formalism, as well as how excitations in the true interacting system are connected to those occurring in the noninteracting KS ensemble, is discussed in a separate work [68]. Still, it is important to stress that, whatever the nature of the neutral excitation $\nu > 0$ under study, Eq. (48), from which excited-state IPs can be evaluated, remains exact. The possible mixture of single and double (or even higher) excitations in the true interacting states, which may not appear explicitly in the KS states, will be recovered, energywise, *via* the ensemble Hxc functional and its weight derivatives [see the second and third lines of Eq. (48)].

As pointed out previously [see Eq. (47)], the IP expression of Eq. (52) is invariant under any constant shift in the ensemble Hxc potential. Therefore, we can always adjust the latter potential in order to exactify Koopmans' theorem for a given ground or excited N-electron state ν and a given choice of ensemble weight values $\boldsymbol{\xi}$:

$$
\begin{aligned}
& I_\nu^N \underset{\nu\geqslant 0}{=} -\varepsilon^{\xi}_{i(\nu)} \\
& \Updownarrow \\
& \int d\mathbf{r}\, v^{\xi}_{\rm Hxc}(\mathbf{r}) n^{\xi}(\mathbf{r}) = E^{\xi}_{\rm Hxc}[n^{\xi}] - (N + \xi_-)\left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_-}\right|_{n=n^{\xi}} \\
& \qquad + \sum_{\lambda>0}\left(N\delta_{\lambda\nu} - \xi_\lambda^N\right)\left.\frac{\partial E^{\xi}_{\rm Hxc}[n]}{\partial \xi_\lambda^N}\right|_{n=n^{\xi}}.
\end{aligned}
\tag{53}
$$

Equation (53), which is the second key result of this work, uniquely defines (not up to a constant anymore) the Hxc potential. Interestingly, unlike in traditional DFT approaches to electronic excitations [69], this alternative and explicit adjustment procedure of the Hxc potential does *not* rely on the asymptotic behavior of the density (see Refs. [37,57] for a comparison of the two formalisms in the ground state), which means that it is not only applicable to *ab initio* molecular systems but it should also be transferable to finite-size lattice models or extended systems, in principle.

Finally, in order to revisit the concept of derivative discontinuity within the present ensemble density functional formalism, let us have a closer look at the ionization of both the ground N-electron state (first scenario) and a specific νth neutral excited state (second scenario), separately. For that purpose, we should first realize that, in order to reach the latter state ν variationally, we only need to include into the ensemble the neutral states that are lower in energy than ν, i.e., we can set to zero the ensemble weights ξ_λ^N corresponding to $\lambda > \nu$. In this case, the collection of ensemble weights further reduces to

$$
\boldsymbol{\xi} \equiv \left(\boldsymbol{\xi}_\nu^N, 0, 0, \ldots, 0, \xi_-\right), \tag{54}
$$

where (note the bold font)

$$
\boldsymbol{\xi}_\nu^N \equiv \left(\xi_1^N, \xi_2^N, \ldots, \xi_\nu^N\right) \tag{55}
$$

is a shorthand notation for the ν nonzero and monotonically decreasing (TGOK) ensemble weights. In the first scenario, we adjust the Hxc potential such that Koopmans' theorem is fulfilled for the ground state ($\nu = 0$). As neutral excited states are not involved *at all* in this case, the ensemble can be reduced to a regular N-centered ensemble [46] where the TGOK ensemble weights are strictly set to zero:

$$
\boldsymbol{\xi}_1 \equiv \left(\boldsymbol{\xi}_\nu^N = \mathbf{0}, 0, 0, \ldots, 0, \xi_- > 0\right). \tag{56}
$$

On the other hand, in the second scenario (ionization of the νth excited state), assigning an infinitesimal weight to the ionized ground state, in addition to strictly positive and monotonically decreasing weights in $\boldsymbol{\xi}_\nu^N$, is sufficient, i.e.,

$$
\boldsymbol{\xi}_2 \equiv \left(\boldsymbol{\xi}_\nu^N > 0, 0, 0, \ldots, 0, \xi_- \rightarrow 0^+\right), \tag{57}
$$

so that the ensemble weight derivative $\partial E^{\xi}_{\rm Hxc}[n]/\partial \xi_-$ in Eq. (53) can still be evaluated, like in the first scenario. As a consequence of Eq. (53), we finally reach from Eq. (5), and without ever invoking fractional electron numbers nor referring to the asymptotic behavior of the ensemble density, the desired exactification of the KS orbital energies

$$
E_\nu^N - E_0^N \underset{\nu>0}{=} \varepsilon^{\xi_2}_{i(\nu)} - \varepsilon_N^{\xi_1}, \tag{58}
$$

where $i(\nu) > N$, with a clear and explicit construction of the corresponding Hxc potentials.

Equation (58) generalizes Levy's exact formula for the optical gap [55]. It also offers a different perspective on its more recent extension to higher neutral single-electron excitations [35]. Most importantly, the first and second scenarios have a connection point which is reached when $\xi_- \rightarrow 0^+$ and $\boldsymbol{\xi}_\nu^N \rightarrow \mathbf{0}^+$, respectively, and which corresponds to the regular N-electron ground-state formulation of DFT (the density equals $n_{\Psi_0^N}$ in this case). If we use the shorthand notation

$$\boldsymbol{\xi}_\nu^N \underset{\text{notation}}{\equiv} \left(\boldsymbol{\xi}_\nu^N, 0, 0, \ldots, 0, \xi_- \rightarrow 0^+\right), \tag{59}$$

then equating, at this connection point, the Hxc potentials associated with these two scenarios via Eq. (53) leads to our third key result:

$$E_\nu^N - E_0^N = \varepsilon_{i(\nu)}^{\boldsymbol{\xi}_\nu^N \rightarrow \mathbf{0}^+} - \varepsilon_N^{\boldsymbol{\xi}_\nu^N = \mathbf{0}}, \tag{60}$$

where

$$\begin{aligned} &\int \frac{d\mathbf{r}}{N}\left(v_{\text{Hxc}}^{\boldsymbol{\xi}_\nu^N \rightarrow \mathbf{0}^+}(\mathbf{r}) - v_{\text{Hxc}}^{\boldsymbol{\xi}_\nu^N = \mathbf{0}}(\mathbf{r})\right) n_{\Psi_0^N}(\mathbf{r}) \\ &= \left.\frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}_\nu^N}[n_{\Psi_0^N}]}{\partial \boldsymbol{\xi}_\nu^N}\right|_{\boldsymbol{\xi}_\nu^N = \mathbf{0}}. \end{aligned} \tag{61}$$

If we use the following decomposition of the ensemble Hxc energy in terms of the regular weight-independent Hartree functional and the weight-dependent xc functional,

$$E_{\text{Hxc}}^{\boldsymbol{\xi}}[n] = E_{\text{H}}[n] + E_{\text{xc}}^{\boldsymbol{\xi}}[n], \tag{62}$$

which is formally convenient but problematic in practice, because of the ghost interaction errors it may induce [37,64], then all Hartree terms can be removed from Eq. (61). Thus we recover, from a completely different (N-centered) ensemble perspective a feature that was originally highlighted by Levy [55], namely, that the exactification of neutral KS excitation energies is conditioned by the appearance of a derivative discontinuity in the xc potential, once the excitation of interest has been incorporated into the ensemble. Moreover, as readily seen from Eq. (61), that derivative discontinuity matches the weight derivative (taken at $\boldsymbol{\xi}_\nu^N = \mathbf{0}$) of the ensemble Hxc functional, which, on the other hand, corresponds to the deviation in excitation energy between the physical and KS systems [see Eq. (30)]. The equivalence of the two concepts in this special limit, already mentioned at the end of Sec. III, is recovered from Eqs. (60) and (61).

Equation (60) echoes Eq. (1) of Ref. [35] taken in the so-called "$w \rightarrow 0^+$" limit, which is the foundation of perturbative ensemble DFT (pEDFT) [35]. It explains how exact neutral excitation energies can be evaluated from extended N-centered ensemble limits towards regular N-electron ground-state DFT. From a practical point of view, Eq. (60) offers an alternative approach, in the evaluation of gaps, to the still challenging design of weight-dependent density functional approximations [31]. While the latter would in principle allow for a straightforward evaluation of the former from a single ensemble DFT calculation [see Eq. (30) and Ref. [59]], two different limits towards regular DFT need to be considered instead. In both of them, the N-centered ensemble weight ξ_- infinitesimally deviates from zero. Revisiting pEDFT in the present context deserves further attention. This is left for future work.

VI. APPLICATION TO THE HUBBARD DIMER

The present section is a proof of concept, illustrating how derivative discontinuities emerge for neutral electronic excitations in the context of extended N-centered (eN-centered) ensemble DFT. For this purpose, the eN-centered ensemble formalism is applied to both symmetric and asymmetric Hubbard dimer models [70].

A. Key features of the model

The Hubbard dimer has become in recent years a model of choice for assessing density functional approximations in various contexts but also for exploring new concepts [26,37,59,66,70–78]. In the (second-quantized) Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{V}_{\text{ext}}$ of the Hubbard dimer model, the kinetic energy, electron repulsion, and local (external) potential operators are simplified as follows:

$$\hat{\mathcal{T}} = -t \sum_{\sigma=\uparrow,\downarrow} (\hat{c}_{0\sigma}^\dagger \hat{c}_{1\sigma} + \hat{c}_{1\sigma}^\dagger \hat{c}_{0\sigma}), \tag{63a}$$

$$\hat{\mathcal{U}} = U \sum_{i=0}^{1} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \tag{63b}$$

$$\hat{V}_{\text{ext}} = \frac{\Delta v_{\text{ext}}}{2}(\hat{n}_1 - \hat{n}_0), \tag{63c}$$

where $i \in \{0, 1\}$ labels the two atomic sites, $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$ is the spin-site occupation operator, and $\hat{n}_i = \sum_{\sigma=\uparrow,\downarrow} \hat{n}_{i\sigma}$ plays the role of the density operator. While the difference in external potential Δv_{ext} controls the asymmetry of the model, the ratio U/t of the onsite electronic repulsion parameter U to the hopping parameter t can be used to tune electron correlation effects in the model. In the following, the central number of electrons in the eN-centered ensemble is set to $N = 2$. With this choice, the ensemble electronic density $\{n_i = \langle \hat{n}_i \rangle\}_{i=0,1}$ reduces to a single variable n with site occupations equal to $n_0 = n$ and $n_1 = 2 - n$ [see Eq. (15)]. Note that $n = 1$ in the symmetric dimer.

As for the construction of the eN-centered ensemble, we consider the singlet N-electron ground state, which also determines the choice for the $(N-1)$-electron ground state, that is, the one-electron ground state of the noninteracting $(U = 0)$ Hamiltonian. We also include into the ensemble the lowest singlet N-electron (neutral) excited state which, in the noninteracting limit, is described by a single-electron (HOMO to LUMO) excitation. The collection $\boldsymbol{\xi} \equiv (\xi, \xi_-)$ of eN-centered ensemble weights consists of the weight ξ assigned to the neutral (two-electron) excited state and the weight ξ_- that is assigned to the one-electron ground state. According to Eq. (33a), the eN-centered ensemble weight assigned to the reference two-electron ground state ($N = 2$ in this case) reads as

$$\xi_0 \equiv \xi_0(\boldsymbol{\xi}) = 1 - \frac{(N-1)\xi_-}{N} - \xi = 1 - \frac{\xi_-}{2} - \xi. \tag{64}$$

Note that the ensemble weight constraints of Eqs. (33) and (35) read as

$$\xi_0 = 1 - \frac{\xi_-}{2} - \xi \geqslant 0, \tag{65a}$$

$$\xi_- \geqslant 0, \tag{65b}$$

and

$$\xi_0 \geqslant \xi \geqslant 0, \tag{66}$$

respectively, or, equivalently [according to Eqs. (65a) and (66)]

$$1 - \frac{\xi_-}{2} - \xi \geqslant \xi \tag{67}$$

and [according to Eqs. (65a) and (65b)]

$$0 \leqslant \xi_- \leqslant 2(1-\xi), \tag{68}$$

thus leading to $0 \leqslant \xi \leqslant \frac{1}{2} - (\xi_-/4)$ for ξ_- varying in $0 \leqslant \xi_- \leqslant 2$. The e$N$-centered KS ensemble is described by two fractionally occupied orbitals that we simply refer to as HOMO and LUMO in the following, as we use the two-electron ground state as reference in the ensemble. Their expansions in the site basis as well as their energies can be obtained by diagonalizing the following one-electron KS Hamiltonian matrix [see Eq. (63)]:

$$\left[\hat{h}^{\mathrm{KS}}(\Delta v)\right] = \begin{bmatrix} -\frac{\Delta v}{2} & -t \\ -t & +\frac{\Delta v}{2} \end{bmatrix}. \tag{69}$$

In Eq. (69), Δv corresponds to the ensemble density functional KS potential difference whose exact expression is given later in Eq. (76) [see the proof that follows Eq. (A9) in Appendix A 1 a]. According to Eq. (64), the fractional occupations $n_i^{\boldsymbol{\xi}}$ ($i = \mathrm{H}$ or L) of the HOMO and LUMO are controlled by the ensemble weights $\boldsymbol{\xi}$ as follows [see Eq. (28)]:

$$n_{\mathrm{H}}^{\boldsymbol{\xi}} = \xi_0(\boldsymbol{\xi}) \times 2 + \xi_- \times 1 + \xi \times 1 = 2 - \xi \tag{70}$$

and

$$n_{\mathrm{L}}^{\boldsymbol{\xi}} = \xi_0(\boldsymbol{\xi}) \times 0 + \xi_- \times 0 + \xi \times 1 = \xi, \tag{71}$$

respectively. Note finally that, for a given choice of $\boldsymbol{\xi}$, we can arbitrarily shift the external potential (or the KS potential) introduced in Eq. (63) by a constant, i.e.,

$$\pm\frac{\Delta v}{2} \rightarrow \pm\frac{\Delta v}{2} - \mu, \tag{72}$$

without modifying the eN-centered ensemble under study. As further discussed in the following, the adjustment of the latter constant in the KS potential will be essential for satisfying exact Koopmans' theorems and, consequently, observing Hxc derivative discontinuities.

A key feature of the model is that all individual energy levels have exact analytical expressions in terms of t, U, and Δv_{ext} [22,37,46,70], thus allowing for the evaluation (to any arbitrary numerical accuracy) of ensemble density functional Hxc energies. More precisely, the eN-centered ensemble noninteracting kinetic energy and the ensemble exact Hartree-exchange (simply denoted EEXX) functionals have the following exact closed-form expressions:

$$T_{\mathrm{s}}^{\boldsymbol{\xi}}(n) = -2t\sqrt{(1-\xi)^2 - (1-n)^2}, \tag{73a}$$

$$E_{\mathrm{Hx}}^{\boldsymbol{\xi}}(n) = \frac{U}{2}\left[1 + \xi - \frac{\xi_-}{2} + \left(1 - 3\xi - \frac{\xi_-}{2}\right)\left(\frac{1-n}{1-\xi}\right)^2\right]. \tag{73b}$$

As readily seen from Eq. (73a), $T_{\mathrm{s}}^{\boldsymbol{\xi}}(n)$ does not vary with the weight ξ_- assigned to the ground ionized state, unlike the EEXX functional, which exhibits such a variation through the weight $\xi_0(\boldsymbol{\xi})$ assigned to the two-electron ground state [see Eq. (A14)]. This is a consequence of the fact that the KS orbitals occupancies within the ensemble are independent of ξ_- [see Eqs. (70) and (71), and Eq. (A9) from Appendix A 1 a]. Note that EEXX will refer later on to the following EEXX-only approximation:

$$E_{\mathrm{Hxc}}^{\boldsymbol{\xi}}(n) \overset{\mathrm{EEXX}}{\approx} E_{\mathrm{Hx}}^{\boldsymbol{\xi}}(n). \tag{74}$$

The missing ensemble density functional correlation energy $E_{\mathrm{c}}^{\boldsymbol{\xi}}(n) = F^{\boldsymbol{\xi}}(n) - T_{\mathrm{s}}^{\boldsymbol{\xi}}(n) - E_{\mathrm{Hx}}^{\boldsymbol{\xi}}(n)$ [see Eq. (21)] can be evaluated from the eN-centered ensemble extension $F^{\boldsymbol{\xi}}(n)$ of Lieb's functional [22,46,62]. The detailed computation of the exact ensemble Hxc density functional and its ensemble weight derivatives is discussed in further detail in Appendix A.

On that basis, the exact ensemble Hxc potential can be computed within the Hubbard dimer model, as further discussed in the following. First, the Hxc potential difference (between sites 1 and 0) is obtained from the exact ensemble density functional KS potential difference [see Eq. (76)]. The last step consists of shifting the values of the Hxc potential on sites 0 and 1 [see Eq. (72)] such that the exact Koopmans' theorem of the key Eq. (53) is fulfilled, either for the two-electron ground state [$\nu = 0$ in this case and the associated weight is $\xi_0(\boldsymbol{\xi})$] or the first (singlet) neutral excited state ($\nu = 1$ in this case and the associated weight is ξ). The computation of the appropriate shift requires the evaluation of the eN-centered ensemble density functional Hxc energy [first term on the right-hand side of Eq. (53)], which has been discussed previously, as well as the derivatives with respect to ξ_- and ξ of the ensemble Hxc functional [second and third terms on the right-hand side of Eq. (53), where $\xi_1^N = \xi$]. The correlation part of the latter derivatives can be determined *via* the Hellmann-Feynman theorem from the variational Legendre-Fenchel expression of $F^{\boldsymbol{\xi}}(n)$ [see Eqs. (A11) and (A12) in Appendix A 1 a].

B. Observation of derivative discontinuities

Let us first summarize the key findings of Appendix A. For a given choice of U, t, and Δv_{ext}, as well as given ensemble weight values $\boldsymbol{\xi}$, the ensemble Hxc potential difference (between sites 1 and 0) can be expressed exactly as follows:

$$\Delta v_{\mathrm{Hxc}}^{\boldsymbol{\xi}} = \Delta v_{\mathrm{KS}}^{\boldsymbol{\xi}}(n^{\boldsymbol{\xi}}) - \Delta v_{\mathrm{ext}}, \tag{75}$$

where the ensemble density functional KS potential difference (see Appendix A and Ref. [22])

$$\Delta v_{\mathrm{KS}}^{\boldsymbol{\xi}}(n) = \frac{\partial T_{\mathrm{s}}^{\boldsymbol{\xi}}(n)}{\partial n} = \frac{2t(n-1)}{\sqrt{(1-\xi)^2 - (1-n)^2}} \tag{76}$$

is a *continuous* function of both the density n (in the range $\xi \leqslant n \leqslant 2-\xi$) and the ensemble weight ξ assigned to the neutral excited state, and n^{ξ} denotes the true interacting ensemble density (on site 0). The ensemble Hxc potential on site i can be expressed as [see Eq. (72)]

$$v^{\xi}_{\mathrm{Hxc},i} = (-1)^{i-1}\frac{\Delta v^{\xi}_{\mathrm{Hxc}}}{2} - \mu^{\xi}_{\mathrm{Hxc}}, \qquad i = 0, 1 \tag{77}$$

where the uniform shift μ^{ξ}_{Hxc} is determined, for a given ionization process, from Eq. (53).

We now turn to the results and their discussion. All the calculations, exact and approximate, have been carried out with $t = \frac{1}{2}$. For convenience, EEXX results have been generated without density-driven errors. In other words, exact interacting ensemble densities have been employed in conjunction with Eq. (75). Therefore, the EEXX approximation has been used only when evaluating μ^{ξ}_{Hxc} through the neglect of the ensemble correlation density functional and its weight derivatives in Eq. (53).

Figure 1 shows the variation of the ensemble Hxc potential on site 1 with respect to the ensemble weights for two separate physical processes (see Appendix A 2 a for the detailed derivation of the potential in both cases). The first one (red curve in Fig. 1) corresponds to the ionization of the two-electron ground state ($0 \leqslant \xi_- \leqslant 2$ and $\xi = 0$ in this case). In the second process (blue curve in Fig. 1), the neutral excitation is included into the ensemble ($0 < \xi \leqslant \frac{1}{2}$) where the ionized ground state contributes infinitesimally. In other words, ensemble weight derivatives are evaluated for $\xi_- = 0$ in this case. As readily seen from Fig. 1, the exact Hxc potential, constructed according to Eq. (53), does exhibit a discontinuity when switching from one process to the other, whether the dimer is symmetric or not. As expected from Eqs. (30) and (61), this Hxc derivative discontinuity, which reduces to a xc derivative discontinuity if the regular weight-independent Hartree functional is employed, equals

$$\begin{aligned}\Delta^{0}_{\mathrm{Hxc}} &:= v^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc},1} - v^{(\xi=0,0^+)}_{\mathrm{Hxc},1}\\ &= v^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc},0} - v^{(\xi=0,0^+)}_{\mathrm{Hxc},0}\\ &= \left.\frac{\partial E^{(\xi,0)}_{\mathrm{Hxc}}(n_{\Psi^N_0})}{\partial \xi}\right|_{\xi=0},\end{aligned} \tag{78}$$

and corresponds to the deviation of the regular KS gap from its exact interacting optical counterpart.

As readily seen from Eqs. (75)–(77), the derivative discontinuity is solely induced by the readjustment of the constant shift in the Hxc potential when moving from the ionization of the ground state to the neutral excitation process, i.e.,

$$\Delta^{0}_{\mathrm{Hxc}} = \mu^{(\xi=0,0^+)}_{\mathrm{Hxc}} - \mu^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc}}. \tag{79}$$

This appears clearly in the symmetric dimer, for which $n^{\xi} = 1$, thus leading to $\Delta v^{\xi}_{\mathrm{Hxc}} = \Delta v_{\mathrm{ext}} = 0$ and, therefore, $v^{\xi}_{\mathrm{Hxc},i} = -\mu^{\xi}_{\mathrm{Hxc}}$. In this special case, the eN-centered ensemble Hx and correlation energies read as [see Eqs. (73b) and (A36)]

$$\left.E^{\xi}_{\mathrm{Hx}}(n)\right|_{n=1} = \frac{U}{2}\left(1+\xi-\frac{\xi_-}{2}\right), \tag{80a}$$

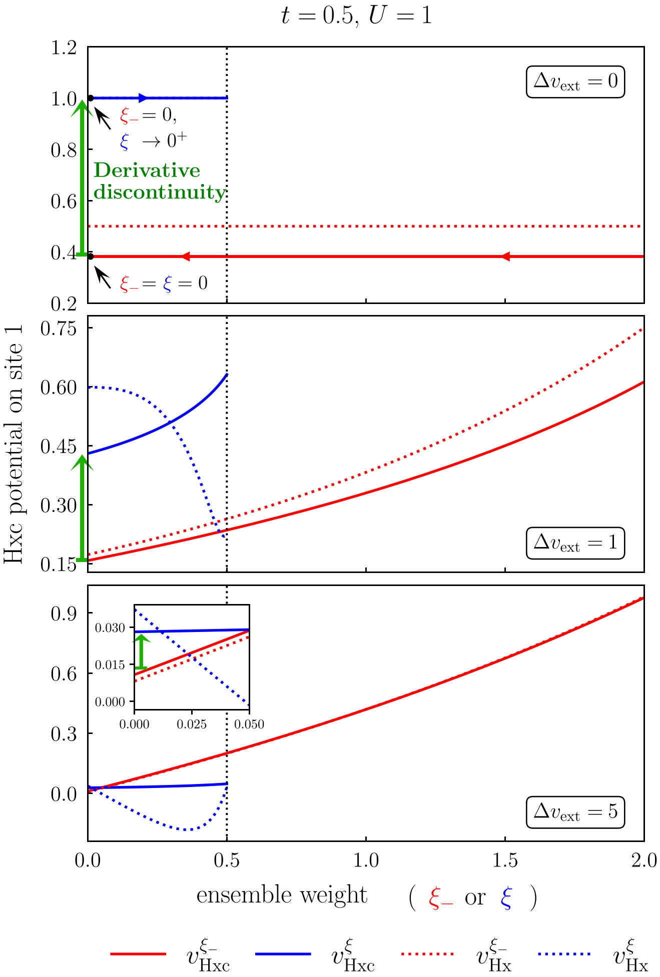

FIG. 1. Exact Hxc and EEXX-only (Hx) potentials on site 1 of the Hubbard dimer plotted as functions of the ensemble weights [ξ_- for the ionization (in red) of the two-electron ground state and ξ for the neutral excitation process (in blue)] for $U = 2t = 1$ and various external potential values. The derivative discontinuity that occurs when switching from one excitation process to the other is highlighted in green. The vertical black line at $\xi = \frac{1}{2}$ (dotted) indicates the TGOK equiensemble.

$$\left.E^{\xi}_{\mathrm{c}}(n)\right|_{n=1} = \left(1-\xi-\frac{\xi_-}{2}\right)E_{\mathrm{c}}, \tag{80b}$$

respectively, where $E_{\mathrm{c}} = 2t - \frac{1}{2}\sqrt{U^2+16t^2}$ is the regular ground-state correlation energy of the symmetric two-electron Hubbard dimer. Consequently, for the ionization of the excited state, the Hx and correlation contributions to the right-hand side of Eq. (61) can be simplified as follows (we recall that $N = 2$):

$$E^{\xi}_{\mathrm{Hx}}(n) - (N+\xi_-)\frac{\partial E^{\xi}_{\mathrm{Hx}}(n)}{\partial \xi_-} + (N-\xi)\frac{\partial E^{\xi}_{\mathrm{Hx}}(n)}{\partial \xi} \overset{n=1}{=} 2U, \tag{81a}$$

$$E^{\xi}_{\mathrm{c}}(n) - (N+\xi_-)\frac{\partial E^{\xi}_{\mathrm{c}}(n)}{\partial \xi_-} + (N-\xi)\frac{\partial E^{\xi}_{\mathrm{c}}(n)}{\partial \xi} \overset{n=1}{=} 0, \tag{81b}$$

respectively. If, instead, we consider the ionization of the two-electron ground state, we obtain

$$\left[E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n)-(N+\xi_-)\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n)}{\partial \xi_-}\right]_{\xi=0} \overset{n=1}{=} U, \tag{82a}$$

$$\left[E^{\boldsymbol{\xi}}_{\mathrm{c}}(n)-(N+\xi_-)\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{c}}(n)}{\partial \xi_-}\right]_{\xi=0} \overset{n=1}{=} 2E_{\mathrm{c}}, \tag{82b}$$

respectively. As a result, we deduce the following weight-independent Hxc potential expressions (with the same value on both sites) for each excitation process (see Appendix A 2 b), $v^{(0,\xi_-)}_{\mathrm{Hxc}} = (U+4t-\sqrt{U^2+16t^2})/2$ with $\xi_- > 0$ and $v^{(\xi,0^+)}_{\mathrm{Hxc}} = U$ with $\xi > 0$, respectively. Thus, we recover the derivative discontinuity expression of Ref. [22], i.e., $\Delta^0_{\mathrm{Hxc}} = (U-4t+\sqrt{U^2+16t^2})/2$. As the ratio $\Delta v_{\mathrm{ext}}/U$ (and, therefore, the asymmetry of the model) increases for a fixed U value, the derivative discontinuity decreases (see the central and bottom panels of Fig. 1), as expected for a system where electron correlation becomes weaker.

Turning finally to the EEXX-only approximation, we obtain for the symmetric dimer the exact ensemble Hxc potential associated to the neutral excitation $v^{(\xi,0^+)}_{\mathrm{Hx}} = v^{(\xi,0^+)}_{\mathrm{Hxc}} = U$, as a consequence of Eq. (81b). However, EEXX overestimates the N-centered ensemble Hxc potential associated to the ionization of the two-electron ground state, giving $v^{(0,\xi_-)}_{\mathrm{Hx}} = U/2$, so that the Hx contribution to the derivative discontinuity is $\Delta^0_{\mathrm{Hx}} = U/2$. These results are in perfect agreement with the top panel of Fig. 1. In the asymmetric case, EEXX is still able to model (approximately) the derivative discontinuity because the EEXX functional is ensemble weight dependent. When comparing the EEXX-only and exact Hxc ensemble potentials that describe the neutral excitation, in the particular case where $U = \Delta v_{\mathrm{ext}} = 1$ (see the solid and dotted blue lines in the central panel of Fig. 1), it becomes clear that electron correlation can drastically change the variation in the TGOK ensemble weight ξ of the Hxc potential. In this specific correlation regime, the Hx potential decreases drastically as ξ approaches $\frac{1}{2}$, unlike the full Hxc potential. This feature originates from the Hx contribution to Koopmans' theorem [see Eq. (53)], from which the Hx potential is uniquely defined. This contribution reads as in the left-hand side of Eq. (81a) and can be simplified as follows, according to Eq. (73b):

$$E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n)-(N+\xi_-)\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n)}{\partial \xi_-}+(N-\xi)\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n)}{\partial \xi}$$
$$\overset{\boldsymbol{\xi}=(\xi,0)}{=} U\left[2+\frac{\xi(1-n)^2(3\xi-5)}{(1-\xi)^3}\right] =: \mathcal{D}^{\xi}_{\mathrm{Hx}}(n). \tag{83}$$

By expressing the Hx potential (on site 1) as follows, according to Eqs. (75) and (77),

$$v^{\xi}_{\mathrm{Hx}} := v^{(\xi,0^+)}_{\mathrm{Hx},1} = \tfrac{1}{2}\left(\Delta v^{\xi}_{\mathrm{KS}}(n^{\xi})-\Delta v_{\mathrm{ext}}\right)-\mu^{\xi}_{\mathrm{Hx}}, \tag{84}$$

where, according to Koopmans' theorem of Eq. (53) and the notation introduced in Eq. (83),

$$\left(\Delta v^{\xi}_{\mathrm{KS}}(n^{\xi})-\Delta v_{\mathrm{ext}}\right)(1-n^{\xi})-2\mu^{\xi}_{\mathrm{Hx}} = \mathcal{D}^{\xi}_{\mathrm{Hx}}(n^{\xi}), \tag{85}$$

we obtain the final expression

$$v^{\xi}_{\mathrm{Hx}} = \frac{n^{\xi}}{2}\left(\Delta v^{\xi}_{\mathrm{KS}}(n^{\xi})-\Delta v_{\mathrm{ext}}\right)+\frac{\mathcal{D}^{\xi}_{\mathrm{Hx}}(n^{\xi})}{2}. \tag{86}$$

When $U = \Delta v_{\mathrm{ext}} = 1$, the ensemble density varies weakly with ξ in the range $1.4 \leqslant n^{\xi} \leqslant 1.5$ [22], so that the contribution $\mathcal{D}^{\xi}_{\mathrm{Hx}}(n^{\xi})$ to the Hx potential varies essentially as $\xi(3\xi-5)/(1-\xi)^3$, which decreases with ξ over the range $0 \leqslant \xi \leqslant 1/2$, in agreement with the middle panel of Fig. 1. On the other hand, in the more pronounced $\Delta v_{\mathrm{ext}}/U = 5$ asymmetric regime (see the bottom panel of Fig. 1), the ensemble density varies as $n^{\xi} \approx 2-\xi$ [22]. Consequently, the prefactor $(1-n^{\xi})^2 \approx (1-\xi)^2$ in the second term of $\mathcal{D}^{\xi}_{\mathrm{Hx}}(n^{\xi})$ [see Eq. (83)] does now contribute to the weight dependence of the Hx potential, thus leading to a variation as $\xi(3\xi-5)/(1-\xi)$ and, therefore, a substantially different behavior (still decreasing though) when approaching $\xi = \frac{1}{2}$. The increase of the Hx potential observed in the vicinity of $\xi = \frac{1}{2}$ (see the bottom panel of Fig. 1) can be related to the KS and external potentials as well as to the variation in ξ of the ensemble density [see Eqs. (76) and (86)]. Indeed, in the limit $\Delta v_{\mathrm{ext}}/(2t) = \Delta v_{\mathrm{ext}}/U \to +\infty$, which is taken in order to better understand the strongly asymmetric $\Delta v_{\mathrm{ext}}/U = 5$ regime depicted in the bottom panel of Fig. 1, the ensemble density is essentially a noninteracting one,

$$n^{\xi} \approx 1+\frac{(1-\xi)\Delta v_{\mathrm{ext}}}{\sqrt{(\Delta v_{\mathrm{ext}})^2+4t^2}} \approx 2-\xi-\frac{2(1-\xi)t^2}{(\Delta v_{\mathrm{ext}})^2}, \tag{87}$$

which can, in this form, be introduced into the KS density functional expression of Eq. (76), thus leading to the Hx potential contribution

$$\frac{n^{\xi}}{2}\left(\Delta v^{\xi}_{\mathrm{KS}}(n^{\xi})-\Delta v_{\mathrm{ext}}\right) \approx -\frac{t^2}{\Delta v_{\mathrm{ext}}}(2-\xi), \tag{88}$$

which increases with ξ.

C. Connection with regular ground-state DFT

In order to establish a clearer connection with conventional N-electron ground-state DFT (i.e., the $\boldsymbol{\xi} = \mathbf{0}$ limit of the theory), we adopt in this section a different perspective by using the general and exact IP expressions of Eq. (52), where the ensemble Hxc potential is defined up to a constant. Unlike in Sec. V, and the previous section, we do *not* impose any constraint on the latter constant. According to Eq. (52) [see also Eqs. (A17) and (A18)], the IPs of the N-electron ($N = 2$ here) ground and first neutral singlet excited states can be expressed as follows when $\boldsymbol{\xi} = \mathbf{0}$:

$$I^N_0 = -\tilde{\varepsilon}_{\mathrm{H}}+\left.\frac{\partial E^{\xi_-}_{\mathrm{Hxc}}[n_{\Psi^N_0}]}{\partial \xi_-}\right|_{\xi_-=0}, \tag{89a}$$

$$I^N_1 = -\tilde{\varepsilon}_{\mathrm{L}}+\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}[n_{\Psi^N_0}]}{\partial \xi_-}\right|_{\xi_-=0}-\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}[n_{\Psi^N_0}]}{\partial \xi}\right|_{\xi=0}, \tag{89b}$$

respectively, in terms of the regular (defined up to a constant) KS HOMO and LUMO energies ε_i to which we have applied the Levy-Zahariev (LZ) density functional shift in

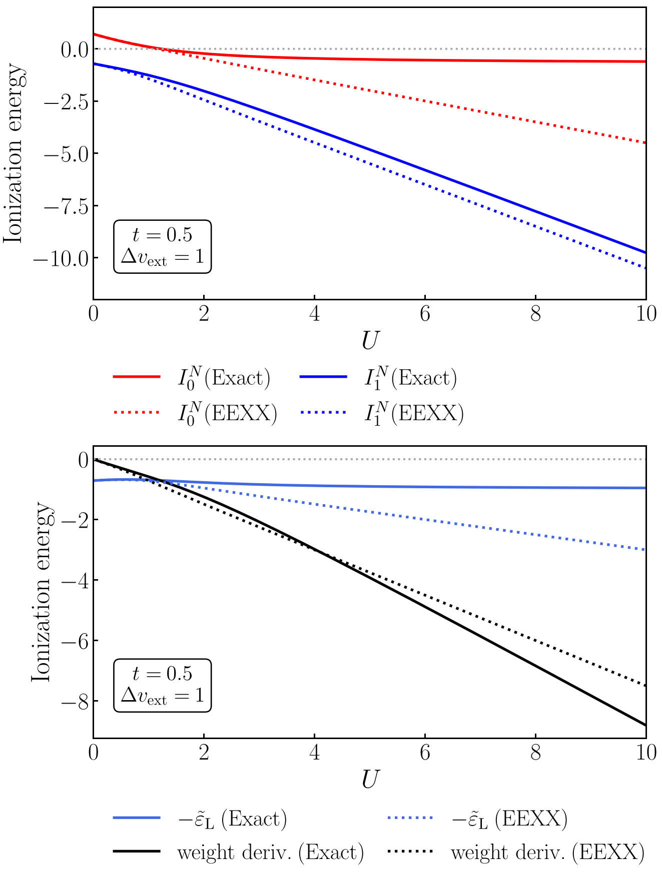

FIG. 2. Top: Variation of ground-state (red) and excited-state (blue) IPs with the onsite repulsion U in the asymmetric two-electron Hubbard dimer ($N = 2$ and $\Delta v_{\mathrm{ext}}/t = 2$). EEXX-only results (dotted lines) are shown for analysis purposes. Bottom: Decomposition of the excited-state IP into LZ-shifted KS LUMO energy and ensemble weight derivatives contributions [see Eq. (89b)].

potential [65]

$$C[n] = \frac{E_{\mathrm{Hxc}}[n] - \int d\mathbf{r}\, v_{\mathrm{Hxc}}(\mathbf{r}) n(\mathbf{r})}{N}, \tag{90}$$

where $E_{\mathrm{Hxc}}[n]$ and $v_{\mathrm{Hxc}}(\mathbf{r})$ are the regular Hxc functional and potential, respectively:

$$\varepsilon_i \rightarrow \tilde{\varepsilon}_i = \varepsilon_i + C[n_{\Psi_0^N}]. \tag{91}$$

The nice feature of LZ-shifted orbital energies is that they are invariant under constant shifts in the Hxc potential. In the present two-electron Hubbard dimer model [see Eqs. (76), (A6), and (A8)], the unshifted KS energies are $\varepsilon_{\mathrm{H}} = -\varepsilon_{\mathrm{L}} \equiv \varepsilon_{\mathrm{H}}[\Delta v_{\mathrm{KS}}^{\boldsymbol{\xi}=\mathbf{0}}(n_{\Psi_0^N})]$ and

$$C(n) = \tfrac{1}{2}[E_{\mathrm{Hxc}}(n) - (1-n)\Delta v_{\mathrm{Hxc}}(n)]. \tag{92}$$

The top panel of Fig. 2 shows the variations in U of the ground-state and first-excited-state IPs at the exact and approximate EEXX levels of calculation in the asymmetric $\Delta v_{\mathrm{ext}}/t = 2$ case. The trends of the ground-state IP in Fig. 2 are qualitatively the same as in Fig. 4 of Ref. [46] (where $\Delta v_{\mathrm{ext}}/t = 5$). As long as electron correlation is weak or moderately strong ($U/t \leqslant 2$), EEXX performs very well. In the stronger correlation regime, the relatively good performance of EEXX in the description of the excited-state IP was expected since, as readily seen from the following energy expressions [22],

$$\frac{E_0^N}{U} = \frac{4}{\left(\frac{\Delta v_{\mathrm{ext}}}{U}\right)^2 - 1}\left(\frac{t}{U}\right)^2 + O\left[\left(\frac{t}{U}\right)^3\right], \tag{93a}$$

$$\frac{E_1^N}{U} = 1 - \frac{\Delta v_{\mathrm{ext}}}{U} + \frac{2}{1 - \frac{\Delta v_{\mathrm{ext}}}{U}}\left(\frac{t}{U}\right)^2 + O\left[\left(\frac{t}{U}\right)^3\right], \tag{93b}$$

for $U \gg \Delta v_{\mathrm{ext}} \gg t$, the first (singlet) excited state has essentially no correlation energy. This is not the case for the ground state, which explains the poor performance of EEXX in the description of the ground-state IP when electron correlation is strong.

For completeness (the following analysis has already been done for the ground-state IP in Ref. [46]), the decomposition into LZ-shifted KS LUMO energy and ensemble Hxc weight derivatives of the excited-state IP [see Eq. (89b)] is plotted as a function of the interaction strength U in the bottom panel of Fig. 2. As U increases, the Hxc ensemble weight derivatives dominate while the LZ-shifted LUMO energy essentially tends to the hopping parameter t, which is the expected result for a perfectly symmetric dimer. Indeed, the ground-state density approaches the value $n = 1$ when $U/\Delta v_{\mathrm{ext}}$ becomes large [22,26]. Note that, at the EEXX level of approximation, the LZ-shifted LUMO energy is overestimated while the (absolute value of the) total weight derivatives contribution is underestimated, so that the errors mostly cancel out when evaluating the total excited-state IP (see the top panel of Fig. 2). Let us stress that, in the present case, being able to model the weight dependence of the ensemble density functional exchange energy is essential.

For analysis purposes, we finally consider deviations from regular ground-state DFT that are more than infinitesimal by increasing the weight assigned to the ionized ground state ($\xi_- > 0$) while remaining infinitesimally close to the ground-state limit (i.e., $\xi \rightarrow 0^+$) for the description of the excited state. The impact on the evaluation of both ground- and excited-state IPs, as well as the optical gap, is shown in Fig. 3. In the symmetric case (top panels), $I_0^N = -t - \frac{1}{2}(U - \sqrt{U^2 + 16t^2})$, which gives the lower value $I_0^N \approx t - \frac{U}{2}$ (i.e., $I_0^N \approx 0$ in Fig. 3, since $U = 2t$) within the EEXX-only approximation, where the correlation energy of the two-electron ground state is missing. Since the exact excited-state IP $I_1^N = -t - U$ is recovered at the EEXX level in this case, the underestimation of the optical gap is solely due to the missing correlation in the ground state.

Turning on asymmetry ($\Delta v_{\mathrm{ext}} = 1$) while remaining in the same moderately correlated regime ($U = 2t$) introduces curvature in ξ_- for both ground- and excited-state approximate EEXX IPs (see the middle left panel of Fig. 3). Note that, in the present case ($U = \Delta v_{\mathrm{ext}} = 2t = 1$), a perfect, and probably fortuitous, compensation of errors on both IPs occurs when computing the EEXX optical gap for the specific weight value of $\xi_- \approx 1.3$. In the stronger correlation regime ($U = 5$), the curvature of EEXX IPs is further enhanced and perfect

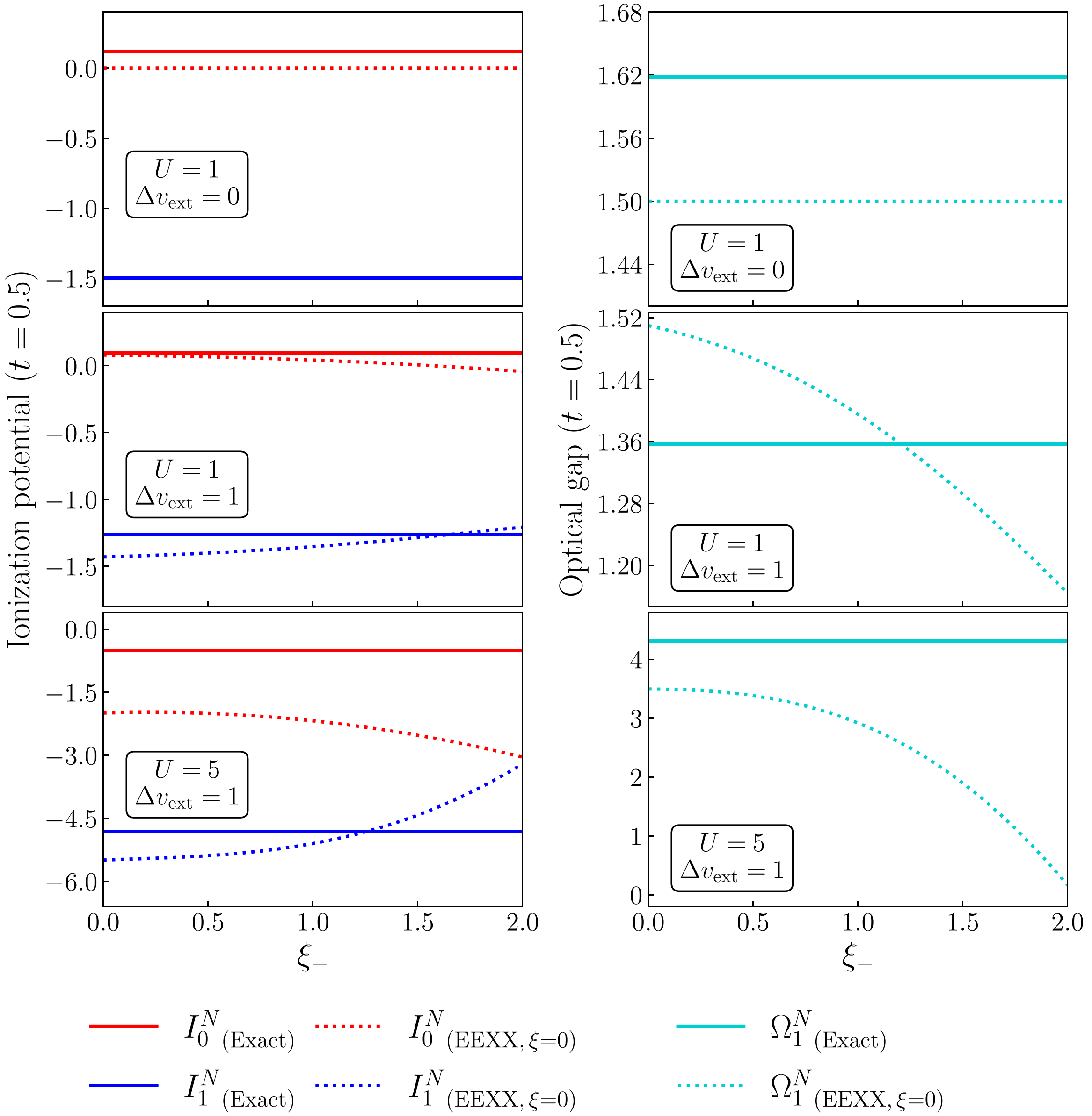

FIG. 3. Left panels: Exact and EEXX-only IPs for the ground state (red curves) and the excited state (blue curves) plotted as functions of the ionization ensemble weight ξ_- in the limit $\xi = 0$ for the symmetric (top), and two asymmetric (middle, bottom) Hubbard dimers. Right panels: Exact and EEXX-only optical gaps plotted as the difference between the two IPs for the same three Hubbard dimers.

error cancellation does not occur anymore (see the bottom panels of Fig. 3). Unlike in the exact theory, the EEXX density functional corrections to the bare weight-dependent KS IPs [see Eq. (52)] do not lead to weight-independent physical IPs. Nevertheless, as shown analytically in Appendix B, the EEXX functional succeeds in reversing, through its weight dependence, the variations in ξ_- of both ground- and first-excited-state KS IPs, thus avoiding a further underestimation of the excited-state IP as ξ_- increases (see the bottom left panel of Fig. 3). As expected in such a strongly correlated regime, a sensible optical gap can only be obtained by retrieving the weight-dependent ensemble correlation energy, which is completely neglected at the EEXX level of approximation (see the bottom right panel of Fig. 3).

VII. CONCLUSIONS AND OUTLOOK

TGOK-DFT [38,40] and the more recent N-centered ensemble DFT [46,47] have been merged, thus allowing for an in-principle exact and simultaneous density functional description of both charged and neutral electronic excitation processes [see the general excitation energy expression of Eq. (48)]. The resulting unified theory is referred to as extended N-centered ensemble DFT. Unlike in conventional DFT, in extended N-centered ensemble DFT, the number of electrons is artificially held constant and equal to the integer (so-called central) number of electrons N of the reference ground state, even when the ensemble under study contains charged excited states in addition to neutral ones, hence the name of the theory. Therefore, and most importantly, the Hxc potential is always defined up to a constant shift within the present formalism.

The concept of derivative discontinuity for neutral excitations, which is much less discussed in the literature [18,35,55] than for charged excitations, has been revisited in this context. When adjusting, for each ground and excited N-electron states separately, the constant shift in the Hxc potential, such that each of them satisfies an exact ionization Koopmans' theorem [see Eq. (53)], a jump (the so-called derivative discontinuity) is indeed observed when switching from the ground to the excited state of interest [see Eq. (61)].

Unlike in previous works, the asymptotic behavior of the density is never invoked nor used in the mathematical construction of the derivative discontinuities. It fully relies, instead, on the weight dependence of the extended N-centered ensemble Hxc density functional energy. This allows for a straightforward application of the theory to lattice models (the Hubbard dimer in this work). It may also open new perspectives in the description of gaps in mesoscopic systems [79]. In principle, the present density functional formalism is general enough to describe excitonic effects (through the inclusion of anionic states into the ensemble), as well as the challenging multiple-electron neutral excitation processes.

Finally, efforts should now be put into the design of weight-dependent density functional approximations, which is essential for turning the theory into a reliable computational method. The (in-principle orbital-dependent) ensemble exact-exchange functional that we studied within the Hubbard dimer model nicely incorporates weight dependencies but it obviously needs a proper (weight-dependent) correlation counterpart whose construction is far from trivial [27,28,31]. Exploring further the extension of ensemble DFT to the time-dependent linear response regime [29], for example, could be a source of inspiration for this task. Work in these directions is currently in progress.

ACKNOWLEDGMENTS

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APPENDIX A: TECHNICAL DETAILS ABOUT THE APPLICATION OF eN-CENTERED ENSEMBLE DFT ON THE HUBBARD DIMER

1. Ensemble functionals

In this Appendix, the exact and EEXX-approximate density functionals of the Hubbard dimer are systematically derived for the eN-centered ensemble in Sec. VI.

a. Exact functionals

We first consider the universal eN-centered ensemble density functional of the interacting system. As stated in Sec. VI A, the central number of electrons was set to $N=2$. For this particular choice, all individual N- and $(N-1)$-electron energies of the Hubbard dimer have analytical expressions, which are available in, for example, Refs. [22,46].

The eN-centered ensemble energy reads as

$$E^{\xi}(\Delta v_{\mathrm{ext}}) = \left(1-\frac{\xi_-}{2}-\xi\right)E_0^N(\Delta v_{\mathrm{ext}}) + \xi_- E_0^{N-1}(\Delta v_{\mathrm{ext}}) + \xi E_1^N(\Delta v_{\mathrm{ext}}), \tag{A1}$$

where the dependence of individual energies on t and U has been omitted for clarity, which will also be the case for other expressions dependent on t and U. The corresponding ensemble density reads as

$$n^{\xi} := n^{\xi}(\Delta v_{\mathrm{ext}}) = \left(1-\frac{\xi_-}{2}-\xi\right)n_{\Psi_0^N}(\Delta v_{\mathrm{ext}}) + \xi_- n_{\Psi_0^{N-1}}(\Delta v_{\mathrm{ext}}) + \xi n_{\Psi_1^N}(\Delta v_{\mathrm{ext}}), \tag{A2}$$

where individual N- and $(N-1)$-electron densities can be straightforwardly obtained from first-order derivatives of individual energies with respect to the external potential. If we introduce the counting operator $\hat{N} = \sum_{i=0}^{1}\hat{n}_i$, it follows from Eq. (63c) and the Hellmann-Feynman theorem that

$$\begin{aligned}\frac{\partial E_I^M(\Delta v_{\mathrm{ext}})}{\partial \Delta v_{\mathrm{ext}}} &= \left\langle \Psi_I^M \middle| \frac{\partial \hat{H}(\Delta v_{\mathrm{ext}})}{\partial \Delta v_{\mathrm{ext}}} \middle| \Psi_I^M \right\rangle \\ &= \left\langle \Psi_I^M \middle| \frac{1}{2}(\hat{N}-2\hat{n}_0) \middle| \Psi_I^M \right\rangle \\ &= \frac{M}{2} - n_{\Psi_I^M}(\Delta v_{\mathrm{ext}}),\end{aligned} \tag{A3}$$

where $M = N-1$ or N, and $I = 0$ or 1.

In the practical calculations reported in Sec. VI, we rely on the Legendre-Fenchel transform definition of the universal eN-centered ensemble density functional, which can be obtained by analogy with TGOK-DFT [22] and N-centered eDFT [46]:

$$F^{\xi}(n) = \sup_{\Delta v}\{E^{\xi}(\Delta v) + \Delta v(n-1)\}. \tag{A4}$$

In the above equation, the maximizing potential $\Delta v^{\xi}(n)$ is equal to the derivative of $F^{\xi}(n)$ with respect to the density,

$$\frac{\partial F^{\xi}(n)}{\partial n} = \Delta v^{\xi}(n). \tag{A5}$$

Despite lacking a closed-form expression as a function of the density, the value of $F^{\xi}(n)$ can still be computed to arbitrary accuracy for any given density from Eq. (A4) via Lieb maximization. However, for the exact ensemble density n^{ξ} which is used in all calculations in Sec. VI, the maximizing potential is simply equal to the external potential $\Delta v^{\xi}(n^{\xi}) = \Delta v_{\mathrm{ext}}$, and $F^{\xi}(n^{\xi}) = E^{\xi}(\Delta v_{\mathrm{ext}}) + \Delta v_{\mathrm{ext}}[n^{\xi}(\Delta v_{\mathrm{ext}}) - 1]$ is an analytical function of Δv_{ext}.

Next, we consider the noninteracting (KS) system which reproduces the eN-centered ensemble density of the interacting system. From the KS Hamiltonian

$$\hat{H}^{\mathrm{KS}}(\Delta v) = \hat{\mathcal{T}} + \frac{\Delta v}{2}(\hat{n}_1 - \hat{n}_0), \tag{A6}$$

we obtain the eN-centered ensemble energy as

$$\mathcal{E}^{\boldsymbol{\xi}}_{\mathrm{KS}}(\Delta v) = \left(1-\xi-\frac{\xi_-}{2}\right)\mathcal{E}^{N}_{0}(\Delta v) + \xi_-\mathcal{E}^{N-1}_{0}(\Delta v) + \xi\mathcal{E}^{N}_{1}(\Delta v), \tag{A7}$$

with the N- and $(N-1)$-electron ground-state energies, and the N-electron excited-state energy written as $\mathcal{E}^{N}_{0}(\Delta v) = 2\varepsilon_{\mathrm{H}}(\Delta v)$, $\mathcal{E}^{N-1}_{0}(\Delta v) = \varepsilon_{\mathrm{H}}(\Delta v)$, and $\mathcal{E}^{N}_{1}(\Delta v) = 0$, respectively, where

$$\varepsilon_{\mathrm{H}}(\Delta v) = -\sqrt{t^2+\frac{\Delta v^2}{4}}. \tag{A8}$$

Similarly to the universal functional in Eq. (A4), the noninteracting kinetic energy $T^{\boldsymbol{\xi}}_{\mathrm{s}}(n)$ can be written as a Legendre-Fenchel transform, which reads as

$$T^{\boldsymbol{\xi}}_{\mathrm{s}}(n) = \sup_{\Delta v}\{2(1-\xi)\varepsilon_{\mathrm{H}}(\Delta v) - \Delta v(1-n)\}. \tag{A9}$$

Since Eq. (A9) is explicitly independent of the ensemble weight for the $(N-1)$-electron ground state ξ_-, it follows that the maximizing KS potential corresponding to the noninteracting eN-centered ensemble is the same one as in TGOK-DFT [22]. Hence, it can be expressed as

$$\Delta v^{\mathrm{KS},\boldsymbol{\xi}}(n) \equiv \Delta v^{\mathrm{KS},\xi}(n) = \frac{2t(n-1)}{\sqrt{(1-\xi)^2-(1-n)^2}}, \tag{A10}$$

which implies that a given density n is noninteracting eN-centered ensemble v representable iff $|n-1| \leqslant 1-\xi$. By plugging Eq. (A10) into Eq. (A9), we obtain the expression for the noninteracting kinetic energy functional $T^{\boldsymbol{\xi}}_{\mathrm{s}}(n)$, as given in Eq. (73a).

Finally, the ensemble weight derivatives of Hxc functional $E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n) = F^{\boldsymbol{\xi}}(n) - T^{\boldsymbol{\xi}}_{\mathrm{s}}(n)$, which are key ingredients for obtaining exact expressions for the IPs and the optical gap, are obtained as follows:

$$\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi} = E^{N}_{1}[\Delta v^{\boldsymbol{\xi}}(n)] - E^{N}_{0}[\Delta v^{\boldsymbol{\xi}}(n)] - \frac{2t(1-\xi)}{\sqrt{(1-\xi)^2-(1-n)^2}} \tag{A11}$$

and

$$\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi_-} = E^{N-1}_{0}[\Delta v^{\boldsymbol{\xi}}(n)] - \frac{E^{N}_{0}[\Delta v^{\boldsymbol{\xi}}(n)]}{2}. \tag{A12}$$

b EEXX functional

The eN-centered ensemble exact (Hartree) exchange (EEXX) functional can be obtained from the formal expression of the Hx energy:

$$E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n) = U\left.\frac{\partial F^{\boldsymbol{\xi}}(n)}{\partial U}\right|_{U=0}, \tag{A13}$$

where we have, according to Eq. (A4),

$$\left.\frac{\partial F^{\boldsymbol{\xi}}(n)}{\partial U}\right|_{U=0} = \left(1-\frac{\xi_-}{2}-\xi\right)\left.\frac{\partial E^{N}_{0}(\Delta v)}{\partial U}\right|_{U=0,\,\Delta v=\Delta v^{\boldsymbol{\xi}}_{\mathrm{KS}}(n)} + \xi\left.\frac{\partial E^{N}_{1}(\Delta v)}{\partial U}\right|_{U=0,\,\Delta v=\Delta v^{\boldsymbol{\xi}}_{\mathrm{KS}}(n)}, \tag{A14}$$

and, according to Eqs. (A8) and (A10), and Eq. (A7) in [22],

$$\left.\frac{\partial E^{N}_{I}(\Delta v)}{\partial U}\right|_{U=0,\,\Delta v=\Delta v^{\boldsymbol{\xi}}_{\mathrm{KS}}(n)} = \frac{I+1}{2}\left[1+(1-2I)\left(\frac{1-n}{1-\xi}\right)^2\right], \tag{A15}$$

for $I=0$ or 1. Finally, inserting Eq. (A15) into Eq. (A13) gives, after some rearrangements of various terms, the following expression for Hx energy of Eq. (73b):

$$E^{\boldsymbol{\xi}}_{\mathrm{Hx}}(n) = \frac{U}{2}\left[1+\xi-\frac{\xi_-}{2}+\left(1-3\xi-\frac{\xi_-}{2}\right)\left(\frac{1-n}{1-\xi}\right)^2\right]. \tag{A16}$$

2. Derivative discontinuity in the Hubbard dimer from the e*N*-centered ensemble perspective

a. General expressions

Within the formalism of extended N-centered ensembles, the derivative discontinuity can be shown to appear in the Hubbard dimer. Starting from Eq. (52), we derive expressions for the IPs of the ground and the first-excited states

$$E^{N-1}_{0} - E^{N}_{0} = -\varepsilon^{\boldsymbol{\xi}}_{\mathrm{H}} - \frac{1}{2}\left(E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n^{\boldsymbol{\xi}}) - \sum_{i=0}^{1} v^{\boldsymbol{\xi}}_{\mathrm{Hxc},i}n^{\boldsymbol{\xi}}_{i}\right) + \left(1+\frac{\xi_-}{2}\right)\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi_-}\right|_{n=n^{\boldsymbol{\xi}}} + \frac{\xi}{2}\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi}\right|_{n=n^{\boldsymbol{\xi}}} \tag{A17}$$

and

$$E^{N-1}_{0} - E^{N}_{1} = -\varepsilon^{\boldsymbol{\xi}}_{\mathrm{L}} - \frac{1}{2}\left(E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n^{\boldsymbol{\xi}}) - \sum_{i=0}^{1} v^{\boldsymbol{\xi}}_{\mathrm{Hxc},i}n^{\boldsymbol{\xi}}_{i}\right) + \left(1+\frac{\xi_-}{2}\right)\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi_-}\right|_{n=n^{\boldsymbol{\xi}}} + \left(\frac{\xi}{2}-1\right)\left.\frac{\partial E^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(n)}{\partial\xi}\right|_{n=n^{\boldsymbol{\xi}}}, \tag{A18}$$

where the integral $\int d\mathbf{r}\, v^{\boldsymbol{\xi}}_{\mathrm{Hxc}}(\mathbf{r})n^{\boldsymbol{\xi}}(\mathbf{r})$ has been replaced by a summation over lattice sites. For the purpose of displaying the derivative discontinuity, the KS Hamiltonian of the Hubbard dimer is written with the KS potential determined up to a constant as follows:

$$\hat{H}^{\mathrm{KS},\boldsymbol{\xi}} = \hat{\mathcal{T}} + v^{\mathrm{KS},\boldsymbol{\xi}}_{1}\hat{n}_1 + v^{\mathrm{KS},\boldsymbol{\xi}}_{0}\hat{n}_0, \tag{A19}$$

where

$$v_i^{\mathrm{KS},\xi} = \frac{(-1)^{i-1}}{2}\Delta v^{\mathrm{KS},\xi} - \mu^{\xi}_{\mathrm{Hxc}}, \tag{A20a}$$

$$\Delta v^{\mathrm{KS},\xi} = \partial T_{\mathrm{s}}^{\xi}(n)/\partial n\big|_{n=n^{\xi}} \equiv \Delta v_{\mathrm{ext}} + \Delta v^{\xi}_{\mathrm{Hxc}}, \tag{A20b}$$

and n^{ξ} is the exact eN-centered ensemble occupation of site 0. The total Hxc potential on site i reads as

$$v^{\xi}_{\mathrm{Hxc},i} = \frac{(-1)^{i-1}}{2}\Delta v^{\xi}_{\mathrm{Hxc}} - \mu^{\xi}_{\mathrm{Hxc}}. \tag{A21}$$

The constant shift $-\mu^{\xi}_{\mathrm{Hxc}}$ is determined to fulfill the constraint for exactification of Koopmans' theorem in Eq. (53).

In order to derive the derivative discontinuity, we consider two specific ensembles. The first ensemble is the regular N-centered ensemble, where the ensemble weights take the values of $\xi = 0$ and $0 \leqslant \xi_- \leqslant 2$, describing the ionization process from the two-electron ground state, with the IP $I_0^N = E_0^{N-1} - E_0^N$. To fulfill Koopman's theorem for the ground-state IP, we set all the terms on the right-hand sides of Eq. (A17) to zero, except the HOMO energy. This gives the following constraint for the Hxc potential in the Hubbard dimer:

$$\sum_{i=0}^{1} v^{(0,\xi_-)}_{\mathrm{Hxc},i} n_i^{\xi_-} = E^{\xi_-}_{\mathrm{Hxc}}(n^{\xi_-}) - (2+\xi_-)\left.\frac{\partial E^{\xi_-}_{\mathrm{Hxc}}(n)}{\partial \xi_-}\right|_{n=n^{\xi_-}}, \tag{A22}$$

where $n^{\xi_-} = n^{(0,\xi_-)}$ and $E^{\xi_-}_{\mathrm{Hxc}} = E^{(0,\xi_-)}_{\mathrm{Hxc}}$. By inserting Eq. (A21) into the above equation, and solving for $-\mu^{(0,\xi_-)}_{\mathrm{Hxc}}$, we get

$$-\mu^{(0,\xi_-)}_{\mathrm{Hxc}} = \frac{1}{2}\Big(\Delta v^{\xi_-}_{\mathrm{Hxc}}[n^{\xi_-} - 1] + E^{\xi_-}_{\mathrm{Hxc}}(n^{\xi_-})\Big) - \frac{2+\xi_-}{2}\left.\frac{\partial E^{\xi_-}_{\mathrm{xc}}(n)}{\partial \xi_-}\right|_{n=n^{\xi_-}}, \tag{A23}$$

where, according to Eqs. (75) and (76), $\Delta v^{\xi_-}_{\mathrm{Hxc}} = \Delta v^{(0,\xi_-)}_{\mathrm{Hxc}}(n^{\xi_-}) = \Delta v^{(0,0)}_{\mathrm{Hxc}}(n^{\xi_-})$.

The second ensemble is the extended N-centered ensemble from Sec. VI, with the full weight range for the neutral excitation ($0 < \xi \leqslant \frac{1}{2}$), and the infinitesimal limit for the ionization from the two-electron ground state, i.e., $\xi_- \to 0^+$. The latter weight limit is imposed so that Koopmans' theorem for the excited-state IP $I_1^N = E_0^{N-1} - E_1^N$ can still be fulfilled. By setting all the terms on the right-hand side of Eq. (A18) to zero, except the LUMO energy, we get

$$\sum_{i=0}^{1} v^{(\xi,0^+)}_{\mathrm{Hxc},i} n_i^{\xi} = E^{\xi}_{\mathrm{Hxc}}(n^{\xi}) + (2-\xi)\left.\frac{\partial E^{\xi}_{\mathrm{xc}}(n)}{\partial \xi}\right|_{n=n^{\xi}} - 2\left.\frac{\partial E^{(\xi,\xi_-)}_{\mathrm{xc}}(n^{\xi})}{\partial \xi_-}\right|_{\xi_-=0}, \tag{A24}$$

where $n^{\xi} = n^{(\xi,0)}$ and $E^{\xi}_{\mathrm{Hxc}} = E^{(\xi,0)}_{\mathrm{Hxc}}$. After inserting Eq. (A21) into the above equation, and solving for $-\mu^{(\xi,0^+)}_{\mathrm{Hxc}}$, we get

$$-\mu^{(\xi,0^+)}_{\mathrm{Hxc}} = \frac{1}{2}\big(\Delta v^{\xi}_{\mathrm{Hxc}}[n^{\xi} - 1] + E^{\xi}_{\mathrm{Hxc}}(n^{\xi})\big) + \frac{2-\xi}{2}\left.\frac{\partial E^{\xi}_{\mathrm{xc}}(n)}{\partial \xi}\right|_{n=n^{\xi}} - \left.\frac{\partial E^{(\xi,\xi_-)}_{\mathrm{xc}}(n)}{\partial \xi_-}\right|_{\xi_-=0}, \tag{A25}$$

where $\Delta v^{\xi}_{\mathrm{Hxc}} = \Delta v^{(\xi,0)}_{\mathrm{Hxc}}(n^{\xi})$. Considering now Eq. (A23), the limit $\xi_- \to 0^+$ determines the value of the constant Hxc shift for the two-electron ground state

$$-\mu^{(\xi=0,0^+)}_{\mathrm{Hxc}} = \frac{1}{2}\big(\Delta v_{\mathrm{Hxc}}[n_{\Psi_0^N} - 1] + E_{\mathrm{Hxc}}(n_{\Psi_0^N})\big) - \left.\frac{\partial E^{\xi_-}_{\mathrm{xc}}(n_{\Psi_0^N})}{\partial \xi_-}\right|_{\xi_-=0}. \tag{A26}$$

In the case of Eq. (A25), the limit $\xi \to 0^+$ returns the value of the Hxc shift for the TGOK ensemble with an infinitesimal amount of neutral excitation from the two-electron ground state

$$-\mu^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc}} = \frac{1}{2}\big(\Delta v_{\mathrm{Hxc}}[n_{\Psi_0^N} - 1] + E_{\mathrm{Hxc}}(n_{\Psi_0^N})\big) + \left.\frac{\partial E^{\xi}_{\mathrm{xc}}(n_{\Psi_0^N})}{\partial \xi}\right|_{\xi=0} - \left.\frac{\partial E^{\xi_-}_{\mathrm{xc}}(n_{\Psi_0^N})}{\partial \xi_-}\right|_{\xi_-=0}. \tag{A27}$$

By subtracting Eq. (A26) from Eq. (A27) and using Eq. (A21), we obtain the following expression for the derivative discontinuity:

$$v^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc},1} - v^{(\xi=0,0^+)}_{\mathrm{Hxc},1} = \mu^{(\xi=0,0^+)}_{\mathrm{Hxc}} - \mu^{(\xi\to 0^+,0^+)}_{\mathrm{Hxc}} = \left.\frac{\partial E^{\xi}_{\mathrm{xc}}(n_{\Psi_0^N})}{\partial \xi}\right|_{\xi=0}. \tag{A28}$$

This is an exact result for the derivative discontinuity in the Hubbard dimer, which is shown in Fig. 1.

b. Symmetric Hubbard dimer

In the symmetric dimer, the Hxc potential and the derivative discontinuity have closed-form expressions. Starting from the formulas for individual N- and $(N-1)$-electron energies, $E_0^N(\Delta v_{\mathrm{ext}} = 0) = \frac{1}{2}(U - \sqrt{U^2 + 16t^2})$, $E_1^N(\Delta v_{\mathrm{ext}} = 0) = U$, and $E_0^{N-1}(\Delta v_{\mathrm{ext}} = 0) = -t$, the universal and the noninteracting kinetic energy eN-centered ensemble density functionals are derived as follows:

$$F^{\xi}(n=1) = E^{\xi}(\Delta v_{\mathrm{ext}} = 0) = \left(1 - \frac{\xi_-}{2} - \xi\right)\frac{U - \sqrt{U^2 + 16t^2}}{2} - \xi_- t + \xi U \tag{A29}$$

and

$$T_{\mathrm{s}}^{\xi}(n=1) = -2t(1-\xi), \tag{A30}$$

while the EEXX functional reads as

$$E^{\boldsymbol{\xi}}_{\rm Hx}(n=1) = \frac{U}{2}\left(1 - \frac{\xi_-}{2} + \xi\right). \tag{A31}$$

For the regular N-centered ensemble ($\xi = 0$ and $0 \leqslant \xi_- \leqslant 2$), the Hxc functional reads as

$$E^{\xi_-}_{\rm Hxc}(n=1) = \left(1 - \frac{\xi_-}{2}\right)\frac{U - \sqrt{U^2 + 16t^2}}{2} - \xi_- t + 2t, \tag{A32}$$

which can also be expressed as

$$E^{\xi_-}_{\rm Hxc}(n=1) = -(2-\xi_-)\frac{\partial E^{\xi_-}_{\rm Hxc}(n=1)}{\partial \xi_-}. \tag{A33}$$

Inserting the above expression into Eq. (A23), and taking into account that $\Delta v^{\xi_-}_{\rm Hxc} = 0$, we obtain from Eq. (A21) that

$$v^{(0,\xi_-)}_{\rm Hxc,1} = -2\frac{\partial E^{\xi_-}_{\rm Hxc}(n=1)}{\partial \xi_-} = \frac{U + 4t - \sqrt{U^2 + 16t^2}}{2}. \tag{A34}$$

Using the EEXX functional [see Eq. (A31)] instead of the exact Hxc functional clearly gives the wrong result:

$$v^{(0,\xi_-)}_{\rm Hx,1} = U/2. \tag{A35}$$

Upon inclusion of the neutral excitation into the ensemble ($0 < \xi \leqslant \frac{1}{2}$), we observe that the EEXX-only and the exact Hxc ensemble potentials coincide in the symmetric dimer. To demonstrate this, we first isolate the eN-centered ensemble correlation functional from Eqs. (A29)–(A31):

$$\begin{aligned} E^{\boldsymbol{\xi}}_{\rm c}(n=1) &= F^{\boldsymbol{\xi}}(n=1) - T^{\boldsymbol{\xi}}_{\rm s}(n=1) - E^{\boldsymbol{\xi}}_{\rm Hx}(n=1) \\ &= \left(1 - \frac{\xi_-}{2} - \xi\right)\frac{4t - \sqrt{U^2 + 16t^2}}{2}, \end{aligned} \tag{A36}$$

which can also be expressed as

$$E^{\boldsymbol{\xi}}_{\rm c}(n=1) = -(2-\xi)\frac{\partial E^{\boldsymbol{\xi}}_{\rm c}(n=1)}{\partial \xi} + (2+\xi_-)\frac{\partial E^{\boldsymbol{\xi}}_{\rm c}(n=1)}{\partial \xi_-}. \tag{A37}$$

In the particular case when $\xi_- \to 0^+$, we have

$$E^{\xi}_{\rm c}(n=1) = -(2-\xi)\frac{\partial E^{\xi}_{\rm c}(n=1)}{\partial \xi} + 2\frac{\partial E^{(\xi_-,\xi)}_{\rm c}(n=1)}{\partial \xi_-}\bigg|_{\xi_-=0}. \tag{A38}$$

By inserting the above expression into Eq. (A25), we can see that the correlation part in the $E^{\boldsymbol{\xi}}_{\rm Hxc}(n=1)$ functional is canceled out by its weight derivatives, which implies that only exchange terms contribute to $v^{(\xi,0^+)}_{\rm Hxc}$, giving the following result:

$$\begin{aligned} v^{(\xi,0^+)}_{\rm Hxc,1} &\equiv v^{(\xi,0^+)}_{\rm Hx,1} \\ &= \frac{1}{2}\left(\frac{U}{2} + 2\frac{\partial E^{\xi}_{\rm Hx}(n=1)}{\partial \xi}\right) - \frac{\partial E^{\boldsymbol{\xi}}_{\rm Hx}(n=1)}{\partial \xi-}\bigg|_{\xi_-=0} \\ &= U. \end{aligned} \tag{A39}$$

Hence, according to Eqs. (A34) and (A39), the exact derivative discontinuity in the symmetric dimer reads as

$$v^{(\xi\to 0^+,0^+)}_{\rm Hxc,1} - v^{(\xi=0,0^+)}_{\rm Hxc,1} = \frac{U - 4t + \sqrt{U^2 + 16t^2}}{2}, \tag{A40}$$

while the EEXX-only approximation, obtained from Eqs. (A35) and (A39), reads as

$$v^{(\xi\to 0^+,0^+)}_{\rm Hx,1} - v^{(\xi=0,0^+)}_{\rm Hx,1} = \frac{U}{2}, \tag{A41}$$

which is always lower than the exact derivative discontinuity.

APPENDIX B: EEXX APPROXIMATION APPLIED TO THE HUBBARD DIMER WITH $U \gg \Delta v_{\rm ext} = 2t = 1$

In the strongly correlated regime $U \gg \Delta v_{\rm ext} = 2t = 1$, the ground-state density is very close to 1 [22], while the one-electron ground-state density $n_{\Psi_0^{N-1}}$ (we recall that the central number of electrons is $N = 2$ in the present model) fulfills, according to Eqs. (A3) and (A8),

$$\frac{\partial \varepsilon_{\rm H}(\Delta v_{\rm ext})}{\partial \Delta v_{\rm ext}} = -\frac{\Delta v_{\rm ext}}{4\sqrt{t^2 + (\Delta v^2_{\rm ext}/4)}} = \frac{1}{2}\left(1 - 2n_{\Psi_0^{N-1}}\right), \tag{B1}$$

or, equivalently, $n_{\Psi_0^{N-1}} = \frac{1}{2}(1 + \frac{1}{\sqrt{2}})$, thus leading to the following expression for the ensemble density under study:

$$\begin{aligned} n^{\xi_-} &= n^{(\xi=0,\xi_-)} \\ &= \left(1 - \frac{\xi_-}{2}\right) \times 1 + \xi_- \times \frac{1}{2}\left(1 + \frac{1}{\sqrt{2}}\right) \\ &= 1 + \frac{\xi_-}{2\sqrt{2}}. \end{aligned} \tag{B2}$$

As a result, the ensemble KS potential varies with ξ_- as follows [see Eq. (76)]:

$$\Delta v^{\xi_-}_{\rm KS} = \frac{2t\left(n^{\xi_-} - 1\right)}{\sqrt{1 - (n^{\xi_-} - 1)^2}} = \frac{\xi_-}{\sqrt{8 - \xi_-^2}}, \tag{B3}$$

and the KS HOMO/LUMO energies read as

$$-\varepsilon^{\xi_-}_{\rm H} = \varepsilon^{\xi_-}_{\rm L} = \sqrt{t^2 + \frac{\left(\Delta v^{\xi_-}_{\rm KS}\right)^2}{4}} = \frac{\sqrt{2}}{\sqrt{8 - \xi_-^2}}. \tag{B4}$$

Therefore, the bare KS ground-state (excited-state) IP increases (decreases) with the ensemble weight ξ_-, unlike the approximate interacting EEXX one (see the bottom left panel of Fig. 3).

In order to identify the origin of the latter trend we need to consider the decomposition of both IPs as given in Eq. (52). The Hxc potential term, which contributes to both IPs, reads as

$$\begin{aligned} \frac{\Delta v^{\xi_-}_{\rm Hxc}}{2N}(2 - 2n^{\xi_-}) &= -\frac{\xi_-\left(\Delta v^{\xi_-}_{\rm KS} - \Delta v_{\rm ext}\right)}{4\sqrt{2}} \\ &= \frac{1}{4\sqrt{2}}\left(-\frac{\xi_-^2}{\sqrt{8 - \xi_-^2}} + \xi_-\right) \end{aligned} \tag{B5}$$

since $N = 2$. Note that, as we approach the $\xi_- = 2$ limit, the above contribution decreases with ξ_-. Therefore, the weight dependence of the approximate EEXX excited-state IP originates from the remaining ensemble Hx energy term and its weight derivatives. The contribution that is common to both ground- and excited-state IPs reads as

$$I^{\xi_-}_{0,\mathrm{Hx}} = \left[-\frac{E^{\xi_-}_{\mathrm{Hx}}(n)}{N} + \left(1+\frac{\xi_-}{N}\right)\frac{\partial E^{\xi_-}_{\mathrm{Hx}}(n)}{\partial \xi_-}\right]_{n=n^{\xi_-}}, \tag{B6}$$

where [see Eq. (73b)]

$$E^{\xi_-}_{\mathrm{Hx}}(n) = \frac{U}{2}\left(1-\frac{\xi_-}{2}\right)[1+(n-1)^2], \tag{B7}$$

thus leading to

$$I^{\xi_-}_{0,\mathrm{Hx}} = -\frac{U}{2}[1+(n^{\xi_-}-1)^2] = -\frac{U}{2}\left(1+\frac{\xi_-^2}{8}\right). \tag{B8}$$

The above contribution is therefore responsible for the net decrease of the EEXX ground-state IP as the ensemble weight ξ_- increases.

Turning to the excited-state IP, we need to consider the following additional contribution [see Eq. (52)]:

$$\begin{aligned} -\Delta^{\xi_-}_{\mathrm{Hx}} &= -\left.\frac{\partial E^{(\xi,\xi_-)}_{\mathrm{Hx}}(n)}{\partial \xi}\right|_{\xi=0,n=n^{\xi_-}} \\ &= -\frac{U}{2}[1-(n^{\xi_-}-1)^2(1+\xi_-)] \\ &= -\frac{U}{2}\left[1-\frac{\xi_-^2(1+\xi_-)}{8}\right], \end{aligned} \tag{B9}$$

which, when it is added to the remaining Hx contribution of Eq. (B8), gives the total Hx term

$$I^{\xi_-}_{0,\mathrm{Hx}} - \Delta^{\xi_-}_{\mathrm{Hx}} = -\frac{U}{2}\left(2-\frac{\xi_-^3}{8}\right). \tag{B10}$$

The above contribution is therefore responsible for the net increase with ξ_- of the EEXX excited-state IP.

In summary, at the EEXX level of approximation and in the considered $U \gg \Delta v_{\mathrm{ext}} = 2t = 1$ regime, the ground- and first-excited-state IPs read as

$$I^N_0 \approx \frac{1}{4\sqrt{2}}\left(\xi_- + \sqrt{8-\xi_-^2}\right) - \frac{U}{2}\left(1+\frac{\xi_-^2}{8}\right), \tag{B11a}$$

$$I^N_1 \approx \frac{1}{4\sqrt{2}}\left(\xi_- - \frac{8+\xi_-^2}{\sqrt{8-\xi_-^2}}\right) - \frac{U}{2}\left(2-\frac{\xi_-^3}{8}\right), \tag{B11b}$$

respectively, thus leading to the following expression for the optical gap:

$$I^N_0 - I^N_1 \approx \frac{2\sqrt{2}}{\sqrt{8-\xi_-^2}} + \frac{U}{2}\left[1-\frac{\xi_-^2(1+\xi_-)}{8}\right]. \tag{B12}$$

As a result, we obtain in the limiting $\xi_- = 0$ and $\xi_- = 2$ cases the following expressions:

$$I^N_0 \overset{\xi_-=0}{\approx} \frac{1}{2} - \frac{U}{2}, \tag{B13a}$$

$$I^N_1 \overset{\xi_-=0}{\approx} -\frac{1}{2} + U, \tag{B13b}$$

$$I^N_0 - I^N_1 \overset{\xi_-=0}{\approx} 1 + \frac{U}{2}, \tag{B13c}$$

and

$$I^N_0 \overset{\xi_-=2}{\approx} \frac{1}{\sqrt{2}} - \frac{3U}{4}, \tag{B14a}$$

$$I^N_1 \overset{\xi_-=2}{\approx} -\frac{1}{\sqrt{2}} - \frac{U}{2}, \tag{B14b}$$

$$I^N_0 - I^N_1 \overset{\xi_-=2}{\approx} \sqrt{2} - \frac{U}{4}, \tag{B14c}$$

respectively, which are in very good agreement with the values obtained numerically for $U = 5$ (see the bottom panels of Fig. 3). Note that, in the latter case, the EEXX optical gap equals $\sqrt{2} - \frac{5}{4} \approx 0.16$ when $\xi_- = 2$, which confirms the dramatic underestimation of the optical gap that is observed in the bottom right panel of Fig. 3 as ξ_- increases.

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