PHYSICAL REVIEW A **94**, 012511 (2016)

Ghost-interaction correction in ensemble density-functional theory for excited states with and without range separation

Md. Mehboob Alam,[1,*] Stefan Knecht,[2] and Emmanuel Fromager[1]

[1]*Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France*

[2]*Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog Weg 2, CH-8093 Zürich, Switzerland*

(Received 17 March 2016; published 19 July 2016)

Ensemble density-functional theory (eDFT) suffers from the so-called "ghost-interaction" error when approximate exchange-correlation functionals are used. In this work, we present a rigorous ghost-interaction correction (GIC) scheme in the context of range-separated eDFT. The method relies on an exact decomposition of the ensemble short-range exchange-correlation energy into a multideterminantal exact exchange term, which involves the long-range interacting ensemble density matrix, instead of the Kohn-Sham (KS) one, and a complementary density-functional correlation energy. A generalized adiabatic connection formula is derived for the latter. In order to perform practical calculations, the complementary correlation functional is simply modeled by its ground-state local density approximation (LDA), while long-range interacting ground- and excited-state wave functions are obtained self-consistently by combining a long-range configuration-interaction calculation with a short-range LDA potential. We show that the GIC reduces the curvature of approximate range-separated ensemble energies drastically while providing considerably more accurate excitation energies, even for charge-transfer and double excitations. Interestingly, the method performs well also in the context of standard KS-eDFT, which is recovered when the range-separation parameter is set to 0.

DOI: 10.1103/PhysRevA.94.012511

I. INTRODUCTION

The low computational cost and good accuracy of the time-dependent density-functional theory (DFT) [1,2] has made it one of the most popular methods for calculating electronic excitation energies. Nevertheless, because of the incorrect asymptotic behavior of approximate density-functional exchange-correlation potentials used in the time-dependent DFT, it suffers from limitations like the poor description of charge-transfer and Rydberg excitations [1]. Additionally, because of the standard adiabatic approximation (i.e., the use of a frequency-independent kernel), excitations of multiple character [3] are completely absent from the spectrum. The present work deals with ensemble DFT (eDFT) [4–7], which is a time-independent alternative to time-dependent DFT for excited states. Its variational nature and hence ease of implementation have caused its recent reappearance in the literature [8–16]. Originally formulated by Theophilou for equiensembles [4], it was generalized by Gross *et al.* [5–7] about three decades ago, but until now it has not gained the status of a standard method. One of the main reasons is the absence of reliable exchange-correlation functionals for ensembles, whose development remains challenging [17–20]. Employing ground-state local or semilocal functionals in practical eDFT calculations usually gives curved ensemble energies [21] and introduces so-called "ghost-interaction" errors [22]. The latter are induced by unphysical interactions between ground and excited states that appear when the Hartree energy is calculated with an ensemble density (i.e., a weighted sum of individual state densities). In spite of these difficulties, the ability of eDFT to account for multiple excitations [21], in particular, motivated recent developments, including its multiconfigurational extension [8,9]. Very recently, Pernal and coworkers [8] introduced range separation in eDFT. In their approach, Boltzmann ensemble weights are defined by means of an effective temperature parameter that can be tuned, in addition to the range separation parameter. In contrast, Senjean *et al.* [21,23] use a linear interpolation method (LIM) in order to obtain weight-independent excitation energies. Since the LIM uses ensemble densities in conjunction with ground-state Hartree-exchange-correlation (Hxc) functionals, it obviously suffers from ghost-interaction errors. In Pernal's scheme, the error is pragmatically removed by defining the individual state energies [16]. So far, rigorous ghost-interaction corrections have been developed in the context of single determinantal Kohn-Sham (KS) eDFT [13,22,24] only. In this work, we present a rigorous strategy for removing ghost-interaction errors in range-separated eDFT which, in the end, proves to be equally applicable to standard KS-eDFT.

The paper is organized as follows: After a brief review on exact range-separated eDFT (Sec. II A) and an introduction to the usual weight-independent density-functional approximation (Sec. II B), the concept of the ghost interaction as well as an exact ghost-interaction-free expression for the range-separated ensemble energy are presented in Sec. II C. Approximate implementable formulations with and without extrapolation corrections are then provided in Sec. II D. Following the computational details (Sec. III), numerical results are discussed in Sec. IV. Conclusions are given in Sec. V.

II. THEORY

A. Range-separated ensemble density-functional theory for excited states

In eDFT, an ensemble consisting of M eigenstates $\{\Psi_k[v]\}_{0\leqslant k\leqslant M-1}$ of the Hamiltonian $\hat{H}[v]=\hat{T}+\hat{W}_{\rm ee}+\int d\mathbf{r}\; v(\mathbf{r})\hat{n}(\mathbf{r})$ with energies $E_0[v]$, $E_1[v]$, $\dots$, $E_{M-1}[v]$ and the associated weights $\mathbf{w}\equiv(w_0,w_1,\dots,w_{M-1})$ is considered.

---

[*] malam@unistra.fr

2469-9926/2016/94(1)/012511(9)

The operators $\hat{T}$, $\hat{W}_{\mathrm{ee}}$, and $\hat{n}(\mathbf{r})$ correspond to the kinetic energy, the regular two-electron repulsion, and the density, respectively. The weights are assigned in such a way that $w_0 \geqslant w_1 \geqslant \ldots \geqslant w_{M-1}$ and $\sum_{k=0}^{M-1} w_k = 1$. According to the Gross-Oliveira-Kohn (GOK) variational principle [5], the following inequality holds for any trial ensemble density matrix $\hat{\gamma}^{\mathbf{w}} = \sum_{k=0}^{M-1} w_k |\overline{\Psi}_k\rangle\langle\overline{\Psi}_k|$:

$$E^{\mathbf{w}}[v] \leqslant \mathrm{Tr}\big[\hat{\gamma}^{\mathbf{w}} \hat{H}[v]\big], \tag{1}$$

where Tr denotes the trace. The lower bound,

$$E^{\mathbf{w}}[v] = \mathrm{Tr}\big[\hat{\Gamma}^{\mathbf{w}}[v]\hat{H}[v]\big] = \sum_{k=0}^{M-1} w_k E_k[v], \tag{2}$$

is the exact ensemble energy, which is reached when the trial density matrix equals the exact ensemble density matrix $\hat{\Gamma}^{\mathbf{w}}[v] = \sum_{k=0}^{M-1} w_k |\Psi_k[v]\rangle\langle\Psi_k[v]|$. An important consequence of this variational principle is that the Hohenberg-Kohn theorem can be extended to ensembles [6], thus leading to the exact variational expression

$$E^{\mathbf{w}}[v] = \min_n \left\{ F^{\mathbf{w}}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}, \tag{3}$$

where

$$\begin{aligned} F^{\mathbf{w}}[n] &= \min_{\hat{\gamma}^{\mathbf{w}} \to n} \mathrm{Tr}[\hat{\gamma}^{\mathbf{w}}(\hat{T} + \hat{W}_{\mathrm{ee}})] \\ &= \mathrm{Tr}[\hat{\Gamma}^{\mathbf{w}}[n](\hat{T} + \hat{W}_{\mathrm{ee}})] \end{aligned} \tag{4}$$

is the analogue of the Levy-Lieb functional for ensembles. Note that the minimization in Eq. (4) is performed over all ensemble density matrices with density $n(\mathbf{r})$:

$$\hat{\gamma}^{\mathbf{w}} \to n \Leftrightarrow \mathrm{Tr}[\hat{\gamma}^{\mathbf{w}} \hat{n}(\mathbf{r})] = n_{\hat{\gamma}^{\mathbf{w}}}(\mathbf{r}) = n(\mathbf{r}). \tag{5}$$

Note also that, for any trial density $n(\mathbf{r})$, the GOK inequality in Eq. (1) can be applied to the minimizing ensemble density matrix $\hat{\Gamma}^{\mathbf{w}}[n]$ with density $n(\mathbf{r})$, thus leading to

$$E^{\mathbf{w}}[v] \leqslant \mathrm{Tr}\big[\hat{\Gamma}^{\mathbf{w}}[n]\hat{H}[v]\big] \tag{6}$$

or, equivalently, according to Eq. (4),

$$E^{\mathbf{w}}[v] \leqslant F^{\mathbf{w}}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}). \tag{7}$$

Since Eq. (7) holds for any potential $v(\mathbf{r})$, $F^{\mathbf{w}}[n]$ can be rewritten as a Legendre-Fenchel transform, exactly like in the ground-state theory [25]:

$$F^{\mathbf{w}}[n] = \sup_v \left\{ E^{\mathbf{w}}[v] - \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}. \tag{8}$$

From a mathematical point of view, the latter expression is well defined since the ensemble energy, in contrast to individual excited-state energies, is concave with respect to the local potential $v(\mathbf{r})$. Indeed, for any potentials $v_a(\mathbf{r})$ and $v_b(\mathbf{r})$, and any ζ in the range $0 \leqslant \zeta \leqslant 1$, the exact ensemble energy associated with the average potential $v^{\zeta}(\mathbf{r}) = (1-\zeta)v_a(\mathbf{r}) + \zeta v_b(\mathbf{r})$ reads [see Eq. (2)]

$$\begin{aligned} E^{\mathbf{w}}[v^{\zeta}] = \mathrm{Tr}[\hat{\Gamma}^{\mathbf{w}}[v^{\zeta}]\hat{H}[v^{\zeta}]] &= (1-\zeta)\mathrm{Tr}[\hat{\Gamma}^{\mathbf{w}}[v^{\zeta}]\hat{H}[v_a]] \\ &\quad + \zeta \mathrm{Tr}[\hat{\Gamma}^{\mathbf{w}}[v^{\zeta}]\hat{H}[v_b]]. \end{aligned} \tag{9}$$

Therefore, applying the GOK principle to both the $\hat{H}[v_a]$ and the $\hat{H}[v_b]$ Hamiltonians leads to the concavity relation,

$$E^{\mathbf{w}}[v^{\zeta}] \geqslant (1-\zeta)E^{\mathbf{w}}[v_a] + \zeta E^{\mathbf{w}}[v_b]. \tag{10}$$

Finally, as in the ground-state theory, differentiability problems of the ensemble Levy-Lieb functional should, in principle, occur in directions that change the number of electrons. It was shown recently by Helgaker and coworkers [26] that a differentiable but exact formulation of DFT can be obtained by using a Moreau-Yosida regularization. It would actually be interesting to explore the extension of this work to eDFT.

Returning to the main focus of this paper, which is the ghost-interaction problem in range-separated eDFT, we decompose the two-electron interaction into long- and short-range contributions [27–29],

$$\hat{W}_{\mathrm{ee}} = \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{W}_{\mathrm{ee}}^{\mathrm{sr},\mu}, \quad \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} \equiv \sum_{i<j} \frac{\mathrm{erf}(\mu|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{11}$$

where erf is the error function and μ is a parameter in $[0, +\infty[$ that controls the range separation. According to Eq. (11), the ensemble Levy-Lieb functional can be range-separated as

$$F^{\mathbf{w}}[n] = F^{\mathrm{lr},\mu,\mathbf{w}}[n] + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n], \tag{12}$$

where, by analogy with Eq. (4),

$$\begin{aligned} F^{\mathrm{lr},\mu,\mathbf{w}}[n] &= \min_{\hat{\gamma}^{\mathbf{w}} \to n} \left\{ \mathrm{Tr}\big[\hat{\gamma}^{\mathbf{w}}\big(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu}\big)\big] \right\} \\ &= \mathrm{Tr}\big[\hat{\Gamma}^{\mu,\mathbf{w}}[n]\big(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu}\big)\big], \end{aligned} \tag{13}$$

and $E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n]$ is the complementary short-range ensemble Hxc functional, which is both $\mathbf{w}$ and μ dependent. Note that $\hat{\Gamma}^{\mu,\mathbf{w}}[n]$ is the density matrix of the long-range-interacting ensemble with density n. The short-range ensemble Hxc energy is usually split as [8,9,21]

$$E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n] = E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] + E_{\mathrm{xc}}^{\mathrm{sr},\mu,\mathbf{w}}[n], \tag{14}$$

where the (weight-independent) short-range Hartree term equals

$$E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] = \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') \frac{\mathrm{erfc}\big(\mu|\mathbf{r} - \mathbf{r}'|\big)}{|\mathbf{r} - \mathbf{r}'|}, \tag{15}$$

with $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$. For a given electronic system with nuclear potential $v_{\mathrm{ne}}(\mathbf{r})$, combining Eq. (3) with Eqs. (12) and (13) leads to the following variational range-separated expression for the exact ensemble energy $E^{\mathbf{w}}[v_{\mathrm{ne}}]$, which we simply denote $E^{\mathbf{w}}$ in the following [21]:

$$\begin{aligned} E^{\mathbf{w}} &= \min_{\hat{\gamma}^{\mathbf{w}}} \left\{ \mathrm{Tr}\big[\hat{\gamma}^{\mathbf{w}}(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}})\big] + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n_{\hat{\gamma}^{\mathbf{w}}}] \right\} \\ &= \mathrm{Tr}\big[\hat{\Gamma}^{\mu,\mathbf{w}}\big(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}}\big)\big] + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n_{\hat{\Gamma}^{\mu,\mathbf{w}}}], \end{aligned} \tag{16}$$

where $\hat{V}_{\mathrm{ne}} = \int d\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) \hat{n}(\mathbf{r})$. The minimizing density matrix $\hat{\Gamma}^{\mu,\mathbf{w}} = \sum_{k=0}^{M-1} w_k |\Psi_k^{\mu,\mathbf{w}}\rangle\langle\Psi_k^{\mu,\mathbf{w}}|$ reproduces the exact physical ensemble density, $n_{\hat{\Gamma}^{\mu,\mathbf{w}}}(\mathbf{r}) = \mathrm{Tr}[\hat{\Gamma}^{\mu,\mathbf{w}} \hat{n}(\mathbf{r})] = n_{\hat{\Gamma}^{\mathbf{w}}[v_{\mathrm{ne}}]}(\mathbf{r})$, and the corresponding wave functions $\{\Psi_k^{\mu,\mathbf{w}}\}_{0 \leqslant k \leqslant M-1}$ fulfill the following self-consistent equations [21]:

$$\begin{aligned} &\left(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}} + \int d\mathbf{r} \frac{\delta E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n_{\hat{\Gamma}^{\mu,\mathbf{w}}}]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) \right) |\Psi_k^{\mu,\mathbf{w}}\rangle \\ &= \mathcal{E}_k^{\mu,\mathbf{w}} |\Psi_k^{\mu,\mathbf{w}}\rangle, 0 \leqslant k \leqslant M-1. \end{aligned} \tag{17}$$

Note that the standard Schrödinger and KS-eDFT equations are recovered from Eq. (17) for $\mu \to +\infty$ and $\mu = 0$, respectively. For the sake of simplicity, we focus in the following on two-state ensembles. In this particular case, one single weight w with $0 \leqslant w \leqslant 1/2$ is needed and $\mathbf{w} \equiv (1-w,w)$, so that the exact ensemble energy reads

$$E^{w} = (1-w)E_0 + wE_1, \tag{18}$$

where $E_k = E_k[v_{\mathrm{ne}}]$, $k = 0,1$. Let us stress that all the methods discussed in the following can be extended straightforwardly to higher excitations simply by considering larger ensembles and expressing the targeted excitation energy in terms of equiensemble energies and lower excitation energies [6,21]. This is discussed in more detail in Sec. II B.

In recent works, Senjean *et al.* [21,23] pointed out that, in the exact theory, the excitation energy can be calculated in (at least) two ways. The first one consists in differentiating the ensemble energy in Eq. (16) with respect to the ensemble weight, thus leading to [21]

$$\begin{aligned}\omega = \frac{dE^{w}}{dw} &= \mathcal{E}_1^{\mu,w} - \mathcal{E}_0^{\mu,w} + \left.\frac{\partial E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,w}[n]}{\partial w}\right|_{n=n_{\hat{\Gamma}^{\mu,w}}} \\ &= \Delta\mathcal{E}^{\mu,w} + \Delta_{\mathrm{xc}}^{\mu,w},\end{aligned} \tag{19}$$

where $\Delta\mathcal{E}^{\mu,w} = \mathcal{E}_1^{\mu,w} - \mathcal{E}_0^{\mu,w}$ is the auxiliary long-range-interacting excitation energy and $\Delta_{\mathrm{xc}}^{\mu,w}$ is the short-range analog of the xc derivative discontinuity for a canonical ensemble [9,30]. In the $\mu = 0$ limit, this derivative with respect to the ensemble weight w corresponds, when $w = 0$, to the jump in the KS HOMO energy that occurs when comparing $w = 0$ and $w \to 0$ situations; hence the name "derivative discontinuity." This was shown by Levy [30] and observed numerically by Yang *et al.* [11] in the He atom. The proof is very similar to that for the discontinuity due to the change of particle number but the two discontinuities are different. Indeed, we consider here a canonical ensemble where both ground and excited states have the same number of electrons.

In an alternative approach, referred to as the LIM [21], the exact excitation energy is simply obtained by linear interpolation,

$$\omega = 2\big(E^{w=1/2} - E^{w=0}\big), \tag{20}$$

where $E^{w=0} = E_0$ is the exact ground-state energy.

B. Weight-independent density-functional approximation

Let us stress that Eqs. (19) and (20) are equivalent if exact functionals and wave functions are used, which is of course not the case in practical calculations [21]. In the standard weight-independent density-functional approximation (WIDFA) [8,21,23], the ensemble energy in Eq. (16) and the auxiliary wave functions in Eq. (17) are calculated by substituting the short-range ensemble functional with the (weight-independent) ground-state one, $E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n] = E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,w=0}[n]$, thus leading to the approximate WIDFA variational ensemble energy,

$$\begin{aligned}\tilde{E}^{\mu,w} &= \min_{\hat{\gamma}^{w}}\left\{\mathrm{Tr}\big[\hat{\gamma}^{w}(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}})\big] + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\hat{\gamma}^{w}}]\right\} \\ &= \mathrm{Tr}[\hat{\gamma}^{\mu,w}(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}})] + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\hat{\gamma}^{\mu,w}}],\end{aligned} \tag{21}$$

to the corresponding WIDFA ensemble density matrix,

$$\hat{\gamma}^{\mu,w} = (1-w)|\tilde{\Psi}_0^{\mu,w}\rangle\langle\tilde{\Psi}_0^{\mu,w}| + w|\tilde{\Psi}_1^{\mu,w}\rangle\langle\tilde{\Psi}_1^{\mu,w}|, \tag{22}$$

and, according to Eqs. (19) and (20), to the weight- and μ-dependent excitation energy expression,

$$\omega \to \Delta\tilde{\mathcal{E}}^{\mu,w} = \tilde{\mathcal{E}}_1^{\mu,w} - \tilde{\mathcal{E}}_0^{\mu,w}, \tag{23}$$

or, alternatively, to

$$\omega \to \tilde{\omega}_{\mathrm{LIM}}^{\mu} = 2\big(\tilde{E}^{\mu,w=1/2} - \tilde{E}^{\mu,w=0}\big). \tag{24}$$

The latter expression is, by construction, weight independent. It depends only on the μ parameter. Note that the ground-state energy $\tilde{E}^{\mu,w=0}$ will be μ dependent in practice since approximate ground-state functionals are used. Let us emphasize that Eq. (24) can be extended to higher excitations and degenerate states through linear interpolations between equiensembles [21], thus leading to the expression for the Ith excitation energy

$$\tilde{\omega}_{\mathrm{LIM},I}^{\mu} = \frac{M_I}{g_I}\big(\tilde{E}_I^{\mu,1/M_I} - \tilde{E}_{I-1}^{\mu,1/M_{I-1}}\big) + \frac{1}{M_{I-1}}\sum_{k=1}^{I-1} g_k\tilde{\omega}_{\mathrm{LIM},k}^{\mu}, \tag{25}$$

where g_k is the degeneracy of the kth energy level, $M_I = \sum_{k=0}^{I} g_k$ is the total number of states in the targeted equiensemble (the one that enables reaching the Ith energy), and $\tilde{E}_I^{\mu,1/M_I}$ is the corresponding WIDFA equiensemble energy (with weight $1/M_I$). Note that each equiensemble is made of multiplets. In other words, all degenerate states should be included.

In the formulation of range-separated eDFT by Pastorczak *et al.* [8], the WIDFA is also used but excitation energies are computed differently. A single ensemble containing all states of interest is calculated (from Eq. (17) with the substitution $E_{\mathrm{Hxc}}^{\mathrm{sr},\mu,\mathbf{w}}[n] \to E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n]$) and individual state energies are pragmatically introduced as follows:

$$\tilde{E}_k^{\mu,\mathbf{w}} = \langle\tilde{\Psi}_k^{\mu,\mathbf{w}}|\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{ne}}|\tilde{\Psi}_k^{\mu,\mathbf{w}}\rangle + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\tilde{\Psi}_k^{\mu,\mathbf{w}}}]. \tag{26}$$

As discussed in Ref. [21], the latter expression is questionable, especially because it uses individual state densities (rather than the ensemble density) in conjunction with the ground-state short-range functional. Let us stress that, in contrast to the LIM, even if exact functionals and wave functions were used, the energies in Eq. (26) would *not*, in principle, be exact. This statement holds for any finite μ value. A simple argument is that, for the ground-state energy, the long-range interacting wave function $\tilde{\Psi}_0^{\mu,\mathbf{w}}$ will not have its density equal to the exact ground-state density of the physical system. The former density will contribute to a long-range interacting ensemble density that is equal to the exact ensemble density of the physical system. Another practical issue that arises when approximations are made is that the state energies in Eq. (26) and, consequently, the excitation energies depend on both the range-separation parameter μ and the ensemble weights $\mathbf{w}$. As Boltzmann weights are used in the scheme of Pastorczak *et al.* [8], they are all controlled by an effective inverse temperature β, which is a tunable parameter in the theory. In this respect, the LIM has the advantage of providing excitation energies that are, by construction, weight independent.

C. Ghost interaction and alternative range-separated ensemble energy expression

Let us return to the two-state ensemble problem. Although the combination of the LIM and WIDFA gave promising results [21,23], the use of local or semilocal ground-state short-range xc functionals inevitably introduces a so-called ghost-interaction error [22] in the equiensemble energy $\tilde{E}^{\mu,w=1/2}$ and, consequently, in the LIM excitation energy [see Eqs. (21) and (24)]. This error arises when inserting the WIDFA ensemble density

$$n_{\hat{\gamma}^{\mu,w}}(\mathbf{r}) = (1-w)n_{\tilde{\Psi}_0^{\mu,w}}(\mathbf{r}) + w\, n_{\tilde{\Psi}_1^{\mu,w}}(\mathbf{r}) \tag{27}$$

into the short-range Hartree term [see Eqs. (14) and (15)]:

$$\begin{aligned} E_{\mathrm{H}}^{\mathrm{sr},\mu}[n_{\hat{\gamma}^{\mu,w}}] &= (1-w)^2 E_{\mathrm{H}}^{\mathrm{sr},\mu}[n_{\tilde{\Psi}_0^{\mu,w}}] + w^2 E_{\mathrm{H}}^{\mathrm{sr},\mu}[n_{\tilde{\Psi}_1^{\mu,w}}] \\ &\quad + w(1-w)\iint d\mathbf{r}d\mathbf{r}' n_{\tilde{\Psi}_0^{\mu,w}}(\mathbf{r}) n_{\tilde{\Psi}_1^{\mu,w}}(\mathbf{r}') \\ &\quad \times \frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}. \end{aligned} \tag{28}$$

As readily seen in Eq. (28), the last term on the right-hand side describes an unphysical ghost interaction between the ground and the first excited states through the product of their densities. This error does not show up in the approach of Pastorczak *et al.* [8,16] since, as shown in Eq. (26), individual state densities are inserted into the short-range density functional. As discussed previously, even though it is convenient, the definition of individual state energies in the context of eDFT is a pragmatic choice. In this work, we intend to remove ghost-interaction errors in the LIM excitation energies by applying a correction scheme to the WIDFA ensemble energy rather than by constructing individual state energies. For that purpose, we consider the following decomposition of the exact short-range ensemble xc energy [23]:

$$E_{\mathrm{xc}}^{\mathrm{sr},\mu,w}[n] = E_{\mathrm{x,md}}^{\mathrm{sr},\mu,w}[n] + E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n], \tag{29}$$

where

$$E_{\mathrm{x,md}}^{\mathrm{sr},\mu,w}[n] = \mathrm{Tr}\big[\hat{\Gamma}^{\mu,w}[n]\hat{W}_{\mathrm{ee}}^{\mathrm{sr},\mu}\big] - E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] \tag{30}$$

is the analog of the multideterminantal (md) short-range exchange functional of Toulouse *et al.* [31] for ensembles and $E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n]$ is the complementary short-range ensemble correlation functional. Note that $\hat{\Gamma}^{\mu,w}[n]$ is defined in Eq. (13) and corresponds to the long-range interacting ensemble density matrix with density $n(\mathbf{r})$. Since, according to Eq. (17) (here we consider the particular case of $M=2$ states) and the Hohenberg-Kohn theorem for ensembles [6],

$$\hat{\Gamma}^{\mu,w}[n_{\hat{\Gamma}^{\mu,w}}] = \hat{\Gamma}^{\mu,w}, \tag{31}$$

combining Eqs. (29) and (30) with Eqs. (11), (14), and (16) leads to an exact alternative expression for the range-separated ensemble energy,

$$E^{w} = \mathrm{Tr}[\hat{\Gamma}^{\mu,w}\hat{H}] + E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n_{\hat{\Gamma}^{\mu,w}}], \tag{32}$$

where $\hat{H} = \hat{H}[v_{\mathrm{ne}}]$ is the true physical Hamiltonian. Note that, even though the true Hamiltonian (without range separation) is used, the energy is obtained from a long-range interacting ensemble density matrix. Therefore, short-range correlation effects are missing in the first term on the right-hand side of Eq. (32). These effects are described by the complementary ensemble multideterminantal short-range correlation functional. As readily seen, this alternative energy expression is free of ghost-interaction errors since only short-range correlation effects are now described with a density functional. Of course, the use of an approximate correlation functional in this context may introduce residual ghost-correlation errors but the numerical results discussed in Sec. IV seem to indicate that the latter are not too significant, at least in the simple two- and four-electron systems considered in this work. Note that, when $\mu = 0$, the ensemble energy expression in Eq. (32) becomes similar to the linear exact exchange expression of Gould and Dobson for grand canonical ensembles (see Eq. (5) in Ref. [32]). In order to implement Eq. (32) for any μ values, we need approximate complementary short-range ensemble correlation functionals. So far, only a ground-state local density approximation (LDA) has been developed [33]. A simple approximation, that is used in Sec. IV, consists in using the ground-state functional,

$$E_{\mathrm{c,md}}^{\mathrm{sr},\mu}[n] = E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w=0}[n], \tag{33}$$

in complete analogy with the WIDFA. In order to get further insight into what would actually be neglected with such an approximation and thus pave the way to the construction of adapted weight-dependent short-range correlation functionals, let us decompose the exact functional as

$$E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n] = E_{\mathrm{c,md}}^{\mathrm{sr},\mu}[n] + \Delta E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n], \tag{34}$$

where the weight dependence has been moved to the contribution $\Delta E_{\mathrm{c,md}}^{\mathrm{sr},\mu,w}[n]$, for which an adiabatic connection (AC) formula can be derived. For that purpose, we consider the following AC path based on the generalized AC formalism for ensembles [9] and the range-separated AC of Rebolini *et al.* [34]:

$$\begin{aligned} &\big(\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \lambda\hat{W}_{\mathrm{ee}}^{\mathrm{sr},\mu} + \hat{V}^{\mu,\lambda,\xi}\big)\big|\Psi_k^{\mu,\lambda,\xi}\big\rangle \\ &\quad = \mathcal{E}_k^{\mu,\lambda,\xi}\big|\Psi_k^{\mu,\lambda,\xi}\big\rangle, \quad k=0,1, \end{aligned} \tag{35}$$

where the local potential $\hat{V}^{\mu,\lambda,\xi} = \int d\mathbf{r}\, v^{\mu,\lambda,\xi}(\mathbf{r})\,\hat{n}(\mathbf{r})$ ensures that the density constraint,

$$\mathrm{Tr}\big[\hat{\Gamma}^{\mu,\lambda,\xi}[n]\hat{n}(\mathbf{r})\big] = n(\mathbf{r}), \tag{36}$$

with

$$\hat{\Gamma}^{\mu,\lambda,\xi}[n] = (1-\xi)|\Psi_0^{\mu,\lambda,\xi}\rangle\langle\Psi_0^{\mu,\lambda,\xi}| + \xi|\Psi_1^{\mu,\lambda,\xi}\rangle\langle\Psi_1^{\mu,\lambda,\xi}|, \tag{37}$$

is fulfilled not only for all interaction strengths in the range $0 \leqslant \lambda \leqslant 1$ but also for all ensemble weights in the range $0 \leqslant \xi \leqslant w$. The constraint is strong and it could potentially lead to representability problems. Let us mention that in recent work on the Hubbard dimer (which will be presented in a separate paper), we have shown that such an AC can be constructed. In particular, it appears that if a density is ensemble representable for a given weight w, then it is ensemble representable for any weight ξ with $0 \leqslant \xi \leqslant w$. This is a promising result whose extension to the exact Hamiltonian should be investigated. Work is currently in progress in that direction.

Note that the multideterminantal decomposition of the ensemble short-range xc energy in Eq. (29) relies on a fictitious long-range interacting system instead of the usual noninteracting KS one. Therefore, in order to recover the former system at $\lambda = 0$, and thus obtain an AC formula for the complementary ensemble short-range correlation energy, the short-range interaction only is scaled by λ in Eq. (35). Therefore, the ensemble density matrix $\hat{\Gamma}^{\mu,\lambda,\xi}[n]$ reduces to $\hat{\Gamma}^{\mu,\xi}[n]$ when $\lambda = 0$. Note that, for $\lambda = 1$, the physical (fully interacting) system is recovered ($\hat{\Gamma}^{\mu,\lambda=1,\xi}[n] = \hat{\Gamma}^{\xi}[n]$), as in a conventional AC. According to Eqs. (4), (12), (13), and (14), the short-range ensemble xc energy can be expressed as

$$E_{\rm xc}^{{\rm sr},\mu,w}[n] = \int_0^1 d\lambda \frac{dF^{\mu,\lambda,w}[n]}{d\lambda} - E_{\rm H}^{{\rm sr},\mu}[n], \tag{38}$$

where

$$F^{\mu,\lambda,w}[n] = {\rm Tr}\big[\hat{\Gamma}^{\mu,\lambda,w}[n](\hat{T} + \hat{W}_{\rm ee}^{{\rm lr},\mu} + \lambda \hat{W}_{\rm ee}^{{\rm sr},\mu})\big]. \tag{39}$$

Using the Hellmann-Feynman theorem in Eq. (38) with the density constraint in Eq. (36) as well as Eqs. (29) and (30) leads to

$$E_{\rm c,md}^{{\rm sr},\mu,w}[n] = \int_0^1 d\lambda\, {\rm Tr}\big[\hat{\Gamma}^{\mu,\lambda,w}[n]\hat{W}_{\rm ee}^{{\rm sr},\mu}\big] - {\rm Tr}\big[\hat{\Gamma}^{\mu,w}[n]\hat{W}_{\rm ee}^{{\rm sr},\mu}\big]. \tag{40}$$

Finally, from the expression

$$E_{\rm c,md}^{{\rm sr},\mu,w}[n] = E_{\rm c,md}^{{\rm sr},\mu,w=0}[n] + \int_0^w d\xi \frac{\partial E_{\rm c,md}^{{\rm sr},\mu,\xi}[n]}{\partial \xi}, \tag{41}$$

we obtain the decomposition in Eq. (34) with the following explicit AC formula for the weight-dependent part:

$$\Delta E_{\rm c,md}^{{\rm sr},\mu,w}[n] = \int_0^1 d\lambda \int_0^w d\xi\, {\rm Tr}\left[\left(\frac{\partial \hat{\Gamma}^{\mu,\lambda,\xi}[n]}{\partial \xi} - \frac{\partial \hat{\Gamma}^{\mu,\xi}[n]}{\partial \xi}\right)\hat{W}_{\rm ee}^{{\rm sr},\mu}\right]. \tag{42}$$

Returning to the energy expression in Eq. (32), we should stress that, unlike the expression in Eq. (16), it is *not* variational with respect to the ensemble density matrix. Ignoring this leads to double-counting problems [35], since the minimizing density matrix will be obtained from a fully interacting Hamiltonian rather than a long-range interacting one (as it should). Nevertheless, the ensemble energy in Eq. (32) is variational with respect to local potentials. In other words, it can be obtained by means of optimized effective potentials [31] as

$$E^w = \min_v \big\{{\rm Tr}[\hat{\Gamma}^{\mu,w}[v]\hat{H}] + E_{\rm c,md}^{{\rm sr},\mu,w}[n_{\hat{\Gamma}^{\mu,w}[v]}]\big\}, \tag{43}$$

where

$$\hat{\Gamma}^{\mu,w}[v] = \arg\min_{\hat{\gamma}^w}\left\{{\rm Tr}\big[\hat{\gamma}^w(\hat{T} + \hat{W}_{\rm ee}^{{\rm lr},\mu})\big] + \int d\mathbf{r}\, v(\mathbf{r}) n_{\hat{\gamma}^w}(\mathbf{r})\right\}. \tag{44}$$

So far, such a scheme has been implemented efficiently only for approximate single-determinantal ground-state wave functions but it can, in principle, be extended to multiconfigurational wave functions [35]. For practical purposes, we propose in the following a much simpler approach where a density-functional potential (the one computed at the WIDFA level) is used rather than an optimized effective potential. In this respect, the scheme of Pastorczak *et al.* [8,16] and the ghost-interaction correction proposed in the following section are similar. Both rely on long-range interacting ensemble density matrices that are computed similarly from a short-range Hxc density-functional potential that actually contains ghost-interaction errors (because of the short-range Hartree potential). Optimized effective potentials would have the advantage of removing such errors. This is left for future work.

Finally, returning to the exact theory and the calculation of the excitation energy, combining Eq. (19) with Eq. (32) leads to

$$\omega = \frac{dE^w}{dw} = \langle \Psi_1^{\mu,w}|\hat{H}|\Psi_1^{\mu,w}\rangle - \langle \Psi_0^{\mu,w}|\hat{H}|\Psi_0^{\mu,w}\rangle + \frac{dE_{\rm c,md}^{{\rm sr},\mu,w}[n_{\hat{\Gamma}^{\mu,w}}]}{dw} + 2w\left\langle \frac{\partial \Psi_1^{\mu,w}}{\partial w}\middle|\hat{H}\middle|\Psi_1^{\mu,w}\right\rangle + 2(1-w)\left\langle \frac{\partial \Psi_0^{\mu,w}}{\partial w}\middle|\hat{H}\middle|\Psi_0^{\mu,w}\right\rangle. \tag{45}$$

Note that the Hellmann-Feynman theorem does not hold because of the nonvariational character (with respect to the ensemble density matrix) of the ensemble energy expression in Eq. (32). As a result, the responses of both ground- and excited-state wave functions to variations in the ensemble weight are, in principle, needed.

D. Ghost-interaction correction and extrapolation schemes

In order to perform practical excitation energy calculations from Eq. (45), we consider the following approximations: (i) The long-range interacting density matrix is calculated at the WIDFA level [see Eq. (21)], for example, within the short-range LDA [28,36]. (ii) We then use, as an additional approximation and by analogy with the WIDFA, the (weight-independent) *ground-state* functional $E_{\rm c,md}^{{\rm sr},\mu}[n]$. So far, only an LDA-type functional has been developed by Paziani *et al.* [33]. If, in addition, (iii) we neglect the response of both the ensemble density and the individual wave functions to variations in w, then approximation (ii) has no impact on the excitation energy, which reduces to a first-order corrected (FOC) expression [34]:

$$\omega \rightarrow \tilde{\omega}_{\rm FOC}^{\mu,w} = \langle \tilde{\Psi}_1^{\mu,w}|\hat{H}|\tilde{\Psi}_1^{\mu,w}\rangle - \langle \tilde{\Psi}_0^{\mu,w}|\hat{H}|\tilde{\Psi}_0^{\mu,w}\rangle. \tag{46}$$

Note that the latter expression becomes exact only in the $\mu \rightarrow +\infty$ limit and it converges as μ^{-4} [34,37].

In order to preserve the ghost-interaction-free character of the FOC excitation energy while taking into account the missing short-range correlation effects, it is in fact simpler to apply the LIM. This is actually relevant since, even if approximate functionals are used, the first term on the right-hand side of Eq. (32) will always be linear in w. Combining LIM with the latter equation within approximations (i) and (ii) leads to the following ghost-interaction-corrected (GIC) ensemble energy expression,

$$E^w \rightarrow \tilde{E}_{\rm GIC}^{\mu,w} = {\rm Tr}\big[\hat{\gamma}^{\mu,w}\hat{H}\big] + E_{\rm c,md}^{{\rm sr},\mu}[n_{\hat{\gamma}^{\mu,w}}], \tag{47}$$

and to the corresponding GIC-LIM excitation energy,

$$\omega \rightarrow \tilde{\omega}_{\rm GIC-LIM}^{\mu} = 2\big(\tilde{E}_{\rm GIC}^{\mu,w=1/2} - \tilde{E}_{\rm GIC}^{\mu,w=0}\big). \tag{48}$$

Note that the LIM [see Eqs. (21) and (24)] and GIC-LIM excitation energies are calculated with the *same* (WIDFA) ensemble density matrix $\hat{\gamma}^{\mu,w}$. GIC-LIM reduces to pure wavefunction theory when $\mu \to +\infty$. In the $\mu = 0$ limit, the ensemble energy in Eq. (47) will be simply written as an ensemble HF energy (calculated with the KS-eDFT orbitals) complemented by the standard (full-range) density-functional correlation energy. In conventional ground-state DFT, the combination of 100% of HF exchange with local or semilocal correlation functionals does not work well. As discussed in Ref. [38], the situation is different in the context of ground-state range-separated DFT. Regarding excited states, in the light of the numerical results in Sec. IV, the use of 100% of the HF exchange actually improves the accuracy of excitation energies in practical KS-eDFT calculations. This should obviously be investigated further in more atomic and molecular systems.

Following Savin [37], we, finally, propose to improve the GIC-LIM further by means of extrapolation techniques. While the LIM excitation energy varies as μ^{-2} when $\mu \to +\infty$ [23], the GIC-LIM one will vary as μ^{-3} [31], thus leading to the extrapolated LIM (ELIM) [23] and extrapolated GIC-LIM (EGIC-LIM) excitation energy expressions:

$$\tilde{\omega}^{\mu}_{\rm ELIM} = \tilde{\omega}^{\mu}_{\rm LIM} + \frac{\mu}{2}\frac{\partial \tilde{\omega}^{\mu}_{\rm LIM}}{\partial \mu},$$

$$\tilde{\omega}^{\mu}_{\rm EGIC-LIM} = \tilde{\omega}^{\mu}_{\rm GIC-LIM} + \frac{\mu}{3}\frac{\partial \tilde{\omega}^{\mu}_{\rm GIC-LIM}}{\partial \mu}. \qquad (49)$$

Note that the GIC-LIM and EGIC-LIM schemes can be extended to higher excitations straightforwardly by using Eq. (25) in conjunction with the GIC equiensemble energies.

III. COMPUTATIONAL DETAILS

All the calculations have been performed with a development version of the DALTON program package [39,40] on a small test set of atoms and molecules consisting of He, Be, H_2 ($R = 1.4a_0, 3.7a_0$), and HeH^+ ($R = 8.0a_0$). The following two-state singlet ensembles in a given space symmetry have been considered: $\{1^1S, 2^1S\}$ for He and Be, $\{1^1\Sigma^+, 2^1\Sigma^+\}$ for the stretched HeH^+ molecule, and $\{1^1\Sigma_g^+, 2^1\Sigma_g^+\}$ for H_2. Note that the $1^1\Sigma^+ \to 2^1\Sigma^+$ excitation in the stretched HeH^+ molecule is a charge transfer excitation, while the $1^1\Sigma_g^+ \to 2^1\Sigma_g^+$ excitation in the stretched H_2 molecule is a double excitation. In order to illustrate the extension of the GIC-LIM and EGIC-LIM to higher excitations, the four-state ensemble $\{1^1S, 2^1S, 1^1D\}$ in A_g symmetry has been considered in Be. The excitation $1^1S \to 1^1D$ is a double excitation. In this case, the ground 1^1S and first excited 2^1S states are not degenerate ($g_0 = 1$ and $g_1 = 1$), while the second excited state, 1^1D in A_g symmetry, is degenerate twice ($g_2 = 2$), thus leading to the following expression for the $1^1S \to 1^1D$ LIM excitation energy, according to Eq. (25):

$$\tilde{\omega}^{\mu}_{{\rm LIM},2} = 2\big(\tilde{E}_2^{\mu,1/4} - \tilde{E}_1^{\mu,1/2}\big) + \tfrac{1}{2}\tilde{\omega}^{\mu}_{{\rm LIM},1}, \qquad (50)$$

where $\tilde{\omega}^{\mu}_{{\rm LIM},1} = 2(\tilde{E}_1^{\mu,1/2} - \tilde{E}_0^{\mu,1})$ corresponds to the $1^1S \to 2^1S$ excitation energy. Wave functions have been computed at the full configuration interaction (FCI) level in one-electron basis sets of augmented quadruple-ζ quality (aug-cc-pVQZ) [41,42]. Therefore, range-separated eDFT excitation energies will all converge towards FCI values when increasing μ. Long-range interacting ensemble density matrices have been computed self-consistently at the WIDFA level with the short-range LDA xc potential of Savin and coworkers [28,36]. The corresponding xc functional was used to compute LIM excitation energies. Finally, the ground-state multideterminantal short-range correlation functional of Paziani *et al.* [33] was used for computing GIC-LIM excitation energies. Let us stress once more that both the LIM and the GIC-LIM use exactly the same long-range interacting ensemble density matrix, i.e., the one optimized at the WIDFA level [see Eq. (21)].

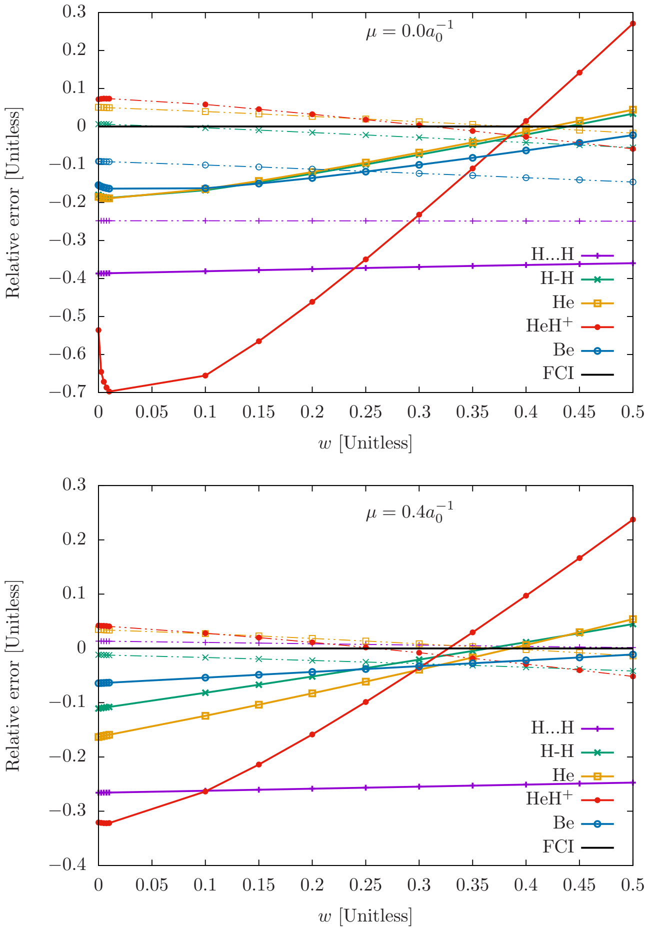

FIG. 1. Relative error with respect to the FCI obtained for the auxiliary (solid lines) and FOC (dash-dotted lines) excitation energies with $\mu = 0$ (top) and $\mu = 0.4a_0^{-1}$ (bottom). The stretched H_2 molecule is represented as H . . . H. Relative errors are calculated as $\frac{\tilde{\omega}-\omega_{\rm FCI}}{\omega_{\rm FCI}}$, where $\tilde{\omega}$ is the approximate excitation energy.

IV. RESULTS AND DISCUSSION

In Fig. 1, we have analyzed the weight dependence of the WIDFA auxiliary excitation energies [see Eq. (23)] and the FOC excitation energies [see Eq. (46)] for $\mu = 0$ (KS-eDFT) and the usual $\mu = 0.4a_0^{-1}$ values [21,23]. Although short-range correlation effects are neglected in FOC energies, following this approximation improves the accuracy of the

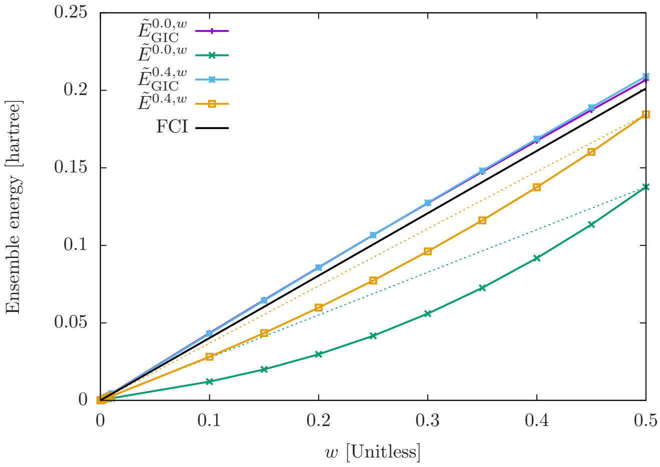

FIG. 2. Weight dependence of the WIDFA and GIC ensemble energies in HeH^+ for $\mu = 0$ and $\mu = 0.4a_0^{-1}$. The FCI and LIM (dashed lines) are also shown. Energies are shifted by their values at $w = 0$ for ease of comparison.

excitation energy and reduces its weight dependence significantly in comparison to the WIDFA auxiliary excitation energy.

As illustrated in Fig. 2 for the charge transfer excitation $1^1\Sigma^+ \rightarrow 2^1\Sigma^+$ in the stretched HeH^+ molecule, the WIDFA ensemble energy can exhibit a significant curvature in the ensemble weight. This is known [21] and actually expected from the expression of the ensemble short-range Hartree energy in Eq. (28). As expected from Eq. (32), the curvature is essentially removed in the GIC scheme, even in the KS-eDFT limit ($\mu = 0$). In this respect, combining the GIC with the LIM is well justified. Let us stress that it is also much simpler than the calculation of excitation energies through the evaluation of ensemble energy derivatives [see Eq. (45)]. We also note that the slope of the GIC ensemble energy is closer to FCI and less μ dependent.

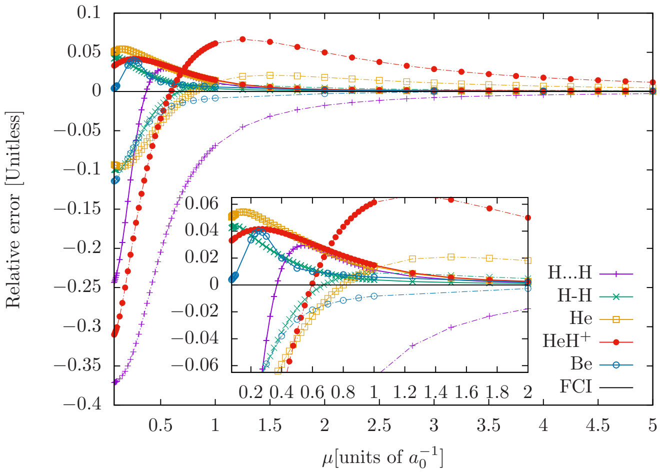

FIG. 3. Relative error with respect to the FCI obtained for the LIM (dash-dotted lines) and GIC-LIM (solid lines) excitation energies when varying μ. Inset: Zoom-in on the range $0 \leqslant \mu \leqslant 2.0a_0^{-1}$. Excitations in the stretched HeH^+ $(1^1\Sigma^+ \rightarrow 2^1\Sigma^+)$ and H ... H $(1^1\Sigma_g^+ \rightarrow 2^1\Sigma_g^+)$ molecules correspond to a charge transfer and a double excitation, respectively.

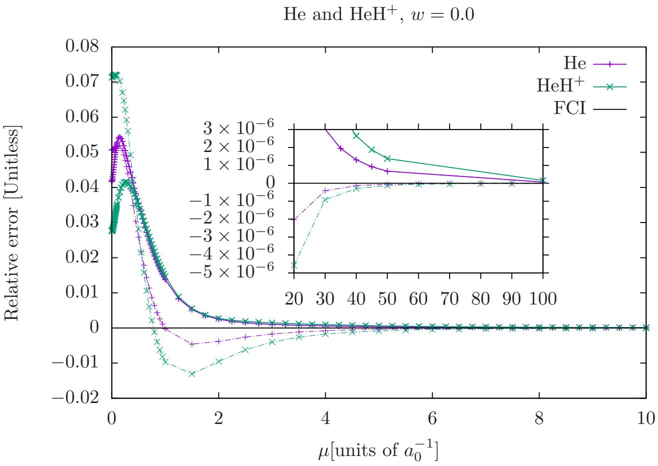

FIG. 4. Relative error with respect to the FCI obtained for the GIC-LIM (solid lines) and FOC [$w = 0$] (dash-dotted lines) excitation energies in He and the stretched HeH^+ molecule. Inset: The convergence towards FCI when $\mu \rightarrow +\infty$.

As shown in Fig. 3, the GIC-LIM outperforms the LIM and converges much more rapidly towards the FCI with increasing μ, as expected. The improvement is substantial for both charge transfer and double excitations in the stretched HeH^+ and H_2 molecules, respectively. It is also remarkable that, in the KS-eDFT limit ($\mu = 0$), the GIC-LIM gives relatively accurate excitation energies also for the charge transfer excitation, despite the fact that 100% of the HF exchange is combined with an LDA correlation functional. The double excitation in H ... H is captured but the excitation energy is still underestimated. In addition, as shown in Figs. 4 and 5 for $w = 0$ and $w = 0.5$, respectively, even though at very large μ values the FOC excitation energy converges more rapidly than the GIC-LIM towards the FCI, it does not

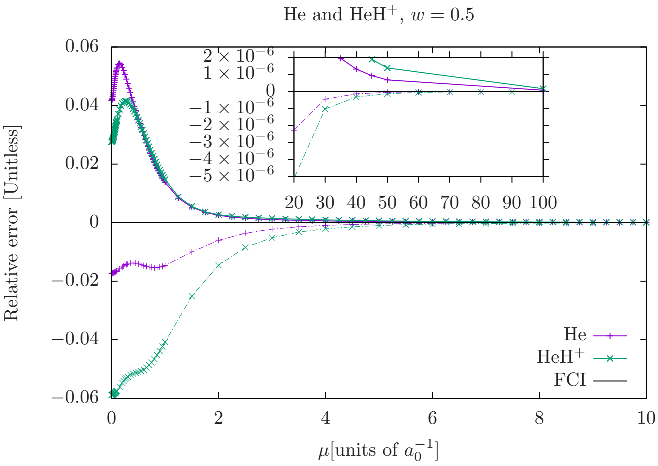

FIG. 5. Relative error with respect to the FCI obtained for the GIC-LIM (solid lines) and FOC [$w = 0.5$] (dash-dotted lines) excitation energies in He and the stretched HeH^+ molecule. Inset: The convergence towards FCI when $\mu \rightarrow +\infty$.

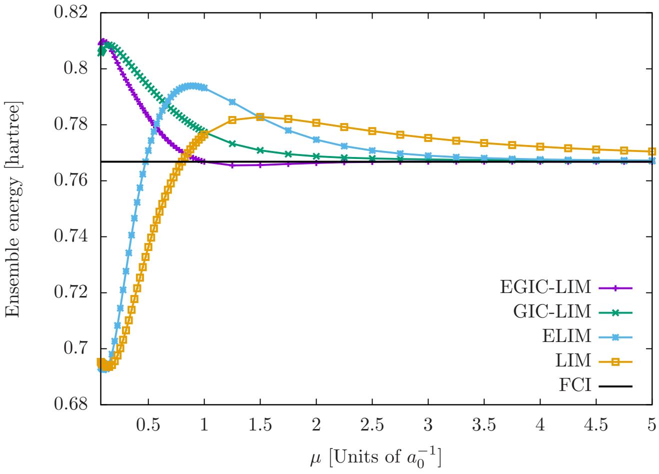

FIG. 6. LIM and GIC-LIM $1^1S \rightarrow 2^1S$ excitation energies obtained in He with and without extrapolation corrections when varying μ. Comparison is made with the FCI. See text for further details.

necessarily perform better than the GIC-LIM in the range of standard values $0.4a_0^{-1} \leqslant \mu \leqslant 1.0a_0^{-1}$ [8,21], which is due to the lack of short-range correlation effects.

Finally, the effect of extrapolation on the GIC-LIM excitation energy is shown for He in Fig. 6. When μ is increased from $0.2a_0^{-1}$, the EGIC-LIM converges monotonically towards the FCI very rapidly, in contrast to GIC-LIM and even ELIM. Convergence is almost reached at the standard $\mu = 1.0a_0^{-1}$ value [8]. This means that accurate ghost-interaction-free excitation energies can, in principle, be obtained with a relatively small μ value, which is highly desirable. Indeed, if μ is not too large, ground- and excited-state long-range interacting wave functions are expected to have a rather compact configuration expansion. Convergence with respect to the atomic basis set will also be faster [43]. In order to illustrate the extension of the (E)GIC-LIM to higher excitations, we consider the double excitation $1^1S \rightarrow 1^1D$ in Be. Results are shown in Fig. 7. We see that the convergence towards the FCI of the EGIC-LIM is slightly slower for the double excitation than for the single $1^1S \rightarrow 2^1S$ excitation. Nevertheless, results are still accurate for both excitations in the range of standard values $0.4a_0^{-1} \leqslant \mu \leqslant 1.0a_0^{-1}$.

V. CONCLUSIONS

A rigorous ghost-interaction correction scheme has been proposed in the context of range-separated ensemble density-functional theory. It is based on an exact decomposition of the short-range ensemble exchange-correlation energy into a multideterminantal exact exchange contribution and a complementary density-functional correlation energy for which an adiabatic connection formula has been derived. In order to perform practical calculations, the latter correlation functional has been simply modeled by its ground-state LDA, while the long-range interacting ensemble density matrix is obtained self-consistently by combining a long-range configuration-interaction calculation with a short-range LDA potential. Excitation energies can then be computed from the GIC ensemble energies by means of a linear interpolation method, with, in addition, an extrapolation correction. Results have been shown for He, Be, and small molecular systems (H_2 and HeH^+). While providing approximate ensemble energies that are essentially linear in the ensemble weight, the GIC scheme gives a significant improvement in the accuracy of excitation energies. In particular, the charge-transfer excitation $1^1\Sigma^+ \rightarrow 2^1\Sigma^+$ in the stretched HeH^+ molecule as well as the double excitation $1^1S \rightarrow 1^1D$ in Be is well described for standard range-separation parameter values. Interestingly, relatively good results are also obtained when the latter parameter is set to 0, which corresponds to standard Kohn-Sham eDFT. In this case, the GIC ensemble energy reduces to an ensemble Hartree-Fock energy (calculated with the ensemble KS orbitals) complemented by a local density-functional correlation energy. Test calculations on larger systems should be performed in order to assess the reliability of the GIC approach, in particular, in fields like photochemistry where the use of ensembles and range separation is appealing. It would also be interesting to construct weight-dependent correlation functionals along the proposed generalized AC for ensembles and to remove from our current GIC scheme the residual ghost-correlation error. Work is currently in progress in these directions.

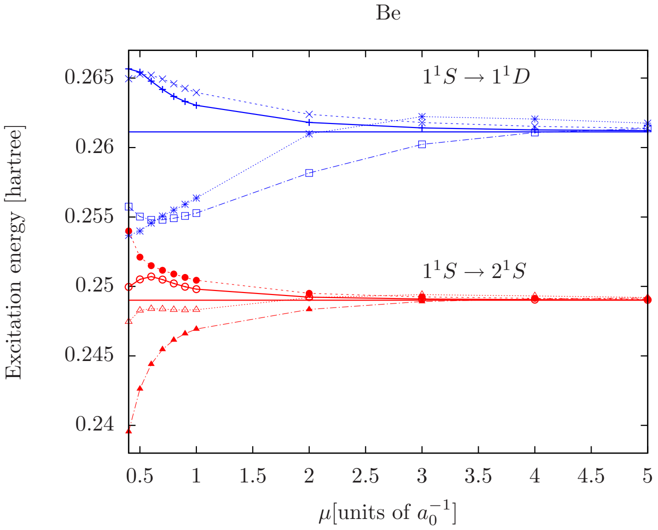

FIG. 7. Convergence towards the FCI (solid horizontal lines) of the LIM (dash-dotted lines with symbols), ELIM (dotted lines with symbols), GIC-LIM (dashed lines with symbols) and EGIC-LIM (solid lines with symbols) excitation energies obtained for the singly excited $1^1S \rightarrow 2^1S$ (bottom, red curves) and doubly-excited $1^1S \rightarrow 1^1D$ (top, blue curves) transitions in Be with increasing μ.

ACKNOWLEDGMENTS

M.M.A. acknowledges Bruno Senjean for fruitful discussions and help. The authors acknowledge financial support from the LABEX "Chemistry of Complex Systems" and the ANR (MCFUNEX project).

[1] M. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. **63**, 287 (2012).

[2] M. Marques and E. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).

[3] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, J. Chem. Phys. **120**, 5932 (2004).

[4] A. K. Theophilou, J. Phys. C: Solid State Phys. **12**, 5419 (1979).

[5] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988).

[6] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988).

[7] L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. A **37**, 2821 (1988).

[8] E. Pastorczak, N. I. Gidopoulos, and K. Pernal, Phys. Rev. A **87**, 062501 (2013).

[9] O. Franck and E. Fromager, Mol. Phys. **112**, 1684 (2014).

[10] A. Pribram-Jones, Z. H. Yang, J. R.Trail, K. Burke, R. J. Needs, and C. A. Ullrich, J. Chem. Phys. **140**, 18A541 (2014).

[11] Z. Yang, J. R. Trail, A. Pribram-Jones, K. Burke, R. J. Needs, and C. A. Ullrich, Phys. Rev. A **90**, 042501 (2014).

[12] A. Nikiforov, J. A. Gamez, W. Thiel, M. Huix-Rotllant, and M. Filatov, J. Chem. Phys. **141**, 124122 (2014).

[13] E. Pastorczak and K. Pernal, J. Chem. Phys. **140**, 18A514 (2014).

[14] M. Filatov, M. Huix-Rotllant, and I. Burghardt, J. Chem. Phys. **142**, 184104 (2015).

[15] M. Filatov, WIREs Comput. Mol. Sci. **5**, 146 (2015).

[16] E. Pastorczak and K. Pernal, Int. J. Quantum Chem. **116**, 880 (2016).

[17] Á. Nagy, J. Phys. B: At. Mol. Opt. Phys. **29**, 389 (1996).

[18] G. Paragi, I. Gyémánt, and V. V. Doren, Chem. Phys. Lett. **324**, 440 (2000).

[19] G. Paragi, I. Gyémánt, and V. V. Doren, J. Mol. Struct. (Theochem.) **571**, 153 (2001).

[20] K. Pernal, N. I. Gidopoulos, and E. Pastorczak, Adv. Quantum Chem. **73**, 199 (2015).

[21] B. Senjean, S. Knecht, H. J. Aa. Jensen, and E. Fromager, Phys. Rev. A **92**, 012518 (2015).

[22] N. I. Gidopoulos, P. G. Papaconstantinou, and E. K. U. Gross, Phys. Rev. Lett. **88**, 033003 (2002).

[23] B. Senjean, E. D. Hedegård, M. M. Alam, S. Knecht, and E. Fromager, Mol. Phys. **114**, 968 (2016).

[24] F. Tasnádi and Á. Nagy, J. Phys. B: At. Mol. Opt. Phys. **36**, 4073 (2003).

[25] E. H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).

[26] S. Kvaal, U. Ekström, A. M. Teale, and T. Helgaker, J. Chem. Phys. **140**, 18A518 (2014).

[27] H. Stoll and A. Savin, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[28] A. Savin, *Recent Developments and Applications of Modern Density Functional Theory* (Elsevier, Amsterdam, 1996), p. 327.

[29] A. Savin, Int. J. Quantum Chem. **34**, 59 (1988).

[30] M. Levy, Phys. Rev. A **52**, R4313 (1995).

[31] J. Toulouse, P. Gori-Giorgi, and A. Savin, Theor. Chem. Acc. **114**, 305 (2005).

[32] T. Gould and J. F. Dobson, J. Chem. Phys. **138**, 014103 (2013).

[33] S. Paziani, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. B **73**, 155111 (2006).

[34] E. Rebolini, J. Toulouse, A. M. Teale, T. Helgaker, and A. Savin, Mol. Phys. **113**, 1740 (2015).

[35] A. Stoyanova, A. M. Teale, J. Toulouse, T. Helgaker, and E. Fromager, J. Chem. Phys. **139**, 134113 (2013).

[36] J. Toulouse, A. Savin, and H. J. Flad, Int. J. Quantum Chem. **100**, 1047 (2004).

[37] A. Savin, J. Chem. Phys. **140**, 18A509 (2014).

[38] Y. Cornaton, A. Stoyanova, H. J. Aa. Jensen, and E. Fromager, Phys. Rev. A **88**, 022516 (2013).

[39] Dalton, *a Molecular Electronic Structure Program*, release dalton2015 (2015); http://daltonprogram.org/.

[40] K. Aidas *et al.*, WIREs Comput. Mol. Sci. **4**, 269 (2015).

[41] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).

[42] D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. **100**, 2975 (1994).

[43] O. Franck, B. Mussard, E. Luppi, and J. Toulouse, J. Chem. Phys. **142**, 074107 (2015).