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Ensemble density variational methods with self- and ghost-interaction-corrected functionals

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Ensemble density functional theory (DFT) offers a way of predicting excited-states energies of atomic and molecular systems without referring to a density response function. Despite a significant theoretical work, practical applications of the proposed approximations have been scarce and they do not allow for a fair judgement of the potential usefulness of ensemble DFT with available functionals. In the paper, we investigate two forms of ensemble density functionals formulated within ensemble DFT framework: the Gross, Oliveira, and Kohn (GOK) functional proposed by Gross *et al.* [Phys. Rev. A **37**, 2809 (1988)] alongside the orbital-dependent eDFT form of the functional introduced by Nagy [J. Phys. B **34**, 2363 (2001)] (the acronym eDFT proposed in analogy to eHF – ensemble Hartree-Fock method). Local and semi-local ground-state density functionals are employed in both approaches. Approximate ensemble density functionals contain not only spurious self-interaction but also the so-called ghost-interaction which has no counterpart in the ground-state DFT. We propose how to correct the GOK functional for both kinds of interactions in approximations that go beyond the exact-exchange functional. Numerical applications lead to a conclusion that functionals free of the ghost-interaction by construction, i.e., eDFT, yield much more reliable results than approximate self- and ghost-interaction-corrected GOK functional. Additionally, local density functional corrected for self-interaction employed in the eDFT framework yields excitations energies of the accuracy comparable to that of the uncorrected semi-local eDFT functional. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4866998]

I. INTRODUCTION

Density functional theory[1,2] (DFT) has been originally formulated as a ground-state formalism and many approximate density functionals for predicting ground-state energies of electronic systems have been proposed since then. Nowadays, DFT is often the method of choice to calculate electronic structure of atoms and molecules in their ground states. Parallel to the development of the ground-state DFT there has been an ongoing effort towards extending DFT to excited states. Since there is no unique way to follow, a few different strategies have been proposed. Some, like ΔSCF method[3,4] are applicable to lowest excited states of different symmetries, but others, including time-dependent DFT (TD-DFT),[5] constricted variational DFT,[6] or ensemble variational DFT,[7,8] allow one to obtain many excitation energies in one calculation. The most widely used DFT method for computing excitation energies – TD-DFT in the adiabatic approximation – relies on approximate ground-state functionals. Despite a continuous progress in improving accuracy of the adiabatic TD-DFT generic limitations of this approach result in large errors or in missing some excitations from spectra of atoms and molecules.[9]

The ensemble DFT formalism for excited states does not involve calculation of the linear response function and its poles like TD-DFT but it is based on minimization of the ensemble density functional.[7,8,10] So in this sense the formalism is closer to the ground-state DFT than to TD-DFT. In principle, the ensemble DFT approach is exact and capable of giving a proper description of all excited states independent of their character. As opposed to TD-DFT in the adiabatic approximation, even if approximate functionals are employed in the ensemble method, it should be possible to reproduce accurately excited states of varied characters, e.g., of both single and multiple character. This is due to the fact that multiconfigurational effects can be taken into account in the ensemble DFT by properly choosing states that enter the ensemble and by not restricting the states to be purely single determinantal. Some initial efforts in this direction have been recently presented in Refs. 11 and 12.

Substantial theoretical investigation of the ensemble DFT[7,8,10,13–19] has not been paralleled by its practical implementations and the amount of numerical examples is rather scarce. Initial attempts of computing excitation energies have been mainly limited to atoms and small molecules and they involved using either local and semi-local functionals,[20–27] or the exact-exchange functional.[15,28,29] Calculations have been carried out via the Kohn-Sham (KS) scheme and, in case of the exact exchange functional, optimal effective potential (OEP) methods have been developed.[15,28]

In the paper, we discuss ensemble density functional methods and apply them to predict ensemble energies and,

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in particular, excitation energies of atomic and molecular systems. We also address the issue of the self- and ghost-interaction corrections, we propose their general definitions in different functional approaches, and analyze their effect on the results. We show that functionals proposed in the ground-state DFT may still provide quite accurate excitation energies if they are employed in the proper ensemble framework.

II. CORRECTIONS TO APPROXIMATE ENSEMBLE FUNCTIONALS

Finite ensemble variational approach is founded on Rayleigh-Ritz variational principle. The ensemble variational principle states that if $\psi_1, \psi_2, \ldots, \psi_M$ are M orthonormal trial N-electron states and if $E_1^{(0)}, E_2^{(0)}, \ldots, E_M^{(0)}$ are M lowest eigenvalues of a Hamiltonian $\hat{H}$ in increasing order, whereas positive weights $\omega_I \geq 0$ are in decreasing order, then the following inequality holds:

$$\sum_{I=1}^{M} \omega_I \langle \psi_I | \hat{H} | \psi_I \rangle \geq \sum_{I=1}^{M} \omega_I E_I^{(0)}. \quad (1)$$

In the case of equal weights (Theophilou's variational principle[7]), the ensemble energy functional $E = \sum_{I=1}^{M} \langle \psi_I | \hat{H} | \psi_I \rangle$ reduces to the trace of the Hamiltonian in the M-dimensional space spanned by the orthonormal basis $\{\psi_I\}$. Since the trace is invariant under rotation of the basis vectors and depends only on the M-dimensional space, Theophilou[7] named the approach based on his theorem of the subspace method. The variational principle formulated by Gross, Oliveira, and Kohn (GOK) with the flexibility of different weights (for non-degenerate states) affords not only the energies of the first M states but also the corresponding wavefunctions.[30] Both Theophilou's[7] and the GOK variational principles have led to several formulations of the ensemble Hartree-Fock method. In one of them, trial states are given as Slater determinants $\{\Phi_I\}$ and the variational principle allows one to find approximate energies of ground and excited states if the ensemble Hartree-Fock (eHF) functional defined as

$$E^{eHF}[\{\varphi_i\}] = \sum_{I=1}^{M} \omega_I \left(\sum_{i=1} n_i^I h_{ii} + \frac{1}{2} \sum_{ij} n_i^I n_j^I \langle ij || ij \rangle \right) \quad (2)$$

is minimized with respect to orthonormal spinorbitals $\{\varphi_i\}$ that build M determinants. In Eq. (2), one-electron integrals $\{h_{ij}\}$ collect contributions from the kinetic and external potential energy operators, $\{\langle ij || ij \rangle\}$ are the antisymmetrized two-electron integrals in the representation of the spinorbitals $\{\varphi_i\}$, and n_i^I is the occupation number of the ith orbital in the Ith single determinantal state, i.e.,

$$n_i^I = \begin{cases} 1 & i \in I \\ 0 & i \notin I \end{cases}. \quad (3)$$

The ensemble variational principle, Eq. (1), has been used as a basis to formulate ensemble density functional theory, within which Hohenberg-Kohn theorem and Kohn-Sham method have been formulated for ensemble density $\rho(x)$[7,8]

$$\rho(x) = \sum_{I}^{M} \omega_I \rho_I(x), \quad (4)$$

where $\rho_I(x)$ represents a density of the interacting system in the Ψ_I state. Similar to the ground-state Kohn-Sham theorem, in its ensemble variant the interacting ensemble density is mapped onto an ensemble of noninteracting particles whose density can be written in the following form:

$$\rho(x) = \sum_{i} n_i \, |\varphi_i(x)|^2 , \quad (5)$$

where we have introduced ensemble occupation numbers for each spinorbital, i.e.,

$$n_i = \sum_{I=1}^{M} \omega_I \, n_i^I , \quad (6)$$

with the definition of n_i^I provided in Eq. (3). Ensemble occupation numbers $\{n_i\}$ sum up to a number of electrons in a system, N, namely,

$$\sum_i n_i = N. \quad (7)$$

Clearly, if a given spinorbital $\varphi_i(x)$ is included in each state in the ensemble, then its occupation number equals 1. Otherwise, the spinorbital is fractionally occupied in the ensemble, i.e., $0 < n_i < 1$. According to the Hohenberg-Kohn theorem for ensembles, the total energy of the interacting ensemble is a functional of an ensemble density and it has been proposed by Gross *et al.*[8] to partition the ensemble functional into components known from the ground-state theory, namely,

$$E^{GOK}[\rho] = T_s[\rho] + V_{ext}[\rho] + E_H[\rho] + E_{xc}[\rho], \quad (8)$$

where ρ is an interacting ensemble density, T_s denotes the kinetic energy functional of the noninteracting ensemble, the external potential energy is given by $V_{ext}[\rho]$, the Hartree functional E_H is defined in the same fashion as in the ground-state theory and after mapping onto a noninteracting system with a density given in Eq. (5) it reads

$$E_H[\rho] = \frac{1}{2} \sum_{ij} n_i n_j \langle ij | ij \rangle . \quad (9)$$

The last term in the GOK functional (8), $E_{xc}[\rho]$, is the ensemble exchange and correlation energy functional. Although a local ensemble density exchange-correlation functional has been derived for a uniform electron gas model at finite temperature[31] most applications presented so far employed either exchange-correlation functionals proposed for ground-state calculations or orbital-dependent Hartree-Fock exchange (exact exchange) that is given as

$$E_{xx}[\gamma] = -\frac{1}{2} \sum_{ij} n_i n_j \langle ij | ji \rangle , \quad (10)$$

where γ is a noninteracting ensemble-state one-electron density matrix

$$\gamma(x, x') = \sum_i n_i \, \varphi_i(x) \varphi_i(x')^*. \quad (11)$$

The ensemble functional (8) with the exchange-correlation functional approximated by the exact exchange given in Eq. (10) is orbital-dependent and if written explicitly in terms of the spinorbitals of a noninteracting system it reads

$$E^{GOK-HF}[\{\varphi_i\}] = \sum_i n_i h_{ii} + \frac{1}{2}\sum_{ij} n_i n_j \langle ij||ij\rangle\,, \quad (12)$$

where the ensemble weights $\{\omega_I\}$ are included in the occupation numbers $\{n_i\}$ defined in Eq. (6). Notice that the ensemble Hartree-Fock energy expression given in Eq. (2) differs from the functional (12) since the former is a weighted sum of energies of states in an ensemble, whereas the latter can be seen as a density matrix functional with fixed occupancies of orbitals. Both expressions, however, share an attractive property, namely, they are self-interaction (SI) free, i.e., spurious self-interactions of spinorbitals present in the Hartree part are exactly cancelled by diagonal terms in the exchange part. It has been recognized that spurious self-interaction may be responsible for yielding too large ensemble energies if local density functionals are employed.[20] Apart from self-interaction ensemble functionals can be plagued by another kind of spurious interaction that has no counterpart in the ground-state theory, namely, the so-called ghost-interaction (GI).[24,28,29] Ghost-interaction terms are unambiguously identified in case of a one-electron system. Consider then an ensemble of M states of a one-electron system whose ensemble density reads

$$\rho^{N=1}(x) = \sum_{i=1}^{M} \omega_i\, |\varphi_i(x)|^2\,. \quad (13)$$

All terms of the Hartree functional

$$E_H[\rho^{N=1}] = \frac{1}{2}\sum_{i=1}^{M} \omega_i^2\, \langle ii|ii\rangle + \frac{1}{2}\sum_{i\neq j}^{M} \omega_i\omega_j\, \langle ij|ij\rangle \quad (14)$$

should be cancelled in this case by the exchange-correlation functional in Eq. (8). The first term in Eq. (14) represents electron self-interaction, which vanishes if SI-free functional is used. However, the second term, attributed to ghost-interaction, is not cancelled unless the functional is not only SI-free but also corrected for GI. So, for example, even though the exchange-only functional E^{GOK-HF} given in Eq. (12) is self-interaction-free it contains spurious ghost-interaction terms. GI is sometimes considered to be a self-interaction between elements of ensemble,[24] which is another way of saying that GI results from self-interaction of an electron fractionally occupying different spinorbitals. Gidopoulos *et al.*[29] have proposed a GI correction to the exchange-only GOK functional, Eq. (12), if an ensemble consists of two states and it has been shown that removing GI leads to significant improvement in the ensemble energies of atoms. On the other hand, Nagy[32] has introduced a functional that is ghost-interaction free by definition

$$E^{eDFT}[\{\varphi_i\}] = \sum_{I=1}^{M} \omega_I \left(\sum_{i=1} n_i^I h_{ii} + \frac{1}{2}\sum_{ij} n_i^I n_j^I \langle ij|ij\rangle + E_{xc}[\rho_I] \right), \quad (15)$$

where ρ_I is a density of the Ith state of a noninteracting system, namely,

$$\rho_I(x) = \sum_i n_i^I\ |\varphi_i(x)|^2\,. \quad (16)$$

If the exchange-correlation functional of ρ_I is replaced by the exact-exchange functional, Eq. (10), of the pertinent density matrix γ_I

$$\gamma_I(x,x') = \sum_i n_i^I\ \varphi_i(x)\varphi_i(x')^*, \quad (17)$$

then the form of eDFT is equivalent to the ensemble HF energy given in Eq. (2). It should be emphasized, however, that despite similarities in their forms the two functionals are fundamentally different, since eHF originates from the wavefunction approach whereas eDFT is a realization of the ensemble density functional. Clearly, in general, the functional (15) does not depend explicitly on the ensemble density ρ [cf. Eqs. (5) and (6)] and its minimization via one-electron equations with a local KS potential requires employment of the OEP approach. The main advantage of eDFT over the GOK functional is that unlike the latter the former is free of the ghost-interaction. It is not, however, free of the self-interaction which has to be removed by adding a correcting term. The Perdew-Zunger SI correction[33] applied to the ensemble functional (15) leads to the following GI- and SI-free functional:[24]

$$E^{eDFT-SIC}[\{\varphi_i\}] = E^{eDFT}[\{\varphi_i\}] - \sum_i n_i \left(\frac{1}{2}\langle ii|ii\rangle + E_{xc}[\rho_i] \right), \quad (18)$$

where the ensemble occupation numbers are defined in Eq. (6) and the spinorbital density reads

$$\rho_i(x) = |\varphi_i(x)|^2\,. \quad (19)$$

Notice that for an ensemble of one-electron states, Eq. (13), the functional (18) yields

$$E^{eDFT-SIC}[\{\varphi_i\}] = \sum_{i=1}^{M} \omega_i h_{ii}, \quad (20)$$

therefore it is indeed self- and ghost-interaction free.

As it has been mentioned already the GOK functional, Eq. (8), may suffer from both ghost- and self-interaction errors if an approximate exchange-correlation functional is employed. Using exact-exchange functional allows for elimination of the self-interaction problem from the GOK method. To correct the exact-exchange GOK functional defined in Eq. (12) for the spurious ghost-interaction, Gidopoulos *et al.*[29] considered two-state ensembles and proposed a pertinent correction. We propose to generalize the correction to M-state ensembles and write the GI-corrected GOK-HF functional as follows:

$$E^{GOK-HF-GIC}[\{\varphi_i\}] = E^{GOK-HF}[\{\varphi_i\}] - \sum_{I>J}^{M}\sum_{i,j} \omega_I\omega_J\ n_i^I\left(1-n_i^J\right) n_j^J\left(1-n_j^I\right) \times \{\langle ij|ij\rangle + E_{xx}[\gamma_i+\gamma_j] - E_{xx}[\gamma_i] - E_{xx}[\gamma_j]\}, \quad (21)$$

where the exact exchange functional is defined in Eq. (10) and γ_i stands for a density matrix pertinent to a spinorbital φ_i, namely,

$$\gamma_i(x, x') = \varphi_i(x)\varphi_i(x')^*. \tag{22}$$

Pairwise Hartree and exchange interactions between (fractionally occupied, $n_i < 1$) spinorbitals belonging to different states of a noninteracting system are therefore removed. It can be immediately verified that, similar to the eDFT-SIC functional introduced in Eq. (18), the ghost-interaction-corrected GOK-HF functional properly reproduces the energy of an ensemble of one-electron states as a weighted sum of one-electron energies. One can generalize the ghost-interaction correction introduced in Eq. (21) to explicitly density-depending GOK functionals. In addition to GI, such functionals should also be corrected for the self-interaction. Using the Perdew-Zunger functional to account for the latter, we propose the following form of the ghost- and self-interaction-corrected GOK ensemble functional:

$$\begin{aligned} E^{GOK-SIC-GIC}[\rho] \\ &= E^{GOK}[\rho] - \sum_{I=1}^{M} \omega_I^2 \sum_i n_i^I \left(\frac{1}{2}\langle ii|ii\rangle + E_{xc}[\rho_i]\right) \\ &\quad - \sum_{I>J}^{M} \sum_{i,j} \omega_I \omega_J \, n_i^I \left(1 - n_i^J\right) n_j^J \left(1 - n_j^I\right) \\ &\quad \times \{\langle ij|ij\rangle + E_{xc}[\rho_i + \rho_j] - E_{xc}[\rho_i] - E_{xc}[\rho_j]\}. \end{aligned} \tag{23}$$

One should notice that generally such a defined functional is not entirely free of ghost-interaction even for an ensemble of one-electron states. Nevertheless, as it will be shown in Sec. III the GI correction removes some part of the ghost-interaction and leads to lowering the ensemble energy.

III. PERFORMANCE OF THE CORRECTED FUNCTIONALS

In this section, we present and analyze the influence of the aforementioned ghost- and self-interaction corrections on the performance of selected functionals. A test set comprises five systems – beryllium atom and H_2, BH, H_2O, and CO molecules (all molecules in their equilibrium geometries). For each system, we built an equiensemble consisting of M-electron configurations, i.e., each configuration enters the ensemble with weight $1/M$. It should be mentioned that for approximate functionals the excitation energies do depend on weights[34] but in this work we chose to focus only on equiensembles. For the first two systems, namely, Be and H_2, all calculations were performed in aug-cc-pVQZ basis set, for the latter three, i.e., BH, H_2O, and CO, in aug-cc-pVTZ basis set.[35,36] As a reference we use the coupled clusters singles doubles (CCSD) results obtained with DALTON quantum chemistry package[37] in the same basis sets.

Unlike in earlier works[24,28] the functionals are not minimized via the optimized effective potential method but in a procedure of direct minimization with respect to the orbitals (with fixed occupation numbers), described in our previous work.[11] By assuming a particular parametrization of the orbitals we assure orthogonality of both the orbitals and the determinants corresponding to the states in the ensembles. Since we are primarily interested in the ensemble energy rather than in the shape of the orbitals or in the eigenvalues of the effective one-electron Hamiltonian direct minimization should yield similar results as the OEP procedure as it is in case of ground-state calculations.[38] The ghost- (in case of GOK-HF and GOK-DFT functionals) and the self- (for all functionals) interaction corrections are added on top of the minimization procedure.

In the absence of exchange-correlation functionals dedicated for ensembles, we chose two ground-state density functionals: one local – local density approximation (LDA)[39] and one generalized gradient approximation (GGA) – Perdew-Burke-Ernzerhof (PBE).[40] Since the ensembles contain states of open-shell character it is appropriate to use the spin-polarized versions of density functionals. Clearly, one must account for that spin polarization while defining the corrections. For instance, in Eq. (18) instead of $-\sum_i n_i E_{xc}[\rho_i]$ the exchange-correlation part of the self-interaction correction will read $-\sum_i n_i E_{xc}[\rho_i^\alpha, 0]$. Equation (23) should also be rewritten accordingly.

First, let us study the ensemble built of three lowest states of hydrogen molecule (Table I): $1^1\Sigma_g^+$, $1^3\Sigma_u^+$, and $1^1\Sigma_u^+$ that are obtained by including $1\sigma_g^2$ and $1\sigma_g 1\sigma_u$ electron configurations with all pertinent spins (thus, there are 5 configurations in total), all equally weighted. The ensemble energy obtained with uncorrected GOK-HF functional, Eq. (12), is too high by over 200 [mHartree]. It is not a surprising result since GOK-HF not only contains spurious ghost-interaction which comes largely from the Hartree part (and it is therefore positive), but also lacks correlation. The GI correction [cf. Eq. (21)] brings the energy slightly below the benchmark value showing that even for this small, two-electron system, the correction is not exact. Functionals GOK-LSDA and GOK-PBE, resulting from employing pertinent exchange-correlation functionals in the GOK functional, Eq. (8), even tainted with self-interaction and ghost-interaction, produce acceptable, although slightly too high, energies. As one could expect, in case of GOK-LSDA the SI correction lowers the energy bringing it closer to the benchmark value. In case of GOK-PBE, the correction rises the energy by 4 [mHartree]. It is likely that if the correction was computed self-consistently, it would not raise the energy. Still, it is known[41] that the performance of semi-local functionals for ground-states is often impaired by the Perdew-Zunger self-interaction correction. By looking at Table I it is clear that for the hydrogen molecule the GIC fails for density functionals. For example, for GOK-LSDA the Hartree part of GI correction is fairly large and amounts to −271 [mHartree] whereas its exchange-correlation counterpart is very small and equals 26 [mHartree]. In this case, a large part of exchange-correlation ghost-interaction is unaccounted for and therefore the GI-corrected energies are too low. This is not the case for the ensemble functionals, which are free of ghost-interaction by definition. Already the eHF energy obtained from the functional given in Eq. (2) is acceptable and SIC-eLSDA and SIC-ePBE energies resulting from employing self-interaction corrected functional defined in Eq. (18) with, respectively, LSDA or PBE exchange-correlation

TABLE I. Ensemble energies in [Hartree] of H_2 at $R = 1.402$ [a.u.]; Be; BH at $R = 2.329$ [a.u.]; H_2O at $R = 1.808$ [a.u.], $\theta = 104.5^\circ$; and CO at $R = 2.132$ [a.u.]. E_{ens} is the ensemble energy, E_{ens}^{SIC} and $E_{ens}^{SIC-GIC}$ stand, respectively, for energies corrected for self-interaction and for both GI and SI.

	GOK-LSDA	GOK-PBE	GOK-HF	eLSDA	ePBE	eHF	CCSD
				H_2			
E_{ens}	−0.788	−0.812	−0.616	−0.815	−0.847	−0.818	−0.831
E_{ens}^{SIC}	−0.793	−0.808	−0.841	−0.837	−0.824		
$E_{ens}^{SIC-GIC}$	−1.038	−1.065					
				Be			
E_{ens}	−14.335	−14.515	−14.320	−14.370	−14.556	−14.520	−14.547
E_{ens}^{SIC}	−14.369	−14.514	−14.561	−14.608	−14.522	−14.522	
$E_{ens}^{SIC-GIC}$	−14.648	−14.804					
				BH			
E_{ens}	−24.913	−25.171	−24.850	−24.944	−25.209	−25.115	−25.202
E_{ens}^{SIC}	−24.980	−25.164	−25.119	−25.290	−25.179		
$E_{ens}^{SIC-GIC}$	−25.310	−25.503					
				H_2O			
E_{ens}	−75.668	−76.148	−75.664	−75.667	−76.153	−75.861	−76.130
E_{ens}^{SIC}	−75.785	−76.099	−75.885	−76.247	−75.908		
$E_{ens}^{SIC-GIC}$	−76.025	−76.346					
				CO			
E_{ens}	−112.305	−113.072	−112.490	−112.308	−113.079	−112.640	−113.017
E_{ens}^{SIC}	−112.622	−112.968	−112.750	−113.252	−112.762		
$E_{ens}^{SIC-GIC}$	−112.763	−113.113					

functionals, are in agreement with the reference value within a few mHartree. As for the GOK-type functionals, the SIC bears more significance for the local functional than for the semi-local one.

Let us now consider a larger system – beryllium atom. The equiensemble for this system contains two states: 1^1S and 1^3P that are formed by including $1s^2 2s^2$ and $1s^2 2s2p$ configurations in all pertinent spin- and spatial-symmetry combinations that make altogether 7 Slater determinants in the ensemble. All the ghost-interaction-free functionals, namely, eLSDA and ePBE functionals and their SI-corrected counterparts, perform fairly well. Notably, eLSDA is most improved by the SI correction. The GOK-HF and GOK-LSDA energies are too high but the corrections lower them to sensible values. The GOK-PBE energy deviates by 32 [mHartree] from the reference value and the corrections (mainly the GI) lower it too much resulting in the error of 257 [mHartree].

The behavior of the functionals observed for Be case is very similar for boron hydride (states $1^1\Sigma^+$ and $1^3\Pi$, 5 configurations: $1\sigma^2 2\sigma^2 3\sigma^2$ and $1\sigma^2 2\sigma^2 3\sigma 1\pi$) and water molecules ($1^1A_1$, 1^3B_1, 1^1B_1, configurations: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ and $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^3$). Interestingly, the SI correction of ePBE functional raises significantly the energies of those ensembles, by up to even 245 [mHartree] for H_2O molecule.

In case of the largest system in the set – carbon monoxide molecule (ensemble built of two states: $1^1\Sigma$ and $1^3\Pi$, configurations: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$ and $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma 1\pi^3$) – both of the Hartree-Fock-based methods fail, as well as the local functionals. Even though for both eLSDA and GOK-LSDA the corrections bring energy closer to the benchmark value, their accuracy leaves a lot to be desired, which shows that the deficiency of eHF and GOK-HF is here not simply a matter of lacking correlation. Similar to what has been observed for BH and H_2O molecules, both ePBE and GOK-PBE perform well, while their corrected counterparts fail.

The example of CO molecule once again proves that while introduced corrections work fairly well for the exact exchange functional and the local functionals, they are too naïve for the semi-local ones. It is also clear that it is more rewarding to create functionals that are ghost-interaction free by construction (i.e., eLSDA, ePBE) than to introduce corrections that account for spurious interactions.

The results presented above paint a clear picture of the influence of self- and ghost-interaction corrections on the behavior of ensemble functionals. Nonetheless, the methods in question are primarily dedicated to calculating low-lying excitation energies of atoms and molecules. Therefore, their performance should also be assessed on that ground.

The inequality (1) does not provide a straightforward way to obtain excitation energies within ensemble DFT. However, for a given equiensemble with all weights being identical, i.e., $\forall_{I \leq M}\, \omega_I = 1/M$, Gross *et al.*[8] proposed to obtain an excitation energy for an Ith state by taking a difference $E_I - E_0$, where E_0 is the ground-state energy, whereas the energy of the Ith state, E_I, results from the following equation:

$$E_I = E_{ens}(I) + \frac{I-g}{g}\left[E_{ens}(I) - E_{ens}(I-g)\right], \qquad (24)$$

where g is the degeneracy factor of Ith state and $E_{ens}(I)$ and $E_{ens}(I-g)$ are energies of ensembles consisting of I and $I-g$ states, respectively. Thus, in order to obtain excitation energies up to the Ith level, one must perform separate calculations for the ground-state and for ensembles including ground and an increasing number of excited states. Note that this strategy can be employed for any functional, whether it is an explicit

TABLE II. Excitation energies in [eV] of H_2, Be, BH, H_2O, CO obtained with formulas (24) and (26).

	Excitation energies, Eq. (24)				Excitation energies, Eq. (26)					
	eLSDA	eLSDA-SIC	ePBE	ePBE-SIC	eLSDA	eLSDA-SIC	ePBE	ePBE-SIC	eHF	CCSD
H_2										
$1^3\Sigma_u^+$	10.66	11.76	10.56	11.56	10.00	10.96	9.84	10.53	9.32	10.59
$1^1\Sigma_u^+$	11.10	11.68	10.98	11.29	11.05	12.01	10.97	11.66	11.23	12.53
Be										
1^3P	2.41	2.78	2.32	3.53	2.39	2.69	2.29	2.63	1.65	2.71
BH										
$1^3\Pi^+$	1.06	1.10	1.01	0.99	0.93	1.08	0.88	1.02	0.35	1.32
H_2O										
1^3B_1	8.15	8.02	7.87	7.48	6.27	6.46	5.93	5.28	4.73	7.23
1^1B_1	7.89	7.61	7.59	7.03	6.49	6.69	6.15	5.50	4.96	7.62
CO										
$1^3\Pi^+$	6.29	7.79	6.17	7.75	6.12	6.85	6.00	6.87	5.56	6.76

density functional like GOK given in Eq. (8) or an orbital-dependent functional defined in Eq. (15).

Another, less computationally demanding, method is to perform a single calculation for an ensemble including all states of interest and then compute their energies either as the expectation values of the Hamiltonian

$$E_I = \langle \Phi_I | H | \Phi_I \rangle \tag{25}$$

or, in case of a density functional, as values of the functional each taken for the density of the Ith state, namely,

$$E_I = E\left[\rho_I\right]. \tag{26}$$

One should notice that Eq. (25) should be used with caution for equiensembles for which the energy is invariant to unitary transformation of states. The expression given in Eq. (26) is applicable to eDFT functionals defined in Eq. (15). Since in case of the GOK-type functionals, Eq. (8), one cannot expect to obtain accurate densities of components of the ensemble using Eq. (24) is more appropriate in calculation of excitation energies than that of Eq. (26).

It is also possible to calculate a first excitation energy from orbital energies resulting from an ensemble calculation[14] but we did not explore this method as it is the least universal of the three mentioned methods. For our test set, the uncorrected GOK-LSDA and GOK-PBE functionals yield reasonable excitation energies if Eq. (24) is employed, with the root mean square error amounting to 0.87 [eV] and 0.72 [eV] for the two methods, respectively. For their SI- and GI-corrected counterparts, the excitation energies (not shown in Table II) are dramatically less accurate, differing from the benchmark value even by several [eV].

For the eLSDA and ePBE functionals, we employed both methods [i.e., Eqs. (24) and (26)] of calculating excitation energies. The results collected in Table II show that for the considered ensembles the quality of excitation energies does not heavily depend on the choice between formulae (24) and (26). The eLSDA-SIC excitation energies are improved with respect to the uncorrected eLSDA ones and a mean error drops from 0.33 [eV] to 0.20 [eV] for the method defined by Eq. (26). For the method given by Eq. (24), adding the SIC correction on average also brings an improvement but the mean error is reduced by only 0.02 [eV] from 0.28 [eV] to 0.26 [eV]. For the ePBE functional, the effect of the self-interaction correction is more erratic. For example, ePBE-SIC performs better than ePBE for CO molecule (absolute error of 0.11 [eV] vs. 0.77 [eV] with formula (26)), while it fails for beryllium atom when using formula (24) (error of 0.82 [eV] vs. 0.39 [eV]) and the 1^1B_1 excitation of water molecule while using both formulae (error of 0.60 [eV] vs. 0.03 [eV] with formula (24) and 2.13 [eV] vs. 1.48 [eV] with formula (26)). On average, however, the SIC correction does not significantly influence the quality of the results of ePBE. The mean error changes from 0.43 [eV] to 0.40 [eV] if the SI correction is employed for the method governed by Eq. (26) and from 0.26 [eV] to 0.31 [eV] for the approach defined in Eq. (24). All the density functionals perform better than eHF. Too low excitation energies with the mean error of 0.64 [eV] produced by eHF can be attributed to its lack of dynamical correlation.

The eLSDA-SIC functional produces excitation energies as accurately as ePBE. One can observe that for small ensembles used in our calculations, the excitation energies obtained with methods defined in Eqs. (24) and (26) are of the same quality, but usage of the latter method is preferred for its modest cost.

IV. CONCLUSIONS

In this paper, we have studied the ensemble DFT methods for predicting excited state energies when local or semi-local functionals proposed for the ground-state DFT are used. Two forms of functionals have been employed: the GOK functional,[8] Eq. (8), the exchange-correlation part of which depends explicitly on ensemble density, and the eDFT functional, Eq. (15), which approximates the total energy of an ensemble as a weighted sum of energies of noninteracting states.[32] We have also considered the problem of self- and ghost-interaction in ensemble functionals. Since the physical understanding of self-interaction in ensembles is the same as in the ground state theory, ensemble functionals have been corrected for SI by adopting the Perdew-Zunger correction. Self-interaction is removed for each spinorbital from every state separately both in the eDFT and GOK functionals, cf. Eqs. (18) and (23), respectively. We have generalized the concept of the ghost-interaction to ensembles comprising more than two states and being described by local or semi-local functionals. The ghost-interaction correction proposed for the GOK functional in Eq. (23) involves pairs of fractionally occupied spinorbitals belonging to different states in the ensemble. In case of approximating the exchange-correlation functional with the exact exchange, the ghost-interaction correction reduces to the one proposed by Gidopoulos *et al.*[28] By construction, the eDFT functional should be free of ghost-interaction. Indeed, we have verified that the SI-corrected eDFT functional applied to an ensemble of one-electron states is exact, i.e., it does not involve any contribution from the Hartree and exchange-correlation terms. In general, the SI- and GI-corrected GOK functional does not possess such a property unless the exact exchange approximation is employed.

After applying the GOK and eDFT approaches with LSDA and PBE functionals to a test set, one concludes that corrected eDFT yields much more reliable results than GOK not only for ensemble energies but, what is more important, for excitation energies. Thus, it is more effective to employ ensemble functionals that are free of ghost-interaction by construction than to remove GI by adding pertinent correcting terms to the functional. We have also observed that the SI-GI-corrected GOK functional is prone to producing excitation energies suffering from errors much larger than the uncorrected functional. The eDFT functional, on the other hand, benefits from removing the self-interaction correction especially if the local approximation (LSDA) is employed and the errors of excitation energies are lower than for the uncorrected functional. If PBE is used the improvement brought by the SI correction is erratic but this could be expected from a similar behavior of the correction in the ground state theory. Overall, we conclude that the eDFT approach applied to predicting excitation energies with the corrected LSDA or PBE functionals yields more accurate results than eHF even though the latter functional is better founded theoretically in ensemble methods than the ground-state local or GGA ground-state functionals. The accuracy of eDFT cannot in general compete with the TD-DFT method for the low-lying single excitations. However, eDFT is potentially capable of predicting excitations problematic to approximate TD-DFT, i.e., those of a double or mixed character, which are plentiful in spectra of molecules with stretched bonds. Work along this line is in progress.

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