A weight-dependent local correlation density-functional approximation for ensembles

Pierre-François Loos\textsuperscript{1, a)} and Emmanuel Fromager\textsuperscript{2, b)}
\textsuperscript{1}Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France
\textsuperscript{2}Laboratoire de Chimie Quantique, Institut de Chimie, CNRS, Université de Strasbourg, Strasbourg, France

We report a local, weight-dependent correlation density-functional approximation that incorporates information about both ground and excited states in the context of density-functional theory for ensembles (eDFT). This density-functional approximation for ensembles is specially designed for the computation of single and double excitations within Gross–Oliveira–Kohn (GOK) DFT (i.e., eDFT for neutral excitations), and can be seen as a natural extension of the ubiquitous local-density approximation in the context of ensembles. The resulting density-functional approximation, based on both finite and infinite uniform electron gas models, automatically incorporates the infamous derivative discontinuity contributions to the excitation energies through its explicit ensemble weight dependence. Its accuracy is illustrated by computing single and double excitations in one-dimensional many-electron systems in the weak, intermediate and strong correlation regimes. Although the present weight-dependent functional has been specifically designed for one-dimensional systems, the methodology proposed here is general, i.e., directly applicable to the construction of weight-dependent functionals for realistic three-dimensional systems, such as molecules and solids.

I. INTRODUCTION

Over the last two decades, density-functional theory (DFT)\textsuperscript{1–3} has become the method of choice for modeling the electronic structure of large molecular systems and materials. The main reason is that, within DFT, the quantum contributions to the electronic repulsion energy — the so-called exchange-correlation (xc) energy — is rewritten as a functional of the electron density $n \equiv n(r)$, the latter being a much simpler quantity than the many-electron wave function. The complexity of the many-body problem is then transferred to the xc density functional. Despite its success, the standard Kohn–Sham (KS) formulation of DFT\textsuperscript{2} (KS-DFT) suffers, in practice, from various deficiencies.\textsuperscript{4–15} The description of strongly multiconfigurational ground states (often referred to as “strong correlation problem”) still remains a challenge.\textsuperscript{16–18} Another issue, which is partly connected to the previous one, is the description of low-lying quasi-degenerate states.

The standard approach for modeling excited states in a DFT framework is linear-response time-dependent DFT (TDDFT).\textsuperscript{19–21} In this case, the electronic spectrum relies on the (unperturbed) pure-ground-state KS picture, which may break down when electron correlation is strong. Moreover, in exact TDDFT, the xc energy is in fact an xc action\textsuperscript{22} which is a functional of the time-dependent density $n \equiv n(r,t)$ and, as such, it should incorporate memory effects. Standard implementations of TDDFT rely on the adiabatic approximation where these effects are neglected.\textsuperscript{23} In other words, the xc functional is assumed to be local in time.\textsuperscript{20,21} As a result, double electronic excitations (where two electrons are simultaneously promoted by a single photon) are completely absent from the TDDFT spectrum, thus reducing further the applicability of TDDFT.\textsuperscript{24–34}

When affordable (i.e., for relatively small molecules), time-independent state-averaged wave function methods\textsuperscript{35–40} can be employed to fix the various issues mentioned above. The basic idea is to describe a finite (canonical) ensemble of ground and excited states altogether, i.e., with the same set of orbitals. Interestingly, a similar approach exists in DFT. Referred to as Gross–Oliveira–Kohn (GOK) DFT,\textsuperscript{41–43} it was proposed at the end of the 80’s as a generalization of Theophilou’s DFT for equiensembles.\textsuperscript{44} In GOK-DFT, the ensemble xc energy is a functional of the density and a function of the ensemble weights. Note that, unlike in conventional Boltzmann ensembles,\textsuperscript{45} the ensemble weights (each state in the ensemble is assigned a given and fixed weight) are allowed to vary independently in a GOK ensemble. The weight dependence of the xc functional plays a crucial role in the calculation of excitation energies.\textsuperscript{42,46–50} It actually accounts for the derivative discontinuity contribution to energy gaps.\textsuperscript{51,52}

Even though GOK-DFT is in principle able to describe near-degenerate situations and multiple-electron excitation processes, it has not been given much attention until quite recently.\textsuperscript{45–49,53–80} One of the reason is the lack, not to say the absence, of reliable density-functional approximations for ensembles. The most recent works dealing with this particular issue are still fundamental and exploratory, as they rely either on simple (but nontrivial) model systems\textsuperscript{47–50,63,64,66,75,78,79,81,82} or atoms.\textsuperscript{46,77,83} Despite all these efforts, it is still unclear how weight dependencies can be incorporated into density-functional approximations. This problem is actually central not only in GOK-DFT but also in conventional (ground-state) DFT as the infamous derivative discontinuity problem that occurs when crossing an integral number of electrons can be recast into a weight-dependent ensemble one.\textsuperscript{49,50}

The present work is an attempt to address the ensemble weight dependence problem in GOK-DFT, with the ambition to turn the theory, in the forthcoming future, into a (low-cost) practical computational method for modeling excited states in molecules and extended systems. Starting from the ubiquitous local-density approximation (LDA), we design a weight-dependent ensemble correction based on a finite uniform electron gas from which density-functional excitation energies can be extracted. The present density-functional ap-

\textsuperscript{a)}Electronic mail: loos@irsamc.ups-tlse.fr
\textsuperscript{b)}Electronic mail: fromagere@unistra.fr
proximation for ensembles, which can be seen as a natural extension of the LDA, will be referred to as eLDA in the remaining of this paper. As a proof of concept, we apply this general strategy to ensemble correlation energies (that we combine with ensemble exact exchange energies) in the particular case of strict one-dimensional (1D) spin-polarized systems.\textsuperscript{84–87} In other words, the Coulomb interaction used in this work corresponds to particles which are strictly restricted to move within a 1D sub-space of three-dimensional space. Despite their simplicity, 1D models are scrutinized as paradigms for quasi-1D materials\textsuperscript{88–90} such as carbon nanotubes\textsuperscript{90–92} or nanowires.\textsuperscript{93,94} This description of 1D systems also has interesting connections with the exotic chemistry of ultra-high magnetic fields (such as those in white dwarf stars), where the electronic cloud is dramatically compressed perpendicular to the magnetic field.\textsuperscript{95–97} In these extreme conditions, where magnetic effects compete with Coulombic forces, entirely new bonding paradigms emerge.\textsuperscript{95–102}

The paper is organized as follows. Exact and approximate formulations of GOK-DFT are discussed in Sec. II, with a particular emphasis on the extraction of individual energy levels. In Sec. III, we detail the construction of the weight-dependent local correlation functional specially designed for the computation of single and double excitations within GOK-DFT. Computational details needed to reproduce the results of the present work are reported in Sec. IV. In Sec. V, we illustrate the accuracy of the present eLDA functional by computing single and double excitations in 1D many-electron systems in the weak, intermediate and strong correlation regimes. Finally, we draw our conclusions in Sec. VI. Atomic units are used throughout.

II. THEORY

A. GOK-DFT

In this section we give a brief review of GOK-DFT and discuss the extraction of individual energy levels\textsuperscript{48,82} with a particular focus on exact individual exchange energies. Let us start by introducing the GOK ensemble energy\textsuperscript{41}

\[
E^w = \sum_{K=0} w_K E^{(K)},
\]

where the \(K\)th energy level \(E^{(K)}\) \((K = 0\) refers to the ground state\) is the eigenvalue of the electronic Hamiltonian \(\hat{H} = \hat{h} + \hat{W}_{ee}\), where

\[
\hat{h} = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 + V_{nc}(r_i) \right)
\]

is the one-electron operator describing kinetic and nuclear attraction energies, and \(\hat{W}_{ee}\) is the electron repulsion operator. The (positive) ensemble weights \(w_K\) decrease with increasing index \(K\). They are normalized, i.e.,

\[
w_0 = 1 - \sum_{K>0} w_K,
\]

so that only the weights \(w \equiv (w_1, w_2, \ldots, w_K, \ldots)\) assigned to the excited states can vary independently. For simplicity we will assume in the following that the energies are not degenerate. Note that the theory can be extended to multiplets simply by assigning the same ensemble weight to all degenerate states.\textsuperscript{42} In the KS formulation of GOK-DFT, which is simply referred to as KS ensemble DFT (KS-eDFT) in the following, the ensemble energy is determined variationally as follows:\textsuperscript{42}

\[
E^w = \min_{\Omega} \left[ \text{Tr} [\hat{\Gamma}^w \hat{h}] + E_{\text{Hx}}^w [\eta^w] + E_{\text{c}}^w [\eta^w] \right],
\]

where \(\text{Tr}\) denotes the trace and the trial ensemble density matrix operator reads

\[
\hat{\Gamma}^w = \sum_{K=0} w_K |\Phi^{(K)}\rangle \langle \Phi^{(K)}|.
\]

The KS determinants [or configuration state functions\textsuperscript{61}] \(\Phi^{(K)}\) are all constructed from the same set of ensemble KS orbitals that are variationally optimized. The trial ensemble density in Eq. (4) is simply the weighted sum of the individual KS densities, i.e.,

\[
\eta^w(r) = \sum_{K=0} w_K \eta_{\Phi^{(K)}}(r).
\]

As readily seen from Eq. (4), both Hartree-exchange (Hx) and correlation (c) energies are described with density functionals that are weight dependent. We focus in the following on the (exact) Hx part, which is defined as\textsuperscript{61}

\[
E_{\text{Hx}}^w [n] = \sum_{K=0} w_K \langle \Phi^{(K),w} | \hat{W}_{ee} | \Phi^{(K),w} [n] \rangle,
\]

where the KS wavefunctions fulfill the ensemble density constraint

\[
\sum_{K=0} w_K \eta_{\Phi^{(K),w}}[n] (r) = n(r).
\]

The (approximate) description of the correlation part is discussed in Sec. III.

In practice, the ensemble energy is not the most interesting quantity, and one is more concerned with excitation energies or individual energy levels (for geometry optimizations, for example). As pointed out recently in Ref. 48, the latter can be extracted exactly from a single ensemble calculation as follows:

\[
E^{(i)} = E^w + \sum_{K=0} (\delta_{IK} - w_K) \frac{\partial E^w}{\partial w_K},
\]

where, according to the normalization condition of Eq. (3),

\[
\frac{\partial E^w}{\partial w_K} = E^{(K)} - E^{(0)} \equiv \Omega^{(K)}
\]

corresponds to the \(K\)th excitation energy. According to the variational ensemble energy expression of Eq. (4), the derivative with respect to \(w_K\) can be evaluated from the minimizing
weight-dependent KS wavefunctions \( \Phi^{(K)} \equiv \Phi^{(K,w)} \) as follows:

\[
\frac{\partial E^w}{\partial w_K} = \langle \Phi^{(K)} | \hat{H} | \Phi^{(K)} \rangle - \langle \Phi^{(0)} | \hat{H} | \Phi^{(0)} \rangle \\
+ \left\{ \int \frac{\delta E^w_n}{\delta n(r)} \left[ n_{\Phi^{(K)}}(r) - n_{\Phi^{(0)}}(r) \right] dr + \frac{\partial E^w_c[n]}{\partial w_K} \right\}_{n=\hat{n}_w}.
\]

The Hx contribution from Eq. (11) can be recast as

\[
\frac{\partial}{\partial E^w_c} \left\{ E^w_{\text{Hx}}[n^{w,\xi}] - E^w_{\text{Hx}}[n^{w,\xi}] \right\}_{\xi=w}, \tag{12}
\]

where \( \xi \equiv (\xi_1, \xi_2, \ldots, \xi_K, \ldots) \) and the auxiliary double-weight ensemble density reads

\[
n^{w,\xi}(r) = \sum_{K \geq 0} w_K n_{\Phi^{(K)}}(r). \tag{13}
\]

Since, for given ensemble weights \( w \) and \( \xi \), the ensemble densities \( n^{w,\xi} \) and \( n^{w,\xi} \) are obtained from the same KS potential (which is unique up to a constant), it comes from the exact expression in Eq. (7) that

\[
E^w_{\text{Hx}}[n^{w,\xi}] = \sum_{K \geq 0} \xi_K \langle \Phi^{(K)} | \hat{W}_{\text{ec}} | \Phi^{(K)} \rangle, \tag{14}
\]

and

\[
E^w_{\text{Hx}}[n^{w,\xi}] = \sum_{K \geq 0} w_K \langle \Phi^{(K)} | \hat{W}_{\text{ec}} | \Phi^{(K)} \rangle. \tag{15}
\]

This yields, according to Eqs. (11) and (12), the simplified expression

\[
\frac{\partial E^w}{\partial w_K} = \langle \Phi^{(K)} | \hat{H} | \Phi^{(K)} \rangle - \langle \Phi^{(0)} | \hat{H} | \Phi^{(0)} \rangle \\
+ \left\{ \int \frac{\delta E^w_c[n]}{\delta n(r)} \left[ n_{\Phi^{(K)}}(r) - n_{\Phi^{(0)}}(r) \right] dr + \frac{\partial E^w_c[n]}{\partial w_K} \right\}_{n=\hat{n}_w}. \tag{16}
\]

Since, according to Eqs. (4) and (7), the ensemble energy can be evaluated as

\[
E^w = \sum_{K \geq 0} w_K \langle \Phi^{(K)} | \hat{H} | \Phi^{(K)} \rangle + E^w_c[\hat{n}_w]. \tag{17}
\]

with \( \Phi^{(K)} = \Phi^{(K,w)} \) [note that, when the minimum is reached in Eq. (4), \( \hat{n}_w = n^{w,w} \)], we finally recover from Eqs. (6) and (9) the exact expression of Ref. 82 for the 4th energy level:

\[
E^{(4)} = \langle \Phi^{(4)} | \hat{H} | \Phi^{(4)} \rangle + E^w_c[\hat{n}_w] \\
+ \int \frac{\delta E^w_c[n]}{\delta n(r)} \left[ n_{\Phi^{(4)}}(r) - n_{\Phi^{(0)}}(r) \right] dr \\
+ \sum_{K \geq 0} (\delta_{1K} - w_K) \frac{\partial E^w_c[n]}{\partial w_K} \bigg|_{n=\hat{n}_w}. \tag{18}
\]

Note that, when \( w = 0 \), the ensemble correlation functional reduces to the conventional (ground-state) correlation functional \( E_c[n] \). As a result, the regular KS-DFT expression is recovered from Eq. (18) for the ground-state energy:

\[
E^{(0)} = \langle \Phi^{(0)} | \hat{H} | \Phi^{(0)} \rangle + E_c[n_{\Phi^{(0)}}]. \tag{19}
\]

or, equivalently,

\[
E^{(0)} = \langle \Phi^{(0)} | \hat{H} | n_{\Phi^{(0)}} \rangle | \Phi^{(0)} \rangle, \tag{20}
\]

where the density-functional Hamiltonian reads

\[
\hat{H}[n] = \hat{H} + \sum_{K=1}^{N} \left( \frac{\partial E_c[n]}{\partial n(r)} + C_c[n] \right), \tag{21}
\]

and

\[
C_c[n] = E_c[n] - \int \frac{\delta E_c[n]}{\delta n(r)} n(r) dr \\
\int n(r) dr \tag{22}
\]

is the correlation component of Levy–Zahariev’s constant shift in potential. Similarly, the excited-state \((I > 0)\) energy level expressions can be recast as follows:

\[
E^{(I)} = \langle \Phi^{(I)} | \hat{H} | n_{\Phi^{(I)}} \rangle | \Phi^{(I)} \rangle + \frac{\partial E^w_c[n_{\Phi^{(I)}}]}{\partial w_I} \bigg|_{w=0}. \tag{23}
\]

As readily seen from Eqs. (21) and (22), introducing any correlation components \( E_c[n] \) or, equivalently, \( E^{(0)} = \langle \Phi^{(0)} | \hat{H} | n_{\Phi^{(0)}} \rangle | \Phi^{(0)} \rangle \), will be fully described by the correlation ensemble derivatives [second term on the right-hand side of Eq. (23)].

B. One-electron reduced density matrix formulation

For implementation purposes, we will use in the rest of this work (one-electron reduced) density matrices as basic variables, rather than Slater determinants. As the theory is applied later on to spin-polarized systems, we drop spin indices in the density matrices, for convenience. If we expand the ensemble KS orbitals (from which the determinants are constructed) in an atomic orbital (AO) basis,

\[
\phi_{\mu}(r) = \sum_{\mu} c_{\mu \mu} \chi_{\mu}(r), \tag{24}
\]

then the density matrix of the determinant \( \Phi^{(K)} \) can be expressed as follows in the AO basis:

\[
\Gamma^{(K)} \equiv \Gamma^{(K)}_{\mu \nu} \equiv \sum_{\nu \in \Phi^{(K)}} c_{\mu \nu} c_{\nu \nu}, \tag{25}
\]

where the summation runs over the orbitals that are occupied in \( \Phi^{(K)} \). The electron density of the \( K \)th KS determinant can then be evaluated as follows:

\[
n_{\nu \nu}(r) = \sum_{\mu \nu} \chi_{\mu}(r) \Gamma_{\mu \nu}^{(K)} \chi_{\nu}(r), \tag{26}
\]
while the ensemble density matrix and the ensemble density read
\[
\Gamma^w = \sum_{K \geq 0} w_K \Gamma^{(K)} \equiv \Gamma_{\nu \mu}^w = \sum_{K \geq 0} w_K \Gamma^{(K)}_{\nu \mu},
\]  
where the antisymmetrized two-electron integrals read
\[
\chi_{\mu \nu}(r) = \sum_{\nu' \mu'} \chi_{\mu \nu}(r) \Gamma_{\nu' \mu'}^w \chi_{\nu' \mu'}(r),
\]
respectively. The exact individual energy expression in Eq. (18) can then be rewritten as
\[
E^{(i)} = \text{Tr}[\Gamma^{(i)} h] + \frac{1}{2} \text{Tr}[\Gamma^{(i)} G \Gamma^{(i)}] + E^w_{\nu \mu}[n_{\nu \mu}]
+ \int \frac{\delta E^w_{\nu \mu}[n_{\nu \mu}]}{\delta n(r)} \chi_{\nu \mu}(r) dr
+ \sum_{K > 0} (\delta_{IK} - w_K) \frac{\delta E^w_{\nu \mu}[n]}{\delta w_K} |_{n=n_{\nu \mu}},
\]
where
\[
h \equiv h_{\nu \mu} = \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle
\]
denotes the matrix of the one-electron integrals. The exact individual Hx energies are obtained from the following trace formula
\[
\text{Tr}[\Gamma^{(K)} G \Gamma^{(L)}] = \sum_{\mu \nu \sigma \rho} \Gamma^{(K)}_{\mu \nu} G_{\mu \nu \sigma \rho} \Gamma^{(L)}_{\sigma \rho},
\]
where the antisymmetrized two-electron integrals read
\[
G \equiv G_{\mu \nu \sigma \rho} = (\mu \nu | \sigma \rho) = (\mu \nu | \sigma \rho) - (\mu \sigma | \nu \rho),
\]
with
\[
(\mu \nu | \sigma \rho) = \int \frac{\chi_{\mu}(r) \chi_{\nu}(r) \chi_{\sigma}(r) \chi_{\rho}(r)}{|r_1 - r_2|} dr_1 dr_2.
\]

### C. Approximations

In the following, GOK-DFT will be applied to 1D spin-polarized systems where Hartree and exchange energies cannot be separated. For that reason, we will substitute the Hartree–Fock (HF) density-matrix-functional interaction energy,
\[
W_{\text{HF}}[\Gamma] = \frac{1}{2} \text{Tr}[\Gamma G \Gamma],
\]
for the Hx density-functional energy in the variational energy expression of Eq. (4), thus leading to the following approximation:
\[
\Gamma^w \rightarrow \arg \min \left\{ \text{Tr}[\gamma^w h] + W_{\text{HF}}[\gamma^w] + E^w_{\nu \mu}[n_{\nu \mu}] \right\}.
\]
The minimizing ensemble density matrix in Eq. (35) fulfills the following stationarity condition
\[
F^w \Gamma^w S = S F^w,
\]
where \(S \equiv S_{\nu \mu} = \langle \chi_{\mu} | \chi_{\nu} \rangle\) is the overlap matrix and the ensemble Fock-like matrix reads
\[
F^w \equiv F_{\nu \mu}^w = h_{\nu \mu}^w + \sum_{\sigma \rho} G_{\mu \nu \sigma \rho} \Gamma_{\sigma \rho}^w,
\]
with
\[
h_{\nu \mu}^w = h_{\nu \mu} + \int \chi_{\nu \mu}(r) \frac{\delta E^w_{\nu \mu}[n_{\nu \mu}]}{\delta n(r)} \chi_{\nu \mu}(r) dr.
\]
Note that, within the approximation of Eq. (35), the ensemble density matrix is optimized with a non-local exchange potential rather than a density-functional local one, as expected from Eq. (4). This procedure is actually general, i.e., applicable to not-necessarily spin-polarized and real (higher-dimensional) systems. As readily seen from Eq. (34), inserting the ensemble density matrix into the HF interaction energy functional introduces unphysical ghost-interaction errors\(^{61,69,70,74,104}\) as well as curvature:\(^{69,70}\)
\[
W_{\text{HF}}[\Gamma^w] = \frac{1}{2} \sum_{K \geq 0} w_K \text{Tr}[\Gamma^{(K)} G \Gamma^{(K)}]
+ \sum_{L \leq K \geq 0} w_K w_L \text{Tr}[\Gamma^{(K)} G \Gamma^{(L)}].
\]
The ensemble energy is of course expected to vary linearly with the ensemble weights [see Eq. (1)]. The explicit linear weight dependence of the ensemble Hx energy is actually restored when evaluating the individual energy levels on the basis of Eq. (29).

Turning to the density-functional ensemble correlation energy, the following ensemble local-density approximation (eLDA) will be employed
\[
E^w_{\nu \mu}[n] \approx \int n(r) \epsilon^w_{\nu \mu}(n(r)) dr,
\]
where the ensemble correlation energy per particle
\[
\epsilon^w_{\nu \mu}(n) = \sum_{K \geq 0} w_K \tilde{\epsilon}^{(K)}(n)
\]
is explicitly weight dependent. As shown in Sec. III, the latter can be constructed from a finite uniform electron gas model.

The resulting KS-eLDA ensemble energy obtained via Eq. (35) reads
\[
E_{\text{eLDA}} = \text{Tr}[\Gamma^w h] + W_{\text{HF}}[\Gamma^w] + \int \epsilon^w_{\nu \mu}(n_{\nu \mu}(r)) n_{\nu \mu}(r) dr.
\]
Combining Eq. (29) with Eq. (42) leads to our final expression of the KS-eLDA energy levels
\[
E^{(i)}_{\text{eLDA}} = E^{(i)}_{\text{HF}} + \Xi^{(i)} + \Upsilon^{(i)},
\]
where
\[
E^{(i)}_{\text{HF}} = \text{Tr}[\Gamma^{(i)} h] + \frac{1}{2} \text{Tr}[\Gamma^{(i)} G \Gamma^{(i)}]
\]
is the analog for ground and excited states (within an ensemble) of the HF energy, and
\[
\Xi_c^{(1)} = \int \varepsilon^w(n_{\Gamma}) n_{\Gamma_0}(r) dr 
+ \int n_{\Gamma_0}(r) \left[ n_{\Gamma}(r) - n_{\Gamma_0}(r) \right] \frac{\partial \varepsilon^w(n)}{\partial n} \bigg|_{n=n_{\Gamma}(r)} dr, \quad (45) 
\]
\[
\Upsilon_c^{(1)} = \int \sum_{k>0} (\delta_{IK} - w_K) n_{\Gamma}(r) \frac{\partial \varepsilon^w(n)}{\partial w_K} \bigg|_{n=n_{\Gamma}(r)} dr \quad (46) 
\]
If, for analysis purposes, we Taylor expand the density-functional correlation contributions around the $I$th KS state density $n_{\Gamma_0}(r)$, the second term on the right-hand side of Eq. (43) can be simplified as follows through first order in $n_{\Gamma_0}(r) - n_{\Gamma_0}(r)$:
\[
\Xi_c^{(1)} = \int \varepsilon^w(n_{\Gamma_0}(r)) n_{\Gamma_0}(r) dr + O\left[ (n_{\Gamma_0}(r) - n_{\Gamma_0}(r))^2 \right]. \quad (47) 
\]
Therefore, it can be identified as an individual-density-functional correlation energy where the density-functional correlation energy per particle is approximated by the ensemble one for all the states within the ensemble.

Let us stress that, to the best of our knowledge, eLDA is the first density-functional approximation that incorporates ensemble weight dependencies explicitly, thus allowing for the description of derivative discontinuities [see Eq. (23) and the comment that follows] via the third term on the right-hand side of Eq. (43). According to the decomposition of the ensemble correlation energy per particle in Eq. (41), the latter can be recast
\[
\Upsilon_c^{(1)} = \int \left[ \varepsilon^w(n_{\Gamma})(r) - \varepsilon^w(n_{\Gamma_0}(r)) \right] n_{\Gamma_0}(r) dr, \quad (48) 
\]
thus leading to the following Taylor expansion through first order in $n_{\Gamma_0}(r) - n_{\Gamma_0}(r)$:
\[
\Upsilon_c^{(1)} = \int \varepsilon^w(n_{\Gamma_0}(r)) n_{\Gamma_0}(r) dr + \int \left[ n_{\Gamma_0}(r) \left( \frac{\partial \varepsilon^w(n)}{\partial n} \bigg|_{n=n_{\Gamma}(r)} - \frac{\partial \varepsilon^w(n)}{\partial n} \bigg|_{n=n_{\Gamma_0}(r)} \right) \right] n_{\Gamma_0}(r) dr 
+ \int \varepsilon^w(n_{\Gamma_0}(r)) - \varepsilon^w(n_{\Gamma_0}(r)) \left[ n_{\Gamma_0}(r) - n_{\Gamma_0}(r) \right] dr 
+ O\left[ (n_{\Gamma_0}(r) - n_{\Gamma_0}(r))^2 \right]. \quad (49) 
\]
As readily seen from Eqs. (47) and (49), the role of the correlation ensemble derivative contribution $\Upsilon_c^{(1)}$ is, through zeroth order, to substitute the expected individual correlation energy per particle for the ensemble one.

Let us finally mention that, while the weighted sum of the individual KS-eLDA energy levels delivers a ghost-interaction-corrected (GIC) version of the KS-eLDA ensemble energy, i.e.,
\[
E_{GIC-eLDA} = \sum_{I \geq 0} W_I E_{eLDA}^{(I)} = E_{eLDA}^{(w)} - W_{HF}^{(w)} + \sum_{I \geq 0} W_I W_{HF}^{(I)}, \quad (50) 
\]
the excitation energies computed from the KS-eLDA individual energy level expressions in Eq. (43) can be simplified as follows:
\[
\Omega_{eLDA}^{(1)} = \Omega_{HF}^{(1)} + \int \varepsilon^w(n) \frac{\partial \varepsilon^w(n)}{\partial n} n_{\Gamma_0}(r) - n_{\Gamma_0}(r) dr + \Delta_c^{(1)}, \quad (51) 
\]
where the HF-like excitation energies, $\Omega_{HF}^{(1)} = E_{HF}^{(1)} - E_{HF}^{(0)}$, are determined from a single set of ensemble KS orbitals and
\[
\Delta_c^{(1)} = \int n_{\Gamma_0}(r) \frac{\partial \varepsilon^w(n)}{\partial w_I} n_{\Gamma_0}(r) dr \quad (52) 
\]
is the eLDA correlation ensemble derivative contribution to the $I$th excitation energy.

**III. DENSITY-FUNCTIONAL APPROXIMATIONS FOR ENSEMBLES**

**A. Paradigm**

Most of the standard local and semi-local density-functional approximations rely on the infinite uniform electron gas model (also known as jellium).\cite{84,86,87,106–108} One major drawback of the jellium paradigm, when it comes to develop density-functional approximations for ensembles, is that the ground and excited states are not easily accessible like in a molecule.\cite{84,86,87,106–108} Moreover, because the infinite uniform electron gas model is a metal, it is gapless, which means that both the fundamental and optical gaps are zero. From this point of view, using finite uniform electron gases,\cite{106,108} which have, like an atom, discrete energy levels and non-zero gaps, can be seen as more relevant in this context.\cite{86,87,108} However, an obvious drawback of using finite uniform electron gases is that the resulting density-functional approximation for ensembles will inexorably depend on the number of electrons in the finite uniform electron gas (see below). Here, we propose to construct a weight-dependent LDA functional for the calculation of excited states in 1D systems by combining finite uniform electron gases with the usual infinite uniform electron gas paradigm.

As a finite uniform electron gas, we consider the ringium model in which electrons move on a perfect ring (i.e., a circle) but interact through the ring.\cite{84,85,87} The most appealing feature of ringium regarding the development of functionals in the context of GOK-DFT is the fact that both ground- and excited-state densities are uniform, and therefore equal. As a result, the ensemble density will remain constant (and uniform) as the ensemble weights vary. This is a necessary condition for being able to model the correlation ensemble derivatives [last term on the right-hand side of Eq. (18)]. Moreover, it has been shown that, in the thermodynamic limit, the ringium model is equivalent to the ubiquitous infinite uniform electron gas paradigm.\cite{85,108} Let us stress that, in a finite uniform electron
gas like ringium, the interacting and noninteracting densities match individually for all the states within the ensemble (these densities are all equal to the uniform density), which means that so-called density-driven correlation effects\textsuperscript{30,63,82,83} are absent from the model. Here, we will consider the most simple ringium system featuring electronic correlation effects, i.e., the two-electron ringium model.

The present weight-dependent density-functional approximation is specifically designed for the calculation of excited-state energies within GOK-DFT. To take into account both single and double excitations simultaneously, we consider a three-state ensemble including: (i) the ground state \((I = 0)\), (ii) the first singly-excited state \((I = 1)\), and (iii) the first doubly-excited state \((I = 2)\) of the (spin-polarized) two-electron ringium system. To ensure the GOK variational principle,\textsuperscript{41} the triensemble weights must fulfill the following conditions:\textsuperscript{48} 
\[
0 \leq w_2 \leq 1/3 \quad \text{and} \quad w_1 \leq (1 - w_2)/2,
\]
where \(w_1\) and \(w_2\) are the weights associated with the singly- and doubly-excited states, respectively. All these states have the same (uniform) density \(n = 2/(2\pi R)\), where \(R\) is the radius of the ring on which the electrons are confined. We refer the interested reader to Refs. 84, 85, and 87 for more details about this paradigm. Generalization to a larger number of states is straightforward and is left for future work.

\section*{B. Weight-dependent correlation functional}

Based on highly-accurate calculations (see supplementary material for additional details), one can write down, for each state, an accurate analytical expression of the reduced \(i.e.,\) per electron correlation energy\textsuperscript{85,86} via the following Padé approximant

\[
\tilde{\varepsilon}_c^{(I)}(n) = \frac{a_1^{(I)} n}{n + a_2^{(I)} \sqrt{n} + a_3^{(I)}},
\]

where the \(a_k^{(I)}\)'s are state-specific fitting parameters provided in Table I. The value of \(a_1^{(I)}\) is obtained via the exact high-density expansion of the correlation energy.\textsuperscript{85,86} Equation (53) provides three state-specific correlation density-functional approximations based on a two-electron system. Combining these, one can build the following three-state weight-dependent correlation density-functional approximation:

\[
\tilde{\varepsilon}_c^w(n) = (1 - w_1 - w_2)\tilde{\varepsilon}_c^{(0)}(n) + w_1\tilde{\varepsilon}_c^{(1)}(n) + w_2\tilde{\varepsilon}_c^{(2)}(n).
\]

\section*{C. LDA-centered functional}

One of the main driving forces behind the popularity of DFT is its “universal” nature, as xc density functionals can be applied to any electronic system. Obviously, the two-electron-based density-functional approximation for ensemble defined in Eq. (54) does not have this feature as it does depend on the number of electrons constituting the finite uniform electron gas. However, one can partially cure this dependency by applying a simple embedding scheme in which the two-electron finite uniform electron gas (the impurity) is embedded in the infinite uniform electron gas (the bath). The weight-dependence of the correlation functional is then carried exclusively by the impurity \(i.e.,\) the functional defined in Eq. (54), while the remaining correlation effects are provided by the bath \(i.e.,\) the usual LDA correlation functional. Following this simple strategy, which can be further theoretically justified by the generalized adiabatic connection formalism for ensembles (GACE) originally derived from Franck and Fromager,\textsuperscript{53} we propose to shift the two-electron-based density-functional approximation for ensemble defined in Eq. (54) as follows:

\[
\varepsilon_c^w(n) \rightarrow \varepsilon_c^w(n) = (1 - w_1 - w_2)e_c^{(0)}(n) + w_1e_c^{(1)}(n) + w_2e_c^{(2)}(n),
\]

where

\[
e_c^{(I)}(n) = e_c^{(I)}(n) + e_c^{LDA}(n) - e_c^{(0)}(n).
\]

In the following, we will use the LDA correlation functional that has been specifically designed for 1D systems in Ref. 110:

\[
e_c^{LDA}(n) = a_1^{LDA}F \left[ 1, \frac{3}{2} a_3^{LDA} \right],
\]

where \(F(a, b, c, x)\) is the Gauss hypergeometric function,\textsuperscript{111} and

\[
a_1^{LDA} = - \frac{\pi^2}{360},
\]

\[
a_2^{LDA} = \frac{3}{4} \ln 2\pi,
\]

\[
a_3^{LDA} = 2.408779.
\]

Note that the strategy described in Eq. (55) is general and can be applied to real (higher-dimensional) systems. In order to make the connection with the GACE formalism\textsuperscript{77,78} more explicit, one may recast Eq. (55) as

\[
\varepsilon_c^w(n) = \varepsilon_c^{LDA}(n) + w_1\left[ e_c^{(1)}(n) - e_c^{(0)}(n) \right] + w_2\left[ e_c^{(2)}(n) - e_c^{(0)}(n) \right],
\]

or, equivalently,

\[
\varepsilon_c^w(n) = \varepsilon_c^{LDA}(n) + \int_0^n \left[ e_c^{(K)}(n) - e_c^{(0)}(n) \right] d\xi_k,
\]

where the \(K\)th correlation excitation energy (per electron) is integrated over the ensemble weight \(d\xi_k\) at fixed (uniform) density \(n\). Equation (60) nicely highlights the centrality of the LDA in the present density-functional approximation for ensembles. In particular, \(e_c^{(0)}(n) = e_c^{LDA}(n)\). Consequently, in the following, we name this correlation functional “LDA” as it is a natural extension of the LDA for ensembles. Finally, we note that, by construction,

\[
\frac{\partial \varepsilon_c^w(n)}{\partial w_j} = \varepsilon_c^{(j)}(n) - e_c^{(0)}(n).
\]
IV. COMPUTATIONAL DETAILS

Having defined the eLDA functional in the previous section [see Eq. (59)], we now turn to its validation. Our testing playground for the validation of the eLDA functional is the ubiquitous “electrons in a box” model where \( N \) electrons are confined in a 1D box of length \( L \), a family of systems that we call \( N \)-boxium in the following. In particular, we investigate systems where \( L \) ranges from \( \pi/8 \) to \( 8\pi \) and \( 2 \leq N \leq 7 \). These inhomogeneous systems have non-trivial electronic structure properties which can be tuned by varying the box length. For small \( L \), the system is weakly correlated, while strong correlation effects dominate in the large-\( L \) regime.\(^{112,113} \)

We use as basis functions the (orthonormal) orbitals of the one-electron system, i.e.,

\[
\chi_{\mu}(x) = \begin{cases} \sqrt{2/L} \cos(\mu \pi x/L), & \mu \text{ is odd,} \\ \sqrt{2/L} \sin(\mu \pi x/L), & \mu \text{ is even,} \end{cases}
\]

with \( \mu = 1, \ldots, K \) and \( K = 30 \) for all calculations. The convergence threshold \( \tau = \max |F^w F^* - S^w F^w| \) [see Eq. (36)] of the KS-DFT self-consistent calculation is set to \( 10^{-5} \). In order to compute the various density-functional integrals that cannot be performed in closed form, a 51-point Gauss-Legendre quadrature is employed.

In order to test the present eLDA functional we perform various sets of calculations. To get reference excitation energies for both the single and double excitations, we compute full configuration interaction (FCI) energies with the Knowles-Handy FCI program described in Ref. 114. For the single excitations, we also perform time-dependent LDA (TDLDA) calculations [i.e., TDDFT with the LDA functional defined in Eq. (57)]. Its Tamm-Dancoff approximation version (TDA-TDLDA) is also considered.\(^{23} \)

Concerning the ensemble calculations, two sets of weight are tested: the zero-weight (ground-state) limit where \( w = (0, 0) \) and the equi- triensemble (or equal-weight state-averaged) limit where \( w = (1/3, 1/3) \).

V. RESULTS AND DISCUSSION

First, we discuss the linearity of the computed (approximate) ensemble energies. To do so, we consider 5-boxium with box lengths of \( L = \pi/8 \), \( L = \pi \), and \( L = 8\pi \), which correspond (qualitatively at least) to the weak, intermediate, and strong correlation regimes, respectively. The deviation from linearity of the three-state ensemble energy \( E^{(w_1, w_2)} \) (i.e., the deviation from the linearly-interpolated ensemble energy) is represented in Fig. 1 as a function of \( w_1 \) or \( w_2 \) while fulfilling the restrictions on the ensemble weights to ensure the GOK variational principle [i.e., \( 0 \leq w_2 \leq 1/3 \) and \( w_2 \leq w_1 \leq (1 - w_2)/2 \)]. To illustrate the magnitude of the ghost-interaction error, we report the KS-eLDA ensemble energy with and without GIC as explained above [see Eqs. (42) and (50)]. As one can see in Fig. 1, without GIC, the ensemble energy becomes less and less linear as \( L \) gets larger, while the GIC reduces the curvature of the ensemble energy drastically. It is important to note that, even though the GIC removes the explicit quadratic \( H_x \) terms from the ensemble energy, a non-negligible curvature remains in the GIC-eLDA ensemble energy when the electron correlation is strong. This is due to (i) the correlation eLDA functional, which contributes linearly (or even quadratically) to the individual energies [see Eqs. (47) and (49)], and (ii) the optimization of the ensemble KS orbitals in the presence of ghost-interaction errors [see Eqs. (35) and (39)].

Figure 2 reports the behavior of the three KS-eLDA individual energies as functions of the weights. Unlike in the exact theory, we do not obtain straight horizontal lines when plotting these energies, which is in agreement with the curvature of the GIC-eLDA ensemble energy discussed previously. Interestingly, the individual energies do not vary in the same way depending on the state considered and the value of the weights. We see for example that, within the biensemble (i.e., \( w_2 = 0 \)), the energies of the ground and first excited-state increase with respect to the first-excited-state weight \( w_1 \), thus showing that, in this case, we “deteriorate” these states by optimizing the orbitals for the ensemble, rather than for each state separately. The reverse actually occurs for the ground state in the triensemble as \( w_2 \) increases. The variations in the ensemble weights are essentially linear or quadratic. They are induced by the eLDA correlation functional, as readily seen from Eqs. (47) and (49). In the biensemble, the weight dependence of the first excited-state energy is reduced as the correlation increases. On the other hand, switching from a bi- to a triensemble systematically enhances the weight dependence, due to the lowering of the ground-state energy, as \( w_2 \) increases. The reverse is observed for the second excited state.

Figure 3 reports the excitation energies (multiplied by \( L^2 \)) for various methods and box lengths in the case of 5-boxium (i.e., \( N = 5 \)). Similar graphs are obtained for the other \( N \) values and they can be found in the supplementary material alongside the numerical data associated with each method. For small \( L \), the single and double excitations can be labeled as “pure”, as revealed by a thorough analysis of the FCI wavefunctions. In other words, each excitation is dominated by a sole, well-defined reference Slater determinant. However, when the box gets larger (i.e., as \( L \) increases), there is a strong mixing between the different excitation degrees. In particular, the single and double excitations strongly mix, which makes their assignment as single or double excitations more disputable.\(^{24} \)

| State             | \( l \)  | \( a_1^{(l)} \) | \( a_2^{(l)} \) | \( a_3^{(l)} \) |
|-------------------|--------|----------------|----------------|----------------|
| Ground state      | 0      | -0.0137078    | 0.0538982      | 0.0751740      |
| Singly-excited state | 1      | -0.0238184    | 0.00413142     | 0.0568648      |
| Doubly-excited state | 2      | -0.00935749   | -0.0261936     | 0.0336645      |
This can be clearly evidenced by the weights of the different configurations in the FCI wave function.

As shown in Fig. 3, all methods provide accurate estimates of the excitation energies in the weak correlation regime (i.e., small $L$). When the box gets larger, they start to deviate. For the single excitation, TDLDA is extremely accurate up to $L = 2\pi$, but yields more significant errors at larger $L$ by underestimating the excitation energies. TDA-TDLDA slightly corrects this trend thanks to error compensation. Concerning the eLDA functional, our results clearly evidence that the equiweight [i.e., $w = (1/3, 1/3)$] excitation energies are much more accurate than the ones obtained in the zero-weight limit [i.e., $w = (0, 0)$]. This is especially true, in the strong correlation regime, for the single excitation which is significantly improved by using equal weights. The effect on the double excitation is less pronounced. Overall, one clearly sees that, with equal weights, KS-eLDA yields accurate excitation energies for both single and double excitations. This conclusion is verified for smaller and larger numbers of electrons (see supplementary material).

For the same set of methods, Fig. 4 reports the error (in %) in excitation energies (as compared to FCI) as a function of $N$ for three values of $L$ ($\pi/8$, $\pi$, and $8\pi$). We draw similar conclusions as above: irrespectively of the number of electrons, the eLDA functional with equal weights is able to accurately model single and double excitations, with a very significant improvement brought by the equiensemble KS-eLDA orbitals as compared to their zero-weight (i.e., conventional ground-state) analogs. As a rule of thumb, in the weak and intermediate correlation regimes, we see that the single excitation obtained from equiensemble KS-eLDA is of the same quality as the one obtained in the linear response formalism (such as TDLDA). On the other hand, the double excitation energy only deviates from the FCI value by a few tenths of percent. Moreover, we note that, in the strong correlation regime (right graph of Fig. 4), the single excitation energy obtained at the equiensemble KS-eLDA level remains in good agreement with FCI and is much more accurate than the TDLDA and TDA-TDLDA excitation energies which can deviate by up to 60%. This also applies to the double excitation, the discrepancy between FCI and equiensemble KS-eLDA remaining of the order of a few percents in the strong correlation regime. These observations nicely illustrate the robustness of the GOK-DFT scheme in any correlation regime for both single and double excitations. This is definitely a very pleasing outcome, which additionally shows that, even though we have designed the eLDA functional based on a two-electron model system, the present methodology is applicable to any 1D electronic system, i.e., a system that has more than two electrons.

It is also interesting to investigate the influence of the correlation ensemble derivative contribution $\Delta^{(l)}_c$ to the $l$th excitation energy [see Eq. (52)]. In our case, both single ($l = 1$) and double ($l = 2$) excitations are considered. To do so, we have reported in Fig. 5, for $N = 3$, 5, and 7, the error percentage (with respect to FCI) as a function of the box length $L$ on the excitation energies obtained at the KS-eLDA level with and without $\Delta^{(l)}_c$ [i.e., the last term in Eq. (51)]. We first stress that although for $N = 3$ both single and double excitation ener-
Double excitation for \(N = 5\)

\[
\begin{align*}
\Omega_{\text{FCI}}^{(2)} & \quad \Omega_{\text{eLDA}}^{(2)} \text{ with } w = (0,0) \\
\Omega_{\text{eLDA}}^{(2)} \text{ with } w = (1/3,1/3) & \quad \Omega_{\text{eLDA-TDLDA}}^{(2)}
\end{align*}
\]

Box length \(L\)

Single excitation for \(N = 5\)

\[
\begin{align*}
\Omega_{\text{FCI}}^{(1)} & \quad \Omega_{\text{eLDA}}^{(1)} \text{ with } w = (0,0) \\
\Omega_{\text{eLDA}}^{(1)} \text{ with } w = (1/3,1/3) & \quad \Omega_{\text{eLDA-TDLDA}}^{(1)}
\end{align*}
\]

Box length \(L\)

FIG. 3. Excitation energies (multiplied by \(L^2\)) associated with the single excitation \(\Omega^{(1)}\) (bottom) and double excitation \(\Omega^{(2)}\) (top) of 5-boxium for various methods and box lengths \(L\). Graphs for additional values of \(N\) can be found as supplementary material.

Electronic energies are systematically improved (as the strength of electron correlation increases) when taking into account the correlation ensemble derivative, this is not always the case for larger numbers of electrons. For 3-boxium, in the zero-weight limit, the correlation ensemble derivative is significantly larger for the single excitation as compared to the double excitation; the reverse is observed in the equal-weight triensemble case. However, for 5- and 7-boxium, it hardly influences the double excitation (except when the correlation is strong), and slightly deteriorates the single excitation in the intermediate and strong correlation regimes. This non-systematic behavior in terms of the number of electrons might be a consequence of how we constructed eLDA. Indeed, as mentioned in Sec. III, the weight dependence of the eLDA functional is based on a two-electron finite uniform electron gas. Incorporating an \(N\)-dependence in the functional through the curvature of the Fermi hole, in the spirit of Ref. 108, would be valuable in this respect. This is left for future work. Interestingly, for the single excitation in 3-boxium, the magnitude of the correlation ensemble derivative is substantially reduced when switching from a zero-weight to an equal-weight calculation, while giving similar excitation energies, even in the strongly correlated regime. A possible interpretation is that, at least for the single excitation, equiensemble orbitals partially remove the burden of modelling properly the correlation ensemble derivative. This conclusion does not hold for larger numbers of electrons (\(N = 5\) or \(7\)), possibly because eLDA extracts density-functional correlation ensemble derivatives from a two-electron uniform electron gas, as mentioned previously. For the double excitation, the ensemble derivative remains important, even in the equiensemble case. To summarize, the equiensemble calculation is always more accurate than a zero-weight (i.e., a conventional ground-state DFT) one, with or without including the ensemble derivative correction. Note that the second term on the right-hand side of Eq. (51), which involves the weight-dependent correlation potential and the density difference between ground and excited states, has a negligible effect on the excitation energies (results not shown).

Finally, in Fig. 6, we report the same quantities as a function of the electron number for a box of length \(8\pi\) (i.e., in the strong correlation regime). The difference between the solid and dashed curves undoubtedly show that the correlation ensemble derivative has a rather significant impact on the double excitation (around 10%) with a slight tendency of worsening the excitation energies in the case of equal weights, as the number of electrons increases. It has a rather large influence (which decreases with the number of electrons) on the single excitation energies obtained in the zero-weight limit, showing once again that the usage of equal weights has the benefit of significantly reducing the magnitude of the correlation ensemble derivative.

VI. CONCLUDING REMARKS

A local and ensemble-weight-dependent correlation density-functional approximation (eLDA) has been constructed in the context of GOK-DFT for spin-polarized triensembles in 1D. The approach is general and can be extended to real (three-dimensional) systems\(^{108,115–118}\) and larger ensembles in order to model excited states in molecules and solids. Work is currently in progress in this direction.

Unlike any standard functional, eLDA incorporates derivative discontinuities through its weight dependence. The latter originates from the finite uniform electron gas on which eLDA is (partially) based. The KS-eLDA scheme, where exact individual exchange energies are combined with the eLDA correlation functional, delivers accurate excitation energies for both single and double excitations, especially when an equiensemble is used. In the latter case, the same weights are assigned to each state belonging to the ensemble. The improvement on the excitation energies brought by the KS-eLDA scheme is particularly impressive in the strong correlation regime where usual methods, such as TDLDA, fail. We have observed that, although the correlation ensemble derivative has a non-negligible effect on the excitation energies (especially for the single excitations), its magnitude can be significantly reduced by performing equiweight calculations instead of zero-weight calculations.

Let us finally stress that the present methodology can be extended to other types of ensembles like, for example, the \(N\)-centered ones\(^{49,50}\) thus allowing for the design of a LDA-type functional for the calculation of ionization potentials, electron affinities, and fundamental gaps. Like in the present eLDA, such a functional would incorporate the infamous derivative discontinuity contribution to the fundamental gap through its explicit weight dependence. We hope to report on this in the
FIG. 4. Error with respect to FCI in single and double excitation energies for $N$-boxium for various methods and electron numbers $N$ at $L = \pi/8$ (left), $L = \pi$ (center), and $L = 8\pi$ (right).

FIG. 5. Error with respect to FCI (in %) associated with the single excitation $\Omega^{(1)}$ (bottom) and double excitation $\Omega^{(2)}$ (top) as a function of the box length $L$ for 3-boxium (left), 5-boxium (center), and 7-boxium (right) at the KS-eLDA level with and without the contribution of the ensemble correlation derivative $\Delta_{c}^{(1)}$. Zero-weight (i.e., $w_1 = w_2 = 0$, red lines) and equiweight (i.e., $w_1 = w_2 = 1/3$, blue lines) calculations are reported.

ACKNOWLEDGMENTS

The authors thank Bruno Senjean and Clotilde Marut for stimulating discussions. This work has been supported through the EUR grant NanoX ANR-17-EURE-0009 in the framework of the “Programme des Investissements d’Avenir”.

SUPPLEMENTARY MATERIAL

See supplementary material for the additional details about the construction of the functionals, raw data and additional graphs.

1P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
2W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
3R. G. Parr and W. Yang, Density-functional theory of atoms and molecules (Oxford, Clarendon Press, 1989).
FIG. 6. Error with respect to FCI in single and double excitation energies for N-boxium (with a box length of \( L = 8\pi \)) as a function of the number of electrons \( N \) at the KS-eLDA level with and without the contribution of the ensemble correlation derivative \( \Delta_{N}^{\Omega} \). Zero-weight (i.e., \( w_{1} = w_{2} = 0 \), red lines) and equiweight (i.e., \( w_{1} = w_{2} = 1/3 \), blue lines) calculations are reported.

4H. L. Woodcock, H. F. Schaefer, and P. R. Schreiner, J. Phys. Chem. A 106, 11923 (2002).
5D. J. Tozer, J. Chem. Phys. 119, 12697 (2003).
6D. J. Tozer, R. D. Amos, N. C. Handy, B. O. Roos, and L. Serrano-Andres, Mol. Phys. 97, 859 (1999).
7A. Dreuw, J. L. Weissman, and M. Head-Gordon, J. Chem. Phys. 119, 2943 (2003).
8A. L. Sobolewski and W. Domcke, Chem. Phys. 294, 73 (2003).
9A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. 126, 4007 (2004).
10D. J. Tozer and N. C. Handy, J. Chem. Phys. 109, 10180 (1998).
11D. J. Tozer and N. C. Handy, Phys. Chem. Chem. Phys. 2, 2117 (2000).
12M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salaub, J. Chem. Phys. 108, 4439 (1998).
13M. E. Casida and D. R. Salaub, J. Chem. Phys. 113, 8918 (2000).
14E. Tapavicza, I. Tavernelli, U. Rothlisberger, C. Filippi, and M. E. Casida, J. Chem. Phys. 129, 124108 (2008).
15B. G. Levine, C. Ko, J. Quenneville, and T. J. Martinez, Mol. Phys. 104, 1039 (2006).
16P. Gori-Giorgi and M. Seidl, Phys. Chem. Chem. Phys. 14, 14405 (2010).
17E. Fromager, Mol. Phys. 113, 419 (2015).
18E. Gagliardi, D. G. Truhlar, G. L. Manni, R. K. Carlson, C. E. Hoyer, and J. L. Bao, Acc. Chem. Res. 50, 66 (2017).
19E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
20M. E. Casida, “Recent advances in density functional methods,” (World Scientific, Singapore) p. 155.
21M. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. 63, 287 (2012).
22G. Vignale, Phys. Rev. A 77, 062511 (2008).
23A. Dreuw and M. Head-Gordon, Chem. Rev. 105, 4009 (2005).
24T. Maitra, F. Zhang, R. J. Cave, and K. Burke, J. Chem. Phys. 120, 5932 (2004).
25R. J. Cave, F. Zhang, N. T. Maitra, and K. Burke, Chem. Phys. Lett. 389, 39 (2004).
26G. Mazur and R. Włodarczyk, J. Comput. Chem. 30, 811 (2009).
27P. Romaniello, D. Sangalli, J. A. Berger, P. Sottie, L. G. Molinari, L. Reinig, and G. Onida, J. Chem. Phys. 130, 044108 (2009).
28D. Sangalli, P. Romaniello, G. Onida, and A. Marini, J. Chem. Phys. 134, 034115 (2011).
29G. Mazur, M. Makowski, R. Włodarczyk, and Y. Aoki, Int. J. Quantum Chem. 111, 819 (2011).
30M. Huix-Rotllant, A. Ipatov, A. Rubio, and M. E. Casida, Chem. Phys. 391, 120 (2011).
31P. Elliott, S. Goldson, C. Canahui, and N. T. Maitra, Chem. Phys. 391, 110 (2011).
32N. T. Maitra, “Memory, History, initial-state dependence, and double-excitation,” in Fundamentals of Time-Dependent Density Functional Theory, Vol. 837, edited by M. A. Marques, N. T. Maitra, F. M. Nogueira, E. Gross, and A. Rubio (Springer Berlin Heidelberg, Berlin, Heidelberg, 2012) pp. 167–184.
33J. E. Sandstrom and M. Head-Gordon, J. Chem. Phys. 140, 114103 (2014).
34F.-P. Loos, M. Boggio-Pasqua, A. Scemama, M. Caffarel, and D. Jacquemin, J. Chem. Theory Comput. 15, 1939 (2019).
35A. B. O. Roos, M. P. Pulcher, P.-A. Malmqvist, and L. Serrano-Andres, “Adv. chem. phys.” (Wiley, New York, 1996) pp. 219–331.
36K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Phys. Chem. 94, 5483 (1990).
37C. Angeli, R. Cirimiglia, and J.-P. Malrieu, Chem. Phys. Lett. 350, 297 (2001).
38C. Angeli, R. Cirimiglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, J. Chem. Phys. 114, 10252 (2001).
39C. Angeli, R. Cirimiglia, and J.-P. Malrieu, J. Chem. Phys. 117, 9138 (2002).
40H. Helgaker, P. Jørgensen, and J. Olsen, Molecular Electronic-Structure Theory (John Wiley & Sons, Inc., 2013).
41E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2805 (1988).
42E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).
43L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. A 37, 2821 (1988).
44A. K. Theophilou, J. Phys. C 12, 5419 (1979).
45E. Partridge, N. I. Gidopoulos, and K. Pernali, Phys. Rev. A 87, 062501 (2013).
46Z.-H. Yang, J. R. Trail, A. Pribram-Jones, K. Burke, R. J. Needs, and C. A. Ulrich, Phys. Rev. A 90, 042501 (2014).
47K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B 95, 035120 (2017).
48K. Deur and E. Fromager, J. Chem. Phys. 150, 094106 (2019).
49B. Senjean and E. Fromager, Phys. Rev. A 98, 022513 (2018).
50B. Senjean and E. Fromager, Int. J. Quantum Chem. e26190.
51M. Levy, Phys. Rev. A 52, R4313 (1995).
52P. Perdew and M. Levy, Phys. Rev. Lett. 51, 1884 (1983).
53O. Francke and E. Fromager, Mol. Phys. 112, 1684 (2014).
54A. Borgoo, A. M. Teale, and T. Helgaker, AIP Conf. Proc. 1702, 090049 (2015).
55A. Kazaryan, J. Heuver, and M. Filatov, J. Phys. Chem. A 112, 12980 (2008).
56T. Gould and J. F. Dobson, J. Chem. Phys. 138, 014103 (2013).
57T. Gould and J. Toulouse, Phys. Rev. A 90, 050502 (2014).
58M. Filatov, M. Huix-Rotllant, and I. Burghardt, J. Chem. Phys. 142, 184104 (2015).
59M. Filatov, “Ensemble DFT Approach to Excited States of Strongly Correlated Molecular Systems,” in Density-Functional Methods for Excited States, Vol. 368, edited by N. Ferré, M. Filatov, and M. Huix-Rotllant (Springer International Publishing, Cham, 2015) pp. 97–124.
60M. Filatov, WIREs Comput. Mol. Sci. 5, 146 (2015).
61T. Gould and S. Pittalis, Phys. Rev. Lett. 119, 243001 (2017).
62T. Gould, L. Kronik, and S. Pittalis, J. Chem. Phys. 148, 174101 (2018).
63T. Gould and S. Pittalis, Phys. Rev. Lett. 123, 016401 (2019).
64F. Sagredo and K. Burke, J. Chem. Phys. 149, 134103 (2018).
65P. W. Ayers, M. Levy, and A. Nagy, Theor. Chem. Acc., 137 (2018).
66K. Deur, L. Mazouin, B. Senjean, and E. Fromager, Eur. Phys. J. B 91, 162 (2018).
67. E. Kraisler and L. Kronik, Phys. Rev. Lett. 110, 126403 (2013).
68. E. Kraisler and L. Kronik, J. Chem. Phys. 140, 18A540 (2014).
69. M. M. Alam, S. Knecht, and E. Fromager, Phys. Rev. A 94, 012511 (2016).
70. M. M. Alam, K. Deur, S. Knecht, and E. Fromager, J. Chem. Phys. 147, 204105 (2017).
71. A. Nagy, Int. J. Quantum Chem. 69, 247 (1998).
72. A. Nagy, J. Phys. B At. Mol. Opt. Phys. 34, 2363 (2001).
73. A. Nagy, S. Liu, and L. Bartolotti, J. Chem. Phys. 122, 134107 (2005).
74. E. Pastorczak and K. Pernal, J. Chem. Phys. 140, 18A514 (2014).
75. A. Pribram-Jones, Z.-h. Yang, J. R. Trail, K. Burke, R. J. Needs, and C. A. Ullrich, J. Chem. Phys. 140, 18A541 (2014).
76. W. Yang, P. Mori-Sánchez, and A. J. Cohen, J. Chem. Phys. 139, 104114 (2013).
77. Z.-h. Yang, A. Pribram-Jones, K. Burke, and C. A. Ullrich, Phys. Rev. Lett. 119, 033003 (2017).
78. B. Senjean, S. Knecht, H. J. A. Jensen, and E. Fromager, Phys. Rev. A 92, 012518 (2015).
79. B. Senjean, E. D. Hedegård, M. M. Alam, S. Knecht, and E. Fromager, Mol. Phys. 114, 968 (2016).
80. J. C. Smith, A. Pribram-Jones, and K. Burke, Phys. Rev. B 93, 245131 (2016).
81. D. J. Carrascal, J. Ferrer, C. J. Smith, and K. Burke, J. Phys. Condens. Matter 27, 393001 (2015).
82. E. Fromager, (2020), arXiv:2001.08605 [physics.chem-ph].
83. T. Gould and S. Pittalis, (2020), arXiv:2001.09429 [cond-mat.str-el].
84. P.-F. Loos and P. M. W. Gill, Phys. Rev. Lett. 108, 083002 (2012).
85. P.-F. Loos and P. M. W. Gill, J. Chem. Phys. 138, 164124 (2013).
86. P.-F. Loos, Phys. Rev. A 89, 052523 (2014).
87. P.-F. Loos, C. J. Ball, and P. M. W. Gill, J. Chem. Phys. 140, 18A524 (2014).
88. H. J. Schulz, Phys. Rev. Lett. 71, 1864 (1993).
89. M. M. Fogler, Phys. Rev. Lett. 94, 056405 (2005).
90. M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature 397, 598 (1999).
91. H. Ishii, H. Kataura, H. Shiozawa, H. Yoshioka, H. Otsubo, Y. Takayama, T. Miyahara, S. Suzuki, Y. Achiba, M. Nakatake, T. Narimura, M. Higashiguchi, K. Shimada, H. Namatame, and M. Taniguchi, Nature 426, 540 (2003).
92. V. V. Deshpande and M. Bockrath, Nature Physics 4, 314 (2008).
93. S. Meyer and K. A. Matveev, J. Phys.: Condens. Matter 21, 023203 (2009).
94. V. V. Deshpande, M. Bockrath, L. I. Glazman, and A. Yacoby, Nature 464, 209 (2010).
95. P. Schmelcher and L. S. Cederbaum, Phys. Rev. A 41, 4936 (1990).
96. K. K. Lange, E. I. Tellgren, M. R. Hoffmann, and T. Helgaker, Science 337, 327 (2012).
97. P. Schmelcher, Science 337, 302 (2012).
98. P. Schmelcher and L. S. Cederbaum, Int. J. Quantum Chem. 64, 501 (1997).
99. E. I. Tellgren, A. Soncini, and T. Helgaker, J. Chem. Phys. 129, 154114 (2008).
100. E. I. Tellgren, T. Helgaker, and A. Soncini, Phys. Chem. Chem. Phys. 11, 5489 (2009).
101. S. Bobiest, C. Schimeczek, and G. Wunner, Phys. Rev. A 89, 012505 (2014).
102. S. Stopkowicz, J. Gauss, K. K. Lange, E. I. Tellgren, and T. Helgaker, J. Chem. Phys. 143, 074110 (2015).
103. M. Levy and F. Zahariev, Phys. Rev. Lett. 113, 113002 (2014).
104. N. I. Gidopoulos, P. G. Papaconstantinou, and E. K. U. Gross, Phys. Rev. Lett. 88, 033003 (2002).
105. P.-F. Loos and P. M. W. Gill, Wiley Interdiscip. Rev. Comput. Mol. Sci. 6, 410 (2016).
106. P. M. W. Gill and P.-F. Loos, Theor. Chem. Acc. 131, 1069 (2012).
107. D. Agboola, A. L. Knol, P. M. W. Gill, and P.-F. Loos, J. Chem. Phys. 143, 084114 (2015).
108. P.-F. Loos, J. Chem. Phys. 146, 114108 (2017).
109. P.-F. Loos and P. M. W. Gill, J. Chem. Phys. 135, 214111 (2011).
110. P.-F. Loos, J. Chem. Phys. 138, 064108 (2013).
111. W. J. Olver, D. W. Lozier, R. F. Boisvert, and C. W. Clark, eds., NIST Handbook of Mathematical Functions (Cambridge University Press, New York, 2010).
112. J. Rogers and P.-F. Loos, J. Chem. Phys. 146, 044114 (2017).
113. E. J. M. Rogers, C. J. Ball, and P.-F. Loos, Phys. Rev. B 93, 235114 (2016).
114. P. J. Knowles and N. C. Handy, Comput. Phys. Commun. 54, 75 (1989).
115. P.-F. Loos and P. M. W. Gill, J. Chem. Phys. 131, 241101 (2009).
116. P.-F. Loos and P. M. W. Gill, Phys. Rev. Lett. 103, 123008 (2009).
117. P.-F. Loos and P. M. W. Gill, Chem. Phys. Lett. 500, 1 (2010).
118. P.-F. Loos and P. M. W. Gill, Phys. Rev. Lett. 105, 113001 (2010).