Weight Dependence of Local Exchange-Correlation Functionals in Ensemble Density-Functional Theory: Double Excitations in Two-Electron Systems

Clotilde Marut, Bruno Senjean, Emmanuel Fromager, and Pierre-François Loos

1) Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, France
2) Instituut-Lorentz, Universiteit Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands
3) Division of Theoretical Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
4) Laboratoire de Chimie Quantique, Institut de Chimie, CNRS, Université de Strasbourg, Strasbourg, France

Gross–Oliveira–Kohn (GOK) ensemble density-functional theory (GOK-DFT) is a time-independent extension of density-functional theory (DFT) which allows to compute excited-state energies via the derivatives of the ensemble energy with respect to the ensemble weights. Contrary to the time-dependent version of DFT (TD-DFT), double excitations can be easily computed within GOK-DFT. However, to take full advantage of this formalism, one must have access to a weight-dependent exchange-correlation functional in order to model the infamous ensemble derivative contribution to the excitation energies. In the present article, we discuss the construction of first-rung (i.e., local) weight-dependent exchange-correlation density-functional approximations for two-electron atomic and molecular systems (He and H₂) specifically designed for the computation of double excitations within GOK-DFT. In the spirit of optimally-tuned range-separated hybrid functionals, a two-step system-dependent procedure is proposed to obtain accurate energies associated with double excitations.

I. INTRODUCTION

Time-dependent density-functional theory (TD-DFT) has been the dominant force in the calculation of excitation energies of molecular systems in the last two decades. At a moderate computational cost (at least compared to the other excited-state ab initio methods), TD-DFT can provide accurate transition energies for low-lying excited states of organic molecules (see, for example, Ref. 4 and references therein). Importantlty, within the widely-used adiabatic approximation, setting up a TD-DFT calculation for a given system is an almost pain-free process from a user perspective as the only (yet essential) input variable is the choice of the ground-state exchange-correlation (xc) functional.

Similar to density-functional theory (DFT), TD-DFT is an in-principle exact theory which formal foundations rely on the Runge-Gross theorem. The Kohn-Sham (KS) formulation of TD-DFT transfers the complexity of the many-body problem to the xc functional thanks to a judicious mapping between a time-dependent non-interacting reference system and its interacting analog which both have exactly the same one-electron density.

However, TD-DFT is far from being perfect as, in practice, drastic approximations must be made. First, within the commonly used linear-response regime, the electronic spectrum relies on the (unperturbed) pure-ground-state KS picture, which may not be adequate in certain situations (such as strong correlation). Second, the time dependence of the functional is usually treated at the local approximation level within the standard adiabatic approximation. In other words, memory effects are absent from the xc functional which is assumed to be local in time (the xc energy is in fact an xc action, not an energy functional). Third and more importantly in the present context, a major issue of TD-DFT actually originates directly from the choice of the (ground-state) xc functional, and more specifically, the possible (not to say likely) substantial variations in the quality of the excitation energies for two different choices of xc functionals.

Because of its popularity, approximate TD-DFT has been studied in excruciated details by the community, and some researchers have quickly unveiled various theoretical and practical deficiencies. For example, TD-DFT has problems with charge-transfer and Rydberg excited states (the excitation energies are usually drastically underestimated) due to the wrong asymptotic behaviour of the semi-local xc functional. The development of range-separated hybrids provides an effective solution to this problem. From a practical point of view, the TD-DFT xc kernel is usually considered as static instead of being frequency dependent. One key consequence of this so-called adiabatic approximation (based on the assumption that the density varies slowly with time) is that double excitations are completely absent from the TD-DFT spectra. Although these double excitations are usually experimentally dark (which means that they usually cannot be observed in photo-absorption spectroscopy), these states play, indirectly, a key role in many photochemistry mechanisms. They are, moreover, a real challenge for high-level computational methods.

One possible solution to access double excitations within TD-DFT is provided by spin-flip TD-DFT which describes double excitations as single excitations from the lowest triplet state. However, spin contamination might be an issue. Instead of being frequency dependent, the xc functional is made frequency dependent, which allows to treat doubly-excited states. Note that a simple remedy based on a mixed reference reduced density matrix has been recently introduced by Lee et al. In order to go beyond the adiabatic approximation, a dressed TD-DFT approach has been proposed by Maitra and coworkers (see also Refs. 24, 38–41). In this approach the xc kernel is made frequency dependent, which allows to treat doubly-excited states.

Maybe surprisingly, another possible way of accessing double excitations is to resort to a time-independent formalism. With a computational cost similar to traditional KS-DFT, DFT for ensembles (eDFT) is a viable alternative that follows such a strategy and is currently under active development. In the assumption of monotonically de-
increasing weights, eDFT for excited states has the undeniable advantage to be based on a rigorous variational principle for ground and excited states, the so-called Gross–Oliveria–Kohn (GOK) variational principle.\textsuperscript{48} In short, GOK-DFT (i.e., eDFT for neutral excitations) is the density-based analog of state-averaged wave function methods, and excitation energies can then be easily extracted from the total ensemble energy.\textsuperscript{46} Although the formal foundations of GOK-DFT have been set three decades ago,\textsuperscript{48–50} its practical developments have been rather slow. We believe that it is partly due to the lack of accurate approximations for GOK-DFT. In particular, to the best of our knowledge, although several attempts have been made,\textsuperscript{52,83} an explicitly weight-dependent density-functional approximation for ensembles (eDFA) has never been developed for atoms and molecules from first principles. The present contribution paves the way towards this goal.

The local-density approximation (LDA), as we know it, is based on the uniform electron gas (UEG) also known as jellium, an hypothetical infinite substance where an infinite number of electrons “bathe” in a (uniform) positively-charged jelly.\textsuperscript{84} Although the Hohenberg–Kohn theorems\textsuperscript{5} are here to provide firm theoretical grounds to DFT, modern KS-DFT rests largely on the presumed similarity between this hypothetical UEG and the electronic behaviour in a real system.\textsuperscript{6} However, Loos and Gill have recently shown that there exists other UEGs which contain finite numbers of electrons (more like in a molecule),\textsuperscript{85,86} and that they can be exploited to construct ground-state functionals as shown in Refs. 87–89, where the authors proposed generalised LDA exchange and correlation functionals.

Electrons restricted to remain on the surface of a $D$-sphere (where $D$ is the dimensionality of the surface of the sphere) are an example of finite UEGs (FUEGs).\textsuperscript{35} Very recently,\textsuperscript{90} two of the present authors have taken advantages of these FUEGs to construct a local, weight-dependent correlation functional specifically designed for one-dimensional many-electron systems. Unlike any standard functional, this first-rung functional automatically incorporates ensemble derivative contributions thanks to its natural weight dependence,\textsuperscript{91,92} and has shown to deliver accurate excitation energies for both single and double excitations. In order to extend this methodology to more realistic (atomic and molecular) systems, we combine here these FUEGs with the usual infinite UEG (UEG) to construct a weigh-dependent LDA correlation functional for ensembles, which is specifically designed to compute double excitations within GOK-DFT.

The paper is organised as follows. In Sec. II, the theory behind GOK-DFT is briefly presented. Section III provides the computational details. The results of our calculations for two-electron systems are reported and discussed in Sec. IV. Finally, we draw our conclusions in Sec. V. Unless otherwise stated, atomic units are used throughout.

II. THEORY

Let us consider a GOK ensemble of $M$ electronic states with individual energies $E^{(0)} \leq \ldots \leq E^{(M-1)}$, and (normalised) monotonically decreasing weights $w \equiv (w_1, \ldots, w_{M-1})$, i.e., $w_0 = 1 - \sum_{i=1}^{M-1} w_i$, and $w_0 \geq \ldots \geq w_{M-1}$. The corresponding ensemble energy

\[ E^w = \sum_{I=0}^{M-1} w_I E^{(I)} \]  

can be obtained from the GOK variational principle as follows:\textsuperscript{48}

\[ E^w = \min_{\tilde{\Gamma}^w} \text{Tr} \left[ \tilde{\Gamma}^w \hat{H} \right], \]  

where $\hat{H} = \hat{T} + \hat{W}_{\text{xc}} + \hat{V}_{\text{ne}}$ contains the kinetic, electron-electron and nuclei-electron interaction potential operators, respectively, $\text{Tr}$ denotes the trace, and $\tilde{\Gamma}^w$ is a trial density matrix operator of the form

\[ \tilde{\Gamma}^w = \sum_{I=0}^{M-1} w_I |\overline{\Psi}^{(I)}\rangle \langle \overline{\Psi}^{(I)}|, \]  

where $|\overline{\Psi}^{(I)}\rangle_{0 \leq I \leq M-1}$ is a set of $M$ orthonormal trial wave functions.

The lower bound of Eq. (2) is reached when the set of wave functions correspond to the exact eigenstates of $\hat{H}$, i.e., $|\Psi^{(I)}\rangle_{0 \leq I \leq M-1} = |\overline{\Psi}^{(I)}\rangle_{0 \leq I \leq M-1}$. Multiplet degeneracies can be easily handled by assigning the same weight to the degenerate states.\textsuperscript{49} One of the key feature of the GOK ensemble is that excitation energies can be extracted from the ensemble energy via differentiation with respect to the individual excited-state weights $w_I$ ($I > 0$):

\[ \frac{\partial E^w}{\partial w_I} = E^{(I)} - E^{(0)} = \Omega^{(I)}. \]

Turning to GOK-DFT, the extension of the Hohenberg–Kohn theorem to ensembles allows to rewrite the exact variational expression for the ensemble energy as\textsuperscript{49}

\[ E^w = \min_n \left\{ F^w[n] + \int v_{\text{ne}}(r)n(r)dr \right\}, \]

where $v_{\text{ne}}(r)$ is the external potential and $F^w[n]$ is the universal ensemble functional (the weight-dependent analog of the Hohenberg–Kohn universal functional for ensembles). In the KS formulation\textsuperscript{49}, this functional can be decomposed as

\[ F^w[n] = \text{Tr} \left[ \hat{T} \hat{\gamma}^w[n] \hat{T} \right] + E_{\text{xc}}[n] + E^w[n], \]

where $\text{Tr} \left[ \hat{T} \hat{\gamma}^w[n] \hat{T} \right] = T^w[n]$ is the noninteracting ensemble kinetic energy functional,

\[ \hat{\gamma}^w[n] = \sum_{I=0}^{M-1} w_I |\Phi^w_{+}[n]\rangle \langle \Phi^w_{+}[n]| \]  

is the density-functional KS density matrix operator, and $|\Phi^w_{+}[n]\rangle_{0 \leq I \leq M-1}$ are single-determinant wave functions (or configuration state functions). Their dependence on the density is determined from the ensemble density constraint

\[ \sum_{I=0}^{M-1} w_I n|\Phi^w_{+}[n]\rangle(r) = n(r). \]
where a decomposition might be problematic as inserting an ensemble density into $E_{\text{H}}[n]$ causes the infamous ghost-interaction error. The latter should in principle be removed from the density-functional ensemble as follows

$$E^w[n] = \sum_{i=0}^{M-1} w_i \langle \Psi^w_i | \hat{\Psi}_0 | \Psi^w_i \rangle - E_{\text{H}}[n].$$

The minimum in Eq. (5) is reached when the density $n$ equals the exact ensemble one

$$n^w(r) = \sum_{i=0}^{M-1} w_i n_{i}^w(r).$$

In practice, the minimising KS density matrix operator $\hat{\rho}^w[n^w]$ can be determined from the following KS reformulation of the GOK variational principle,

$$E^w = \min_{\hat{\rho}^w} \left[ \text{Tr} \left[ \hat{\rho}^w \left( \hat{H} + \hat{V}_n \right) \right] + E_{\text{H}}[n_{\text{KS}}^w] + E^w_{\text{xc}}[n_{\text{KS}}^w] \right],$$

where $n_{i}^w(r) = \sum_{i=0}^{M-1} w_i n_{i}^w(r)$, is a trial ensemble density. As a result, the orbitals $\{\phi^w_p(r)\}_{i=0}^{M-1}$ from which the KS wave functions $\{\Phi^w_i[n^w]\}_{i=0}^{M-1}$ are constructed can be obtained by solving the following ensemble KS equation

$$\left( \hat{h}(r) + \frac{\delta E^w_{\text{Hac}}[n^w]}{\delta n(r)} \right) \phi^w_p(r) = \epsilon^w_p \phi^w_p(r),$$

where $\delta E^w_{\text{Hac}}[n^w] / \delta n(r) = \int n(r') \frac{\delta E^w_{\text{xc}}[n^w]}{\delta n(r')} dr' + \frac{\delta E^w_{\text{xc}}[n^w]}{\delta n(r)}$. The ensemble density can be obtained directly (and exactly, if no approximation is made) from these orbitals, i.e.,

$$n^w(r) = \sum_{i=0}^{M-1} w_i \left( \sum_{p} f^{(f)}_p [\phi^w_p(r)]^2 \right),$$

where $f^{(f)}_p$ denotes the occupation of $\phi^w_p(r)$ in the $f$th KS wave function $\Phi^w_f[n^w]$. Turning to the excitation energies, they can be extracted from the density-functional ensemble as follows [see Eqs. (4) and (12) and Refs. 46 and 49]:

$$\Omega^{(f)} = \epsilon^{w}_f - \epsilon^0_f + \frac{\delta E^w_{\text{xc}}[n^w]}{\delta \epsilon^{w}_f} \bigg|_{n=n^w},$$

where

$$\epsilon^{w}_f = \sum_{p} f^{(f)}_p \epsilon^w_p$$

is the energy of the $f$th KS state.

Equation (16) is our working equation for computing excitation energies from a practical point of view. Note that the individual KS densities $n_{\sigma}^{\gamma}[r](r) = \sum_{f=1}^{K} f^{(f)}_p [\phi^w_p(r)]^2$ do not necessarily match the exact (interacting) individual-state densities $n_{\sigma}^{\gamma}(r)$ as the non-interacting KS ensemble is expected to reproduce the true interacting ensemble density $n^w(r)$ defined in Eq. (11), and not each individual density. Nevertheless, these densities can still be extracted in principle exactly from the KS ensemble as shown by one of the author.

In the following, we will work at the (weight-dependent) ensemble LDA (eLDA) level of approximation, i.e.

$$E^w_{\text{xc}}[n] \approx \int \epsilon^{w}_{\sigma}(n(r)) n(r) dr,$$

$$\delta E^w_{\text{xc}}[n] \approx \frac{\delta \epsilon^{w}_{\sigma}(n)}{\delta n} n(r) + \epsilon^{w}_{\sigma}(n).$$

We will also adopt the usual decomposition, and write down the weight-dependent xc functional as

$$\epsilon^{w}_{\sigma}(n) = \epsilon^w_1(n) + \epsilon^w_2(n),$$

where $\epsilon^w_1(n)$ and $\epsilon^w_2(n)$ are the weight-dependent density-functional exchange and correlation energies per particle, respectively. The explicit construction of these functionals is discussed at length in Sec. IV.

### III. COMPUTATIONAL DETAILS

The self-consistent GOK-DFT calculations [see Eqs. (13) and (15)] have been performed in a restricted formalism with the QuACN software, freely available on github, where the present weight-dependent functionals have been implemented. For more details about the self-consistent implementation of GOK-DFT, we refer the interested reader to Ref. 90 where additional technical details can be found. For all calculations, we use the aug-cc-pVXZ (X = D, T, Q, and 5) Dunning family of atomic basis sets. Numerical quadratures are performed with the numgrid library using 194 angular points (Lebedev grid) and a radial precision of $10^{-9}$.

This study deals only with spin-unpolarised systems, i.e., $n_\uparrow = n_\downarrow = n/2$ (where $n_\uparrow$ and $n_\downarrow$ are the spin-up and spin-down electron densities). Moreover, we restrict our study to the case of a three-state ensemble (i.e., $M = 3$) where the ground state ($I = 0$ with weight $1 - w_1 - w_2$), a singly-excited state ($I = 1$ with weight $w_1$), as well as the lowest doubly-excited state ($I = 2$ with weight $w_2$) are considered. Assuming that the singly-excited state is lower in energy than the doubly-excited state, one should have $0 \leq w_2 \leq 1/3$ and $w_2 \leq w_1 \leq (1 - w_2)/2$ to ensure the GOK variational principle. If the doubly-excited state (whose weight is denoted $w_2$ throughout this work) is lower in energy than the singly-excited state (with weight $w_1$), which can be the case as one would notice later, then one has to swap $w_1$ and $w_2$ in the above inequalities. Note also that additional lower-in-energy single excitations may have to be included into the ensemble before incorporating the double excitations.
excitation of interest. In the present exploratory work, we will simply exclude them from the ensemble and leave the more consistent (from a GOK point of view) description of all low-lying excitations to future work. Unless otherwise stated, we set the same weight to the two excited states (i.e., \( w \equiv w_1 = w_2 \)). In this case, the ensemble energy will be written as a single-weight quantity, \( E^w \). The zero-weight limit (i.e., \( w \equiv w_1 = w_2 = 0 \)), and the equi-weight ensemble (i.e., \( w \equiv w_1 = w_2 = 1/3 \)) are considered in the following. (Note that the zero-weight limit corresponds to a conventional ground-state KS calculation.)

Let us finally mention that we will sometimes “violate” the GOK variational principle in order to build our weight-dependent functionals by considering the extended range of weights \( 0 \leq w_2 \leq 1 \). The pure-state limit, \( w_1 = 0 \wedge w_2 = 1 \), is of particular interest as it is, like the (ground-state) zero-weight limit, a genuine saddle point of the restricted KS equations [see Eqs. (12) and (13)], and it matches perfectly the results obtained with the maximum overlap method (MOM) developed by Gilbert, Gill and coworkers.\(^{101-103}\) From a GOK-DFT perspective, considering a (stationary) pure-excited-state limit can be seen as a way to construct density-functional approximations to individual exchange and state-driven correlation within an ensemble.\(^{63,93,104}\) However, when it comes to compute excitation energies, we will exclusively consider ensembles where the largest weight is assigned to the ground state.

### IV. RESULTS AND DISCUSSION

In this Section, we propose a two-step procedure to design, first, a weight- and system-dependent local exchange functional in order to remove some of the curvature of the ensemble energy. Second, we describe the construction of a universal, weight-dependent local correlation functional based on FUEGs. This procedure is applied to various two-electron systems in order to extract excitation energies associated with doubly-excited states.

#### A. Hydrogen molecule at equilibrium

##### 1. Weight-independent exchange functional

First, we compute the ensemble energy of the \( \text{H}_2 \) molecule at equilibrium bond length (i.e., \( R_{\text{H-H}} = 1.4 \) bohr) using the aug-cc-pVTZ basis set and the conventional (weight-independent) LDA Slater exchange functional (i.e., no correlation functional is employed),\(^{105,106}\) which is explicitly given by

\[
\epsilon^S_{\text{LDA}}(n) = C_n n^{1/3}, \quad C_n = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}.
\]

In the case of \( \text{H}_2 \), the ensemble is composed by the ground state of electronic configuration \( 1\sigma_g^2 \), the lowest singly-excited state of configuration \( 1\sigma_g 2\sigma_g^* \), and the lowest doubly-excited state of configuration \( 1\sigma_g^2 3\sigma_g^* \) (which has an auto-ionising resonance nature\(^{107}\)) which all are of symmetry \( \Sigma_g^+ \). As mentioned previously, the lower-lying singly-excited states like \( 1\sigma_g 3\sigma_g^* \) and \( 1\sigma_g 4\sigma_g^* \), which should in principle be part of the ensemble (see Fig. 3 in Ref. 108), have been excluded, for simplicity.

The deviation from linearity of the ensemble energy \( E^w \) [we recall that \( w_1 = w_2 = w \)] is depicted in Fig. 1 as a function of weight \( 0 \leq w \leq 1/3 \) (blue curve). Because the Slater exchange functional defined in Eq. (21) does not depend on the ensemble weight, there is no contribution from the ensemble derivative term [last term in Eq. (16)]. As anticipated, \( E^w \) is far from being linear, which means that the excitation energy associated with the doubly-excited state obtained via the derivative of the ensemble energy with respect to \( w_2 \) (and taken at \( w_2 = w = w_1 \)) varies significantly with \( w \) (see blue curve in Fig. 2). Taking as a reference the full configuration interaction (FCI) value of 28.75 eV obtained with the aug-mcc-pV8Z basis set,\(^{102}\) one can see that the excitation energy varies by more than 8 eV from \( w = 0 \) to 1/3. Note that the exact xc ensemble functional would yield a perfectly linear ensemble energy and, hence, the same value of the excitation energy independently of the ensemble weights.

![Fig. 1. H\(_2\) at equilibrium bond length: deviation from linearity of the ensemble energy \( E^w \) (in hartree) as a function of \( w \) for various functionals and the aug-cc-pVTZ basis set. See main text for the definition of the various functional’s acronyms.](image1)

![Fig. 2. H\(_2\) at equilibrium bond length: error (with respect to FCI) in the excitation energy \( \Omega^{(2)} \) (in eV) associated with the doubly-excited state as a function of \( w \) for various functionals and the aug-cc-pVTZ basis set. See main text for the definition of the various functional’s acronyms.](image2)
2. Weight-dependent exchange functional

Second, in order to remove some of this spurious curvature of the ensemble energy (which is mostly due to the ghost-interaction error\textsuperscript{51} but not only\textsuperscript{90}), one can easily reverse-engineer (for this particular system, geometry, basis set, and excitation) a local exchange functional to make $E^{0,w_2}$ as linear as possible for $0 \leq w_2 \leq 1$ assuming a perfect linearity between the pure-state limits $w_1 = w_2 = 0$ (ground state) and $w_1 = 0 \wedge w_2 = 1$ (doubly-excited state). Doing so, we have found that the following weight-dependent exchange functional (denoted as CC-S for “curvature-corrected” Slater functional)

$$
E^{w_2,\text{CC-S}}_x(n) = C^{w_2}_x n^{1/3},
$$

(22)

with

$$
\frac{C^{w_2}_x}{C_x} = 1 - w_2(1-w_2) \left[ \alpha + \beta(w_2-1/2) + \gamma(w_2-1/2)^2 \right],
$$

(23)

and

$$
\alpha = +0.575 178, \quad \beta = -0.021 108, \quad \gamma = -0.367 189,
$$

(24a)

makes the ensemble energy $E^{0,w_2}$ almost perfectly linear (by construction), and removes some of the curvature of $\tilde{E}^w$ (see yellow curve in Fig. 1). It also allows to “flatten the curve” making the excitation energy much more stable (with respect to $w$), and closer to the FCI reference (see yellow curve in Fig. 2).

The parameters $\alpha$, $\beta$, and $\gamma$ entering Eq. (23) have been obtained via a least-square fit of the non-linear component of the ensemble energy computed between $w_2 = 0$ and $w_2 = 1$ by steps of 0.025. Although this range of weights is inconsistent with GOK theory, we have found that it is important, from a practical point of view, to ensure a correct behaviour in the whole range of weights in order to obtain accurate excitation energies. Note that the CC-S functional depends on $w_2$ only, and not $w_1$, as it is specifically tuned for the double excitation. Hence, only the double excitation includes a contribution from the ensemble derivative term [see Eq. (16)].

The present procedure can be related to optimally-tuned range-separated hybrid functionals,\textsuperscript{109} where the range-separation parameters (which control the amount of short- and long-range exact exchange) are determined individually for each system by iteratively tuning them in order to enforce non-empirical conditions related to frontier orbitals (e.g., ionisation potential, electron affinity, etc) or, more importantly here, the piecewise linearity of the ensemble energy for ensemble states described by a fractional number of electrons.\textsuperscript{109-112} In this context, the analog of the “ionisation potential theorem” for the (first) excitations, for example, would read as follows [see Eqs. (1), (4), and (16)]:

$$
2 \left( E^{w_1=1/2}_{\text{CC-S}} - E^{w_1=0}_{\text{CC-S}} \right) = \int d\mathbf{k} \left[ E^{w_1}_{\text{CC-S}} - E^{w_1}_{\text{CC-S}} \right] - \int d\mathbf{k} \left[ \frac{\partial E^{w_1}_{\text{CC-S}}}{\partial w_1} \right]_{w_1=n_1}.
$$

(25)

We enforce this type of exact constraint (to the maximum possible extent) when optimising the parameters in Eq. (23) in order to minimise the curvature of the ensemble energy. As readily seen from Eq. (23) and graphically illustrated in Fig. 3 (red curve), the weight-dependent correction does not affect the two ghost-interaction-free limits at $w_1 = w_2 = 0$ and $w_1 = 0 \wedge w_2 = 1$ (i.e., the pure-state limits), as $C^{w_2}_x$ reduces to $C_x$ in these two limits. Indeed, it is important to ensure that the weight-dependent functional does not alter these pure-state limits, which are genuine saddle points of the KS equations, as mentioned above. Finally, let us mention that, around $w_2 = 0$, the behaviour of Eq. (23) is linear: this is the main feature that one needs to catch in order to get accurate excitation energies in the zero-weight limit. We shall come back to this point later on.

3. Weight-independent correlation functional

Third, we add up correlation effects via the conventional VWN5 local correlation functional.\textsuperscript{113} For the sake of clarity, the explicit expression of the VWN5 functional is not reported here but it can be found in Ref. 113. The combination of the (weight-independent) Slater and VWN5 functionals (SVWN5) yield a highly convex ensemble energy (green curve in Fig. 1), while the combination of CC-S and VWN5 (CC-SVWN5) exhibit a smaller curvature and improved excitation energies (red curve in Figs. 1 and 2), especially at small weights, where the CC-SVWN5 excitation energy is almost spot on.

4. Weight-dependent correlation functional

Fourth, in the spirit of our recent work,\textsuperscript{90} we design a universal, weight-dependent correlation functional. To build this correlation functional, we consider the singlet ground state, the first singly-excited state, as well as the first doubly-excited...
The reduced (i.e., per electron) Hartree-Fock (HF) energies for these three states are
\[
\epsilon_{HF}^{(0)}(n) = \frac{4}{3} \frac{n^{1/3}}{\pi}, \quad (26a)
\]
\[
\epsilon_{HF}^{(1)}(n) = \frac{3\pi^2}{4} n^{2/3} + \frac{16}{10} \frac{n^{1/3}}{\pi}, \quad (26b)
\]
\[
\epsilon_{HF}^{(2)}(n) = \frac{3\pi^2}{2} n^{2/3} + \frac{176}{105} \frac{n^{1/3}}{\pi}. \quad (26c)
\]

Thanks to highly-accurate calculations\(^\text{114-116}\) and the expressions of the HF energies provided by Eqs. (26a), (26b), and (26c), one can write down, for each state, an accurate analytical expression of the reduced correlation energy\(^\text{87,117}\) via the following simple Padé approximant\(^\text{90,118}\)
\[
\epsilon_c^{(l)}(n) = \frac{a_1^{(l)}}{1 + a_2^{(l)} n^{-1/6} + a_3^{(l)} n^{-1/3}}, \quad (27)
\]

where \(a_2^{(l)}\) and \(a_3^{(l)}\) are state-specific fitting parameters, which are provided in Table II. The value of \(a_1^{(l)}\) is obtained via the exact high-density expansion of the correlation energy.\(^\text{88}\) Equation (27) is depicted in Fig. 4 for each state alongside the data gathered in Table I. Combining these, we build a three-state weight-dependent correlation functional:
\[
\epsilon_c^{w}(n) = (1 - w_1 - w_2)\epsilon_c^{(0)}(n) + w_1\epsilon_c^{(1)}(n) + w_2\epsilon_c^{(2)}(n), \quad (28)
\]
where, unlike in the exact theory,\(^\text{93}\) the individual components are weight independent.

| \(R\) | Ground state \(I = 0\) | Single excitation \(I = 1\) | Double excitation \(I = 2\) |
|-------|-----------------|-----------------|-----------------|
| 0     | 0.023 818       | 0.028 281       | 0.014 463       |
| 0.1   | 0.023 392       | 0.027 886       | 0.014 497       |
| 0.2   | 0.022 979       | 0.027 499       | 0.014 523       |
| 0.5   | 0.021 817       | 0.026 394       | 0.014 561       |
| 1     | 0.020 109       | 0.024 718       | 0.014 512       |
| 2     | 0.017 371       | 0.021 901       | 0.014 142       |
| 5     | 0.012 359       | 0.016 295       | 0.012 334       |
| 10    | 0.008 436       | 0.011 494       | 0.009 716       |
| 20    | 0.005 257       | 0.007 349       | 0.006 744       |
| 50    | 0.002 546       | 0.003 643       | 0.003 584       |
| 100   | 0.001 399       | 0.002 025       | 0.002 059       |
| 150   | 0.000 972       | 0.001 414       | 0.001 458       |

Because our intent is to incorporate into standard functionals (which are “universal” in the sense that they do not depend on the number of electrons) information about excited states that will be extracted from finite systems (whose properties may depend on the number of electrons), we employ a simple “embedding” scheme where the two-electron FUEG (the impurity) is embedded in the UEG (the bath). As explained further in Ref. 90, this embedding procedure can be theoretically justified by the generalised adiabatic connection formalism for ensembles originally derived by Franck and Fromager.\(^\text{52}\) The weight-dependence of the correlation functional is then carried exclusively by the impurity \(i.e., \) the functional defined in (28), while the remaining effects are produced by the bath \(i.e., \) the usual ground-state LDA correlation functional.

Consistently with such a strategy, Eq. (28) is “centred” on its corresponding weight-independent VWN5 LDA reference
\[
\epsilon_c^{VWN5}(n) = (1 - w_1 - w_2)\epsilon_c^{(0)}(n) + w_1\epsilon_c^{(1)}(n) + w_2\epsilon_c^{(2)}(n) \quad (29)
\]
via the following global, state-independent shift:
\[
\epsilon_c^{(l)}(n) = \epsilon_c^{(l)}(n) + \epsilon_c^{VWN5}(n) - \epsilon_c^{(0)}(n). \quad (30)
\]
In the following, we name this weight-dependent correlation functional “\(\epsilon^{VWN5}\)” as it is a natural extension of the VWN5
local correlation functional for ensembles. Also, Eq. (29) can be recast as
\[ \epsilon_c^{w\text{eVWN5}}(n) = \epsilon_c^{\text{VWN5}}(n) + w_1[\epsilon_c^{(1)}(n) - \epsilon_c^{(0)}(n)] + w_2[\epsilon_c^{(2)}(n) - \epsilon_c^{(0)}(n)], \]
(31)
which nicely highlights the centrality of VWN5 in the present weight-dependent density-functional approximation for ensembles. In particular, \( \epsilon_c^{(0)},\text{eVWN5}(n) = \epsilon_c^{\text{VWN5}}(n) \). We note also that, by construction, we have
\[ \frac{\partial \epsilon_c^{w\text{eVWN5}}(n)}{\partial w_1} = \epsilon_c^{(1)}(n) - \epsilon_c^{(0)}(n), \]
(32)
showing that the weight correction is purely linear in eVWN5 and entirely dependent on the FUEG model. Contrary to the CC-S exchange functional which only depends on \( w_2 \), the eVWN5 correlation functional depends on both weights.

As shown in Fig. 1, the CC-SeVWN5 ensemble energy (as a function of \( w \)) is very slightly less concave than its CC-SVWN5 counterpart and it also improves (not by much) the excitation energy (see purple curve in Fig. 2).

For a more qualitative picture, Table III reports excitation energies for various methods and basis sets. In particular, we report the excitation energies obtained with GOK-DFT in the zero-weight limit (i.e., \( w = 0 \)) and for equi-weights (i.e., \( w = 1/3 \)). These excitation energies are computed using Eq. (16).

For comparison, we also report results obtained with the linear interpolation method (LIM).\(^{78,79}\) The latter simply consists in extracting the excitation energies (which are weight-independent, by construction) from the equi-ensemble energies, as follows:
\[ \Omega_{\text{LIM}}^{(1)} = 2[E^{w=(1/2,0)} - E^{w=(0,0)}], \]
(33a)
\[ \Omega_{\text{LIM}}^{(2)} = 3[E^{w=(1/3,1/3)} - E^{w=(1/2,0)}] + \frac{1}{2}\Omega_{\text{LIM}}^{(1)}. \]
(33b)
For a general expression with multiple (and possibly degenerate) states, we refer the reader to Eq. (106) of Ref. 78, where LIM is shown to interpolate linearly the ensemble energy between equi-ensembles. Note that two calculations are needed to get the first LIM excitation energy, with an additional equi-ensemble calculation for each higher excitation energy.

Additionally, MOM excitation energies\(^{101–103}\)
\[ \Omega_{\text{MOM}}^{(1)} = E^{w=(1,0)} - E^{w=(0,0)}, \]
(34a)
\[ \Omega_{\text{MOM}}^{(2)} = E^{w=(0,1)} - E^{w=(0,0)}, \]
(34b)
which also require three separate calculations at a different set of ensemble weights, have been computed for further comparisons.

As readily seen in Eqs. (33a) and (33b), LIM is a recursive strategy where the first excitation energy has to be determined in order to compute the second one. In the above equations, we assumed that the singly-excited state (with weight \( w_1 \)) is lower in energy than the doubly-excited state (with weight \( w_2 \)). If the ordering changes (like in the case of the stretched \( H_2 \) molecule, see below), one should substitute \( E^{w=(0,1/2)} \) by \( E^{w=(1/2,0)} \) in Eqs. (33a) and (33b) which then correspond to the excitation energies of the doubly-excited and singly-excited states, respectively. The same holds for the MOM excitation energies in Eqs. (34a) and (34b).

The results gathered in Table III show that the GOK-DFT excitation energies obtained with the CC-SeVWN5 functional at zero weights are the most accurate with an improvement of 0.25 eV as compared to CC-SVWN5, which is due to the ensemble derivative contribution of the eVWN5 functional. The CC-SeVWN5 excitation energies at equi-weights (i.e., \( w = 1/3 \)) are less satisfactory, but still remain in good agreement with FCI. Interestingly, the CC-S functional leads to a substantial improvement of the LIM excitation energy, getting closer to the reference value when no correlation functional is used. When correlation functionals are added (i.e., VWN5 or eVWN5), LIM tends to overestimate the excitation energy by about 1 eV but still performs better than when no correction of the curvature is considered. It is also important to mention that the CC-S functional does not alter the MOM excitation energy as the correction vanishes in this limit (vide supra). Finally, although we had to design a system-specific, weight-dependent exchange functional to reach such accuracy, we have not used any high-level reference data (such as FCI) to tune our functional, the only requirement being the linearity of the ensemble energy (obtained with LDA exchange) between the ghost-interaction-free pure-state limits.

B. Hydrogen molecule at stretched geometry

To investigate the weight dependence of the xc functional in the strong correlation regime, we now consider the \( H_2 \) molecule in a stretched geometry (\( R_{\text{HH}} = 3.7 \) bohr). Note that, for this particular geometry, the doubly-excited state becomes the lowest excited state with the same symmetry as the ground state. Although we could safely restrict ourselves to a bi-ensemble composed by the ground state and the doubly-excited state, we eschew doing this and we still consider the same tri-ensemble defined in Sec. IV A. Nonetheless, one should just be careful when reading the equations reported above, as they correspond to the case where the singly-excited state is lower in energy than the doubly-excited state. We then follow the same protocol as in Sec. IV A, and considering again the aug-cc-pVTZ basis set, we design a CC-S functional for this system at \( R_{\text{HH}} = 3.7 \) bohr. It yields \( \alpha = +0.019226, \beta = -0.017996, \) and \( \gamma = -0.022945 \) [see Eq. (23)]. The weight dependence of \( C_{\alpha,\beta}^{w} \) is illustrated in Fig. 3 (green curve).

One clearly sees that the correction brought by CC-S is much more gentle than at \( R_{\text{HH}} = 1.4 \) bohr, which means that the ensemble energy obtained with the LDA exchange functional is much more linear at \( R_{\text{HH}} = 3.7 \) bohr. Note that this linearity at \( R_{\text{HH}} = 3.7 \) bohr was also observed using weight-independent xc functionals in Ref. 78. Table IV reports, for the aug-cc-pV5Z basis set (which delivers basis set converged results), the same set of calculations as in Table III. As a reference value, we computed a FCI/aug-cc-pV5Z excitation energy of 8.69
TABLE III. Excitation energies (in eV) associated with the lowest double excitation of $\text{H}_2$ with $R_{\text{H-H}} = 1.4$ bohr for various methods, combinations of xc functionals, and basis sets.

| xc functional | GOK         | x  | c     | Basis         | $w = 0$ | $w = 1/3$ | LIM | MOM |
|---------------|-------------|----|-------|---------------|---------|-----------|-----|-----|
| HF            | aug-cc-pVDZ | 35.59 | 33.33 | 28.65 |
|               | aug-cc-pVTZ | 35.01 | 33.51 | 28.65 |
|               | aug-cc-pVQZ | 34.66 | 33.54 | 28.65 |
| HF            | VWN5        | aug-cc-pVDZ | 37.83 | 33.86 | 29.17 |
|               | aug-cc-pVTZ | 37.61 | 33.99 | 29.17 |
|               | aug-cc-pVQZ | 37.07 | 34.01 | 29.17 |
| HF            | eVWN5       | aug-cc-pVDZ | 38.09 | 34.00 | 29.34 |
|               | aug-cc-pVTZ | 37.61 | 34.13 | 29.34 |
|               | aug-cc-pVQZ | 37.32 | 34.14 | 29.34 |
| S             | aug-cc-pVDZ | 19.44 | 28.00 | 25.09 | 26.60 |
|               | aug-cc-pVTZ | 19.47 | 28.11 | 25.20 | 26.67 |
|               | aug-cc-pVQZ | 19.41 | 28.13 | 25.22 | 26.67 |
| S             | VWN5        | aug-cc-pVDZ | 21.04 | 28.49 | 25.90 | 27.10 |
|               | aug-cc-pVTZ | 21.14 | 28.58 | 25.99 | 27.17 |
|               | aug-cc-pVQZ | 21.13 | 28.59 | 26.00 | 27.17 |
| S             | eVWN5       | aug-cc-pVDZ | 21.28 | 28.64 | 25.99 | 27.27 |
|               | aug-cc-pVTZ | 21.39 | 28.74 | 26.08 | 27.34 |
|               | aug-cc-pVQZ | 21.38 | 28.75 | 26.09 | 27.34 |
| CC-S          | aug-cc-pVDZ | 26.83 | 29.29 | 28.83 | 26.60 |
|               | aug-cc-pVTZ | 26.88 | 29.41 | 28.96 | 26.67 |
|               | aug-cc-pVQZ | 26.82 | 29.43 | 28.97 | 26.67 |
| CC-S VWN5     | aug-cc-pVDZ | 28.54 | 29.85 | 29.73 | 27.10 |
|               | aug-cc-pVTZ | 28.66 | 29.96 | 29.83 | 27.17 |
|               | aug-cc-pVQZ | 28.64 | 29.97 | 29.84 | 27.17 |
| CC-S eVWN5    | aug-cc-pVDZ | 28.78 | 29.99 | 29.82 | 27.27 |
|               | aug-cc-pVTZ | 28.90 | 30.10 | 29.92 | 27.34 |
|               | aug-cc-pVQZ | 28.89 | 30.11 | 29.93 | 27.34 |
| B             | LYP         | aug-mcc-pV5Z | 28.42 |       |       |
| B3            | LYP         | aug-mcc-pV5Z | 27.77 |       |       |
| HF            | LYP         | aug-mcc-pV5Z | 29.18 |       |       |
| HF            | aug-mcc-pV5Z | 28.65 |       |       |

Accurate$^b$

$^a$ Equations (33a) and (34a) are used where the first weight corresponds to the singly-excited state.
$^b$ FCI/aug-mcc-pV8Z calculation from Ref. 102.

TABLE IV. Excitation energies (in eV) associated with the lowest double excitation of $\text{H}_2$ at $R_{\text{H-H}} = 3.7$ bohr obtained with the aug-cc-pVTZ basis set for various methods and combinations of xc functionals.

| xc functional | GOK         | x  | c     | Basis         | $w = 0$ | $w = 1/3$ | LIM | MOM |
|---------------|-------------|----|-------|---------------|---------|-----------|-----|-----|
| HF            | aug-cc-pVDZ | 19.09 | 8.82 | 12.92 | 6.52 |
| HF            | VWN5        | 19.40 | 8.81 | 13.02 | 6.49 |
| HF            | eVWN5       | 19.59 | 8.95 | 13.11 | 6.89 |
| S             | aug-cc-pVDZ | 5.31 | 5.67 | 5.46 | 5.56 |
| S             | VWN5        | 5.34 | 5.64 | 5.46 | 5.52 |
| S             | eVWN5       | 5.53 | 5.79 | 5.56 | 5.72 |
| CC-S          | aug-cc-pVDZ | 5.55 | 5.72 | 5.56 | 5.56 |
| CC-S VWN5     | 5.58 | 5.69 | 5.57 | 5.52 |
| CC-S eVWN5    | 5.77 | 5.84 | 5.66 | 5.72 |
| B             | LYP         | 5.28 |       |       |       |
| B3            | LYP         | 5.55 |       |       |       |
| HF            | LYP         | 6.68 |       |       |       |
| srLDA ($\mu = 0.4$)$^d$ | 6.39 | 6.47 |       |       |

Accurate$^a$

$^a$ Equations (33b) and (34b) are used where the first weight corresponds to the doubly-excited state.
$^b$ KS calculation does not converge.
$^c$ Short-range multiconfigurational DFT/aug-cc-pVQZ calculations from Ref. 78.
$^d$ FCI/aug-cc-pVSZ calculation performed with QUANTUM PACKAGE.120

eV, which compares well with previous studies. For $R_{\text{H-H}} = 3.7$ bohr, it is much harder to get an accurate estimate of the excitation energy, the closest match being reached with HF exchange and VWN5 correlation at equi-weights. As expected from the linearity of the ensemble energy, the CC-S functional coupled or not with a correlation functional yield extremely stable excitation energies as a function of the weight, with only a few tenths of eV difference between the zero- and equi-weights limits. As a direct consequence of this linearity, LIM and MOM do not provide any noticeable improvement on the excitation energy. Nonetheless, the excitation energy is still off by 3 eV. The fundamental theoretical reason of such a poor agreement is not clear but it might be that, in this strongly correlated regime, the weight-dependent correlation functional plays a significant role not caught by our approximation.

For additional comparison, we provide the excitation energy calculated by short-range multiconfigurational DFT in Ref. 78, using the (weight-independent) srLDA functional119 and setting the range-separation parameter to $\mu = 0.4$ bohr$^{-1}$. The excitation energy improves by 1 eV compared to the weight-independent SVWN5 functional, thus showing that treating the long-range part of the electron-electron repulsion by wave function theory plays a significant role.

C. Helium atom

As a final example, we consider the He atom which can be seen as the limiting form of the $\text{H}_2$ molecule for very short bond lengths. Similar to $\text{H}_2$, our ensemble contains the ground state of configuration $1s^2$, the lowest singlet excited state of configuration $1s2s$, and the first doubly-excited state of configuration $2s^2$. In He, the lowest doubly-excited state is an auto-ionising resonance state, extremely high in energy and lies in the continuum.121 In Ref. 122, highly-accurate calculations estimate an excitation energy of 2.126 hartree for this $1s^2 \rightarrow 2s^2$ transition. Nonetheless, it can be nicely described with a Gaussian basis set containing enough diffuse functions. Consequently, we consider for this particular example the d-aug-cc-pVQZ basis set which contains two sets of diffuse functions. The excitation energies associated with this double excitation computed with various methods and combinations
of xc functionals are gathered in Table V.

Before analysing the results, we would like to highlight the fact that there is a large number of singly-excited states lying in between the 1s2s and 2s2 states. Therefore, the present ensemble is not consistent with GOK theory. However, it is impossible, from a practical point of view, to take into account all these single excitations. We then restrict ourselves to a trimmable ensemble keeping in mind the possible theoretical loopholes of such a choice.

The parameters of the CC-S weight-dependent exchange functional (computed with the smaller aug-cc-pVTZ basis) are \( \alpha = +1.912\,574, \beta = +2.715\,267, \) and \( \gamma = +2.163\,422 \) [see Eq. (23)], the curvature of the ensemble energy being more pronounced in He than in H\(_2\) (blue curve in Fig. 3). The results reported in Table V evidence this strong weight dependence of the excitation energies for HF or LDA exchange.

The CC-S exchange functional attenuates significantly this dependence, and when coupled with the eVWN5 weight-dependent correlation functional, the CC-SeVWN5 excitation energy at \( w = 0 \) is only 18 millihartree off the reference value. As in the case of H\(_2\), the excitation energies obtained at zero-weight are more accurate than at equi-weight, while the opposite conclusion was made in Ref. 90. This motivates further the importance of developing weight-dependent functionals that yields linear ensemble energies in order to get rid of the weight-dependency of the excitation energy. Here again, the LIM excitation energy using the CC-S functional is very accurate with only a 22 millihartree error compared to the reference value, while adding the correlation contribution to the functional tends to overestimate the excitation energy. Hence, in the light of the results obtained in this paper, it seems that the weight-dependent curvature correction to the exchange functional has the largest impact on the accuracy of the excitation energies.

As a final comment, let us stress again that the present protocol does not rely on high-level calculations as the sole requirement for constructing the CC-S functional is the linearity of the ensemble energy with respect to the weight of the double excitation.

Table V

| xc functional | GOK | MOM | LIM | w = 0 | w = 1/3 |
|---------------|-----|-----|-----|-------|---------|
| HF            | 1.874 | 2.212 | 2.123 | 2.142 |
| HF VWN5       | 1.988 | 2.260 | 2.190 | 2.193 |
| HF eVWN5      | 2.000 | 2.265 | 2.193 | 2.196 |
| S             | 1.062 | 2.056 | 1.675 | 2.030 |
| S VWN5        | 1.163 | 2.104 | 1.735 | 2.079 |
| S eVWN5       | 1.174 | 2.109 | 1.738 | 2.083 |
| CC-S          | 1.996 | 2.264 | 2.148 | 2.030 |
| CC-S VWN5     | 2.107 | 2.318 | 2.215 | 2.079 |
| CC-S eVWN5    | 2.108 | 2.323 | 2.218 | 2.083 |
| B             | LYP | 2.147 |
| B3            | LYP | 2.150 |
| HF            | LYP | 2.171 |

* Equations (33b) and (34b) are used where the first weight corresponds to the singly-excited state.

** Accurately correlated calculations from Ref. 122.

V. CONCLUSION

In the present article, we have discussed the construction of first-rung (i.e., local) weight-dependent exchange-correlation density-functional approximations for two-electron systems (He and H\(_2\)) specifically designed for the computation of double excitations within GOK-DFT, a time-independent formalism capable of extracting excitation energies via the derivative of the ensemble energy with respect to the weight of each excited state.

In the spirit of optimally-tuned range-separated hybrid functionals, we have found that the construction of a system- and excitation-specific weight-dependent local exchange functional can significantly reduce the curvature of the ensemble energy and improves excitation energies. The present weight-dependent exchange functional, CC-S, specifically tailored for double excitations, only depends on the weight of the doubly-

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