AAPG2019	HYPEDFT		PRC
Coordinated by:	Emmanuel FROMAGER	48 months	€ 178740
CES 29 Chimie : analyse, théorie, modélisation			

HYPerspheres in Ensemble Density-Functional Theory: climbing Jacob's ladder for excited states

Summary table of persons involved in the project:

Partner	Name	First name	Current position	Role & responsibilities in the project (4 lines max)	Involvement (person.month) throughout the project's total duration
University of Strasbourg	*FROMAGER*	*Emmanuel*	*Associate Professor*	*Scientific coordinator, Supervisor/collaborator in tasks 1-4, main contributor to task 5.*	*38.4*
CNRS/University Paul Sabatier, Toulouse	*LOOS*	*Pierre-François*	*Researcher*	*Partner's scientific leader, Supervisor/collaborator in tasks 2-5, main contributor to task 1.*	*14.4*
University of Strasbourg			*PhD student to be hired*	*Main contributor to tasks 2-5.*	*36*
CNRS/University Paul Sabatier, Toulouse			*Master 2 students to be hired (3 in total)*	*Contributors to tasks 1, 2 and 4 (calibration studies).*	*15*

Any changes that have been made in the full proposal compared to the pre-proposal

- *While estimating our total budget at the pre-proposal stage we forgot that additional administrative costs would apply (about 13300 € for the two partners). This is the main reason for the substantial discrepancy between the pre-proposal (165000 €) and proposal (178740 €) budgets. As a discrepancy of +15% was tolerated we decided not to reduce the initial budget.*

- *We mentioned in the pre-proposal that it would be interesting, as a second main task, to extend ensemble density-functional theory (DFT), which is central in the project, to the time-dependent regime. Even though this is for sure an (unexplored) exciting topic, as it would enable the calculation of molecular response properties within ensemble DFT, we realized, once the full proposal was written, that it would be far too ambitious (as we plan to hire a single PhD student) to include it in the HYPEDFT proposal. As our main priority will be the development of (time-independent) ab initio functionals for excited states, which is already quite ambitious, we leave the dynamical extension of HYPEDFT for future work.*

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I. Proposal's context, positioning and objective(s)

a. Objectives and research hypothesis

Over the last two decades, density-functional theory (DFT) 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, the latter being a much simpler quantity than the electronic wavefunction. The complexity of the many-body problem is then transferred to the xc functional. Despite its success, the standard (Kohn-Sham) formulation of DFT suffers, in practice, from various deficiencies. The description of strongly multiconfigurational ground states (often referred to as "strong correlation problem"), which is a common feature in *d*- and *f*-element chemistry or in photochemistry, for example, still remains a challenge. Another issue, which is partly connected to the previous one, is the description of electronically-excited states. The standard approach for modeling excited states in DFT is time-dependent (TD) linear response theory**.** In this case, the electronic spectrum relies on the (unperturbed) ground-state Kohn-Sham picture, which may break down when electron correlation is strong. Moreover, in exact TD-DFT, the xc functional is time-dependent. The simplest and most widespread approximation in state-of-the-art electronic structure programs where TD-DFT is implemented consists in neglecting memory effects. In other words, within this (so-called adiabatic) approximation, the xc functional is assumed to be local in time. As a result, double electronic excitations are completely absent from the TD-DFT spectrum [1], thus reducing further the applicability of TD-DFT.

The ultimate goal of the *HYPEDFT* project is to extend the applicability of density-functional theory (DFT) to excited states in a completely **time-independent** framework. Such an extended DFT should essentially have the same computational cost as a regular DFT calculation and, most importantly, it should offer a reliable alternative to the widely used TD-DFT method in numerous situations where the latter fails (near-degenerate situations and multiple excitation processes, for example). For that purpose, we will work within the ensemble DFT formalism [2] where the basic variable is the so-called ensemble density (i.e. the weighted sum of ground- and excited-state densities). In ensemble DFT, the key quantity to model is the universal ensemble xc functional and, more precisely, its variation with the ensemble weights at *fixed* density [2,3]. The latter variation plays a crucial role in the calculation of excited energy levels [3]. It is actually connected to the infamous derivative discontinuity problem of DFT [4].

The lack (not to say the absence) of xc functionals for ensembles in the literature is one of the reason why ensemble DFT is not used routinely nowadays. There is indeed no clear strategy (like a Jacob's ladder, according to the terminology of Perdew [5]) for developing ensemble xc functionals. This is essentially due to the fact that no good reference system to which ensemble DFT is applicable, like the infinite uniform electron gas (so-called jellium [6]) in the case of regular DFT, has been identified yet. We believe that **finite uniform electron gases** (FUEGs) like electrons on hyperspheres [7] can play this role, thus defining the first rung of a Jacob's ladder for ensembles.

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By climbing this ladder we will produce the first generation of *ab initio* semi-local density-functional approximations (DFAs) that incorporate information about both ground and excited states. Interestingly, in this context, we should be able to design new density-functional corrections to the infamous ***ghost-interaction error*** [8]. The latter, which is a specificity of ensemble DFT, arises when the ensemble density is inserted into the conventional Hartree (or Coulomb) density-functional expression. As the latter is quadratic in the density, unphysical interaction terms between ground and excited densities show up.

Our first-rung ensemble DFAs (combined with a general ready-to-use ensemble DFT code) will be made available in the Quantum Package program which is freely distributed on GitHub [9].

b. Position of the project as it relates to the state of the art

When affordable (i.e. for relatively small molecules), time-independent state-averaged wavefunction-based methods can be employed to overcome the various limitations of DFT and TD-DFT. The basic idea is to describe a finite ensemble of states (ground and excited) altogether, i.e. with the same set of orbitals. Ensemble DFT, which was proposed at the end of the 80's by Gross, Oliveira and Kohn [2], follows exactly the same strategy. As stressed previously, in ensemble DFT, the (time-independent) xc functional depends explicitly on the weights assigned to the states that belong to the ensemble of interest. Despite its formal beauty and the fact that it can in principle tackle near-degenerate situations and multiple excitations [10], ensemble DFT has not been given much attention until recently. Works on this topic are still fundamental and exploratory, as they rely either on simple (but nontrivial) models like the Hubbard dimer [3,11,12] or on atoms for which highly accurate or exact-exchange-only [10] calculations have been performed. In both cases, the key problem, namely the design of *ab initio* weight-dependent DFAs, remains open.

Using a FUEG for modeling the weight-dependent part of the ensemble xc density-functional energy, which is central in *HYPEDFT,* has never been explored so far. It is a completely novel approach which extends the usefulness of FUEG models to DFT for excited states and, at the same time, is expected to turn ensemble DFT into a practical and reliable computational method.

The **first partner (E. Fromager)** made the following contributions to the state of the art in ensemble DFT: *(i) derivation of an exact generalized adiabatic connection formula for the xc ensemble functional* [13]*, (ii) derivation and implementation of a linear interpolation method for the computation of excitation energies in ensemble DFT* [14]*, (iii) derivation and implementation of a ghost-interaction correction in both regular and multideterminant range-separated ensemble DFT* [15]*, (iv) first calculation of an exact ensemble xc functional in a (Hubbard dimer) model system* [11]*, (v) derivation of an in-principle-exact extraction procedure for ground and excited energy levels in ensemble DFT* [3].

The second partner (P.-F. Loos) is a pioneer (with Peter Gill) in the modeling of FUEGs in various dimensionalities (see, for example, Refs. 6,7,16-18, 24, 25 and the references therein). He also recently designed ground-state exchange functionals for DFT on the basis of a 3-dimensional (so-called ***glomium***) FUEG [7].

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c. Methodology and risk management

Preliminary comments on the work plan:

- In order to have enough time for selecting the adequate candidate we decided not to involve the *PhD student* during the first year of the project. She/he will start in october 2020. Both partners (as well as a master 2 student to be hired) will be active during year 1 (see the Gantt chart below).

- *Stays in Strasbourg and Toulouse* (see the Gantt chart below) are detailed in the budget section II. b.

- No risks have been mentioned in the tasks. Any failure of the functionals to be developed will be an instructive and important result to publish. Regarding the implementation, the key ingredients of a DFT code (like integration grids, for example) are already available in the *Quantum Package* program [19] that we will use. Once we have our new ensemble functionals (to be fitted on the glomium), it should be straightforward to incorporate them into the DFT routines.

HYPEDFT project		year 1				year 2				year 3				year 4			
		3	6	9	12	3	6	9	12	3	6	9	12	3	6	9	12
Task 1	Implementation of weight-independent DFAs	*		**													
Task 2	Ensemble DFAs for ringium					*		**									
Task 3	Ensemble DFAs for quantum chemistry									*		**					
Task 4	Implementation of weight-dependent DFAs													*			
Task 5	Extensions and improvements of the DFAs															**	

* 5-day stays in Toulouse

** 5-day stays in Strasbourg

PhD projects

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Task 1: Implementation and calibration of weight-independent DFAs in Quantum Package

Main contributor: P.-F. Loos (in collaboration with E. Fromager)
Additional contributor: first Master 2 student to be hired in P.-F. Loos' group.
Deliverables: general ensemble DFT code that computes ground and excited energy levels with standard (ground-state) xc functionals.

The purpose of task 1 is to set up the computational framework that will be used in the rest of the project for implementing and applying DFAs for ensembles to quantum chemical problems. We will (in this task) implement ensemble DFT at the simplest level of approximation, namely the (weight-independent) ground-state density-functional one. This can be seen as a "rung 0" on our Jacob's ladder for ensembles. Within such an approximation, any standard xc functional can be employed. Let us stress that, in this case, the ensemble xc energy will vary with the ensemble weights only through the ensemble density [14], not the functional itself. As a result, the (approximate) ensemble energy should exhibit an unphysical curvature, thus making the definition of excitation energies ambiguous in this context [14]. Note also that xc derivative discontinuities will be completely absent from the method (the incorporation of the latter into ensemble DFAs is left for task 3). Fromager and coworkers have proposed and explored in recent years various strategies for extracting ground- and excited-state energies in the (more general) context of multideterminant range-separated ensemble DFT [13-15, 20]. These strategies apply also to Kohn-Sham ensemble DFT (which is the only approach considered in the proposal) which is recovered when the range separation parameter equals zero. What are these strategies ? The first one is the ***linear interpolation method*** **(LIM)** [14] which uses a sequence of equi-ensemble (i.e. with the same weights assigned to all the states within the ensemble) calculations. A simple *ad hoc* ghost-interaction correction has also been proposed in this context [15]. These methods have been mainly tested within range-separated schemes. An appealing alternative, where a single ensemble calculation is in principle sufficient, consists in extracting all (ground and excited) energy levels by differentiating the ensemble energy with respect to each ensemble weight [3,20]. So far the latter (in-principle-exact) approach has been applied only to the Hubbard dimer model [3]. One important goal of task 1 is to evaluate the performance of these strategies within the Kohn-Sham scheme when ground-state functionals are employed. Charge-transfer excitations, double excitations and conical intersections, which are problematic in TD-DFT, will be studied in (few-electron) atomic and molecular prototypical systems. More challenging chemical applications will be considered (in task 4), once weight dependencies have been incorporated into the functionals.

The above-mentioned methods will be implemented in the Quantum Package program [9] where DFT grids are already available [19]. The code should be flexible enough, in terms of (fractional) orbital occupancies, so that any kind of ensemble (canonical or grand canonical) can be described. Note that, as shown recently by Senjean and Fromager [4], the same formalism can be used for modeling both neutral (i.e. canonical) and charged excitation processes (ionization, affinity).

P.-F. Loos will be in charge of the implementation in Quantum Package (in collaboration with E. Fromager who has expertise in ensemble DFT calculations). The first M2 student to be hired by P.-F. Loos will test the various methods on prototypical atomic and molecular systems.

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Task 2: Construction of weight-dependent ensemble DFAs for the 1D ringium model

Main contributor: PhD student to be hired (under the supervision of the two partners).
Additional contributor: second Master 2 student to be hired in P.-F. Loos' group.
Deliverables: generalized LDA functionals for ensembles in 1D, calibration studies on prototypical 1D systems and quantum dots.

The purpose of task 2 is to set up our strategy for constructing xc DFAs that incorporate derivative discontinuity corrections through their explicit dependence on the ensemble weights. We will, for simplicity, consider two- or three-state ensembles only, thus allowing for the description of single and double excitations, but also charged excitations [4], within the same formalism. The extension to arbitrary-size ensembles will be discussed in task 5. In order to validate (and, if necessary, improve) the strategy discussed in the rest of the task, we will consider (in this task) one-dimensional systems only. As discussed further in the following, despite the drastic reduction in dimensionality, we should be able to address interesting problems in physics like the modeling of quantum dots, which is challenging for DFT [21]. The extension to the real (three-dimensional) case will be treated in task 3.

Our starting point will be the **generalized adiabatic connection** formalism **for ensembles** (GACE) [11], which was originally derived for a two-state ensemble [13], and that we propose to extend to ensembles of arbitrary size (see the top panel of Fig. 1). Within this in-principle-exact formalism, the (weight-dependent) xc energy of the ensemble is constructed from the (weight-independent) ground-state functional. As a practical consequence, different approximations may be used for modeling weight-dependent and weight-independent contributions to the ensemble xc energy (see the bottom panel of Fig. 1). This is a crucial point as we intend to incorporate into standard functionals (which are "universal" in the sense that they do not depend on the number of electrons) informations about excited states that will be extracted from *finite* systems (whose properties may depend on the number of electrons). In the case of a one-dimensional FUEG (the so-called **ringium** [16]), we will start with two electrons and investigate if this is sufficient for capturing most of the correlation effects on the excitation energies. If necessary, we may investigate their dependence on the number of electrons. Note that, as further discussed in task 3, this information can in principle be transferred to the ensemble xc functional by introducing the so-called Fermi hole curvature [16].

The GACE is trivial to implement for a FUEG since both ground and excited states share the same density, namely the (uniform) ensemble density. As a result, the ensemble xc density-functional energy varies linearly with the ensemble weights (see the middle panel of Fig. 1). Let us stress that, in the one-dimensional (1D) case, the Hartree energy cannot be separated from the exchange one [16]. Therefore, we should in principle design a DFA only for the ensemble correlation energy (the procedure will then be the same as in Ref. 16). Note, however, that if we compute the ensemble Hartree-exchange (Hx) energy with the ensemble density matrix, by analogy with Hartree-Fock or DFT calculations for fractional electron numbers, then we will introduce an unphysical curvature in the ensemble energy as well as ghost-interaction errors [8]. Interestingly, in a FUEG, it should be straightforward to design a density-functional correction that removes these errors simply because, in this case, the Hartree-Fock energies of ground and excited states are functionals of the same (uniform) density.

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Exact GACE formula

$$E_{xc}^{(w_1,w_2,\ldots,w_M)}[n] = E_{xc}[n] + \sum_{i=1}^{M} \int_0^{w_i} d\xi_i \frac{\partial E_{xc}^{(0,0,\ldots,0,\xi_i,w_{i+1},\ldots,w_M)}[n]}{\partial \xi_i}$$

ground-state functional

Application to a finite gas with uniform density n

$$\varepsilon_{xc}^{(w_1,w_2,\ldots,w_M)}(n) = \varepsilon_{xc}^{i=0}(n) + \sum_{i=1}^{M} w_i \left(\varepsilon_{xc}^{i}(n) - \varepsilon_{xc}^{i=0}(n) \right)$$

$\varepsilon_{xc}^{i}(n)$: xc energy of state i per particle

Weight-dependent DFA for ensembles

$$E_{xc}^{(w_1,w_2,\ldots,w_M)}[n] \approx E_{xc}^{DFA}[n] + \sum_{i=1}^{M} w_i \int d\boldsymbol{r}\, n(\boldsymbol{r}) \left(\varepsilon_{xc}^{i}(n(\boldsymbol{r})) - \varepsilon_{xc}^{i=0}(n(\boldsymbol{r})) \right)$$
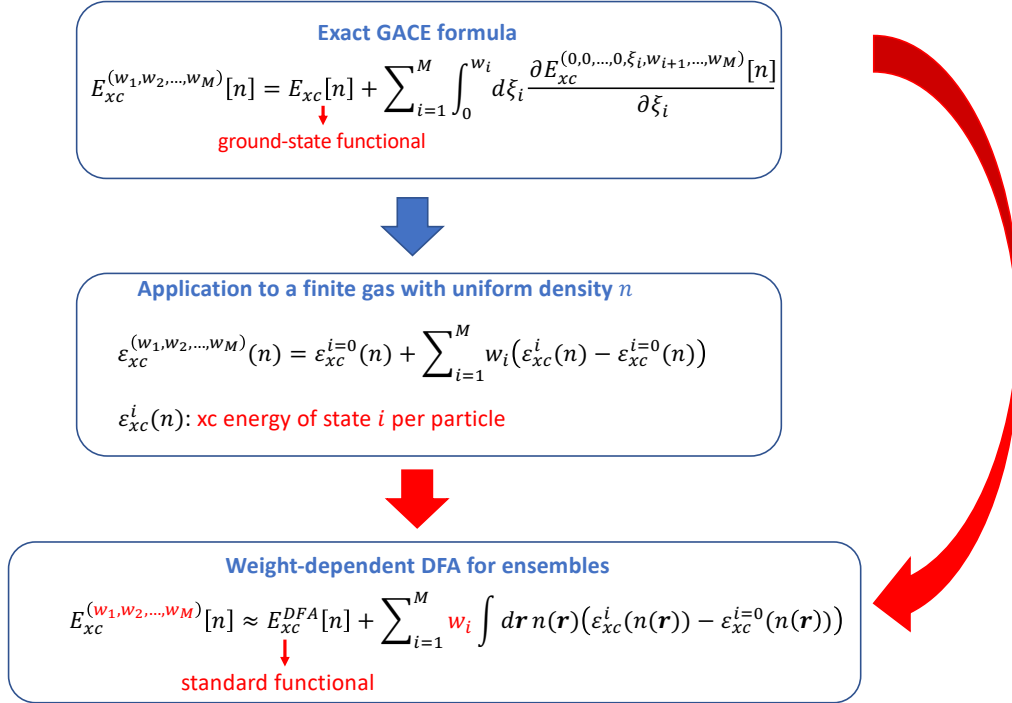
standard functional

Fig. 1: Summary of the procedure that will be used for designing weight-dependent xc functionals for ensembles on the basis of finite uniform electron gases. A non-degenerate ensemble (consisting of M excited states) is considered here for clarity. The ground state is labelled as $i = 0$. The ensemble weight assigned to the ith excited state is denoted w_i.

Our ringium-based ensemble xc functionals will first be tested on two 1D non-uniform prototypical systems with large and small gaps, namely the boxium (electrons in a 1D box) and the hookium (electrons in a 1D harmonic well), respectively [16]. We will evaluate the performance of our functionals in the calculation of optical (or fundamental [4]) energy gaps for these systems. In a second step, we will extend our calibration study to one-dimensional-type quantum dots (so-called quantum rings), which are of high interest in the physics community [21]. Quantum rings (QRs) are tiny, self-organised, ring-shaped semiconductors [22, 23] characterised by three parameters: radius (R), width (δ) and electron number, as shown in Fig. 2. They have been intensively studied, both experimentally and theoretically, because of their rich electronic, magnetic and optical properties, such as the Aharonov-Bohm effect and their potential application in quantum information theory. The Aharonov-Bohm effect is a quantum mechanical phenomenon in which an electrically charged particle is affected by an electromagnetic field, despite being confined to a region in which the electromagnetic field is zero. As a first approximation, they can be modelled by electrons confined on a ring, i.e. a sphere of dimension one [24]. Consequently, the weight-dependent functionals developed in the present proposal would be perfectly adapted for describing the excited states (and therefore the response properties) of such systems. Indeed, QRs are truly quasi-one-dimensional systems, and the influence of this quasi, though dimensionally tiny, can have significant effects on the electronic, magnetic and optical properties (see for example Ref. [25]).

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In particular, we plan to consider finite-width QRs ($\delta > 0$) as well as donut-shaped QRs, where the electrons are confined on the surface of a torus. Following the completion of these computational tasks, we will compare our results with the numerous experimental data found in the literature [22, 23, 26-28]. This will be a strong test for our newly-designed functionals.
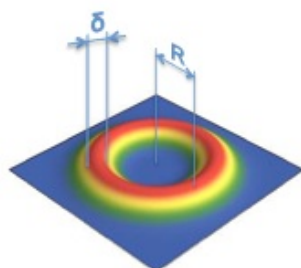

Fig. 2: Quantum ring of radius R *and width* δ

The PhD student to be hired will be in charge of constructing the weight-dependent DFAs for the ringium. He will follow the strategy summarized in Fig. 1. This work will be done under the supervision of E. Fromager (who derived the GACE formalism) and in collaboration with P.-F. Loos who has expertise in the development of such functionals for ground-state DFT. The second Master 2 student to be hired by P.-F. Loos will be in charge of calibrating these functionals and applying them to quantum rings.

Task 3: Construction of weight-dependent ensemble DFAs for quantum chemistry

<u>Main contributor:</u> *PhD student to be hired (under the supervision of the two partners).*
<u>Deliverables:</u> *ab initio weight and spin-dependent xc functionals for ensembles.*

Task 3 is the extension of task 2 to (realistic) three-dimensional systems. The corresponding FUEG (so-called **glomium** [7]) consists of electrons moving on the (three-dimensional) surface of a ball that is constructed in a four-dimensional space. We will follow the same strategy as in task 2 (see Fig. 1). In the following we only discuss the main differences between glomium and ringium models. First of all, in contrast to the 1D case, Hartree and exchange energies can now be separated so that both orbital- and density-functional ensemble exchange energies can in principle be employed. The latter option will clearly be more appealing to condensed matter physicists for computational reasons. Moreover, it may favor error cancellations. For chemical applications it is worth exploring and testing the two options. In both cases, we should be able to construct a ghost-interaction correction density functional, in analogy with the ringium. We should also stress that correlation functionals based on glomium have not been developed yet (even for the ground state [7]). Therefore, as a starting point, we will develop DFAs for the ensemble exchange energy only. Those will then be combined with standard (weight-independent) correlation functionals in practical calculations (see task 4). As shown

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by Loos [7], in the particular case of the ground-state exchange functional, **_finite-size effects_** can be transferred to the functional by introducing an explicit dependence on the Fermi hole curvature.

The latter quantity depends on the density, its gradient, and the kinetic energy density. The corresponding DFA is therefore a particular type of **_meta generalized gradient approximation_** (MGGA). A similar procedure will be investigated for the ensemble exchange energy. More precisely, we will obtain (by numerical fitting) an explicit relation between the exchange energies of all the states in the ensemble (two or three states, as a starting point) and the Fermi hole curvature. This can be achieved thanks to the one-to-one correspondence between the latter curvature and the number of electrons in the glomium. Note that we may be unable to explore situations where the Fermi hole curvature is larger than 1.0 [7], which would reduce the applicability of the functional. A simple solution would consist in using the (weight-independent) extrapolation formula proposed by Loos in Ref. [7]. The functional might be further improved by introducing a weight-dependent extrapolation such that accurate values of ensemble exchange energies of light atoms are well reproduced.

Regarding the construction of correlation DFAs for ensembles, we will combine the results of wave function and Quantum Monte Carlo (QMC) calculations to compile a dataset of energies for low-density glomiums. At high densities, the kinetic energy in glomium dominates the two-electron repulsion energy and traditional perturbation theory (e.g. MP2, MP3, etc.) and coupled cluster approaches (CCSD, CCSD(T), etc) give accurate energies. Therefore, we will combine perturbation theory, coupled cluster and QMC to compile a dataset of energies for high-density glomiums. We will use the same number N of electrons as in the low-density regime, so that direct comparisons of our energies can be made in the intermediate density regions. Agreement (or disparity) between these energies will be used to assess the reliability of our results. The final step will consist in combining the results from the low- and high-density regimes and fit these to a mathematical function of N, V (the volume of glomium) and the relative spin-polarisation $\zeta = (N\alpha - N\beta)/(N\alpha + N\beta)$, where $N\alpha$ and $N\beta$ denote the numbers of spin-up and spin-down electrons, respectively. The fit function is then the kernel of our new weight-dependent correlation DFA.

The PhD student to be hired will be in charge of performing the accurate correlated calculations on glomium and designing the corresponding ensemble xc functionals. This work will be done in collaboration with P.-F. Loos who already constructed the same type of functional for the ground-state exchange energy [7].

Task 4: Implementation and calibration of weight-dependent DFAs in Quantum Package

Main contributor: PhD student to be hired (under the supervision of the two partners).
Additional contributor: third Master 2 student to be hired in P.-F. Loos' group.
Deliverables: first ensemble DFT code that uses weight-dependent DFAs, calibration study of the latter functionals.

The new weight-dependent functionals developed in task 3 will be implemented in the Quantum Package program [19]. Note that the LIM method (see task 1) requires no extra work, which means that the new functionals can be used like any other functional within the implementation already done in task 1. On the other hand, the alternative energy level extraction procedure of Deur and Fromager [3] (which is based on the differentiation of the ensemble energy with respect to the ensemble weights) requires the implementation of ensemble xc derivative corrections. As readily seen from the bottom panel of Fig. 1, these corrections will simply be the density-functional glomium-based xc energy contributions to the excitation energies.

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Turning to the calibration of the new ensemble functionals, excited states presenting double excitation character [29] are notoriously difficult to model using conventional single-reference methods such as adiabatic TD-DFT [30-32]. Double excitations do play a significant role in the proper description of several key physical, chemical and biological processes, e.g., in photovoltaic devices [33], in the photophysics of vision [34], and in photochemistry in general [35-37] involving ubiquitous conical intersections [30]. Another example is intimately linked to the correct location of the excited states of polyenes [38-43], that are closely related to rhodopsin which is involved in visual phototransduction. [44-46] Though doubly-excited states do not appear directly in photo-absorption spectra, these dark states strongly mix with the bright singly-excited states leading to the formation of satellite peaks [47]. It is therefore paramount to design a robust and relatively cheap theoretical method able to tackle such types of excited states. Here, we propose to take advantage of the new weight-dependent DFAs developed in task 3 to obtain excited states of different natures, and in particular doubly-excited states. Regarding conical intersections, one challenging task will be to reproduce, for example, the accurate wavefunction-based results obtained by Gozem *et al.* [48] for the penta-2,4-dieniminium cation taken as a minimal model of the retinal chromophore. Another crucial point is to know whether or not our spin-dependent ensemble DFA is a good alternative to the spin-flip approach, for example, in the description of singlet-triplet splittings [49].

The PhD student to be hired will be in charge of implementing the weight-dependent DFAs in Quantum Package under the supervision of E. Fromager and P.-F. Loos. He will also apply these functionals to the various quantum chemical problems mentioned previously. In particular, he will investigate the impact of the ensemble xc derivatives on properties of interest like the excitation energies. The third Master 2 student to be hired in P.-F. Loos' group will be in charge of testing the new functionals within LIM.

Task 5: Extending and improving glomium-based DFAs for ensembles

Main contributors: E. Fromager and the PhD student to be hired (in collaboration with P.-F. Loos).
Deliverables: new general scheme for constructing DFAs for ensembles at higher levels of approximation.

The purpose of task 5 is to develop a general scheme where ensemble DFAs can be (easily) constructed for arbitrary-size ensembles and at higher levels of approximation. In other words, we are aiming at generalizing the developments proposed in task 3 where two/three-state ensembles only will be considered within the (semi-) local density approximation. For that purpose, we will combine two very recent approaches: the in-principle-exact individual energy level extraction procedure of Deur and Fromager [3] and the decomposition into individual components of the ensemble xc energy proposed by Gould and Pittalis [50]. The latter decomposition makes it in principle easier to construct DFAs for ensembles (because informations about the states within the ensemble appear more explicitly). Moreover, it will enable us to define a clear hierarchy of approximations (i.e. higher rungs in our Jacob's ladder for ensembles), as explained further in the following. The basic idea of Gould and Pittalis is to construct the ensemble xc energy from a weighted sum of (effective) individual ground and excited xc energies. Interestingly, such a decomposition appears naturally if we express the ensemble-density-functional energy levels in terms of the ensemble xc functional and its derivatives, as suggested recently by Deur and Fromager [3]. We can also recover the decomposition of the individual components into **state-driven** and **density-driven**

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contributions [50]. The latter originates from the fact that, in an ensemble, the Kohn-Sham and true physical wavefunctions do not necessarily have the same density.

The ensemble density only is the same. This difference does not exist in regular ground-state DFT (since the ensemble reduces to a single state [50]). Interestingly, in FUEGs like glomium, the density-driven ensemble xc energy contribution vanishes since all the states share the same (uniform) density in both Kohn-Sham and true physical systems. As a result, the glomium-based ensemble DFAs to be developed in task 3 can be considered as "rung 1" functionals on the Jacob's ladder for ensembles.

Two main directions will be explored in task 5. The first one consists in using the Gould-Pittalis decomposition in order to design xc functionals for larger ensembles (on the basis of two- or three-state ensembles), thus allowing for the description of an arbitrary number of states. Note that, in the simple Hubbard dimer model, this can actually be achieved exactly [3]. The key idea here is to describe several states with the same functional and have the possibility to choose the latter functional according to the nature of the excitation (for example single or double excitations). The second direction is the exploration of density-driven effects in ensembles for the purpose of constructing higher-rung DFAs. Both directions will be explored formally and tested on the simple (but non-trivial) Hubbard dimer model [3,11,12] first, as a proof of concept. This work will then be extended to real molecules on the basis of tasks 3 and 4. Regarding the description of density-driven effects in FUEGs, we will explore the possibility of introducing slight deviations from uniformity in glomium, thus allowing for a perturbative treatment of the latter effects.

E. Fromager will be in charge (during the first year of the project) of the derivation and implementation of the theory for the prototypical Hubbard dimer. The PhD student to be hired will test the approximate extensions to larger ensembles in both glomium and real molecular systems. In the latter case, systems mentioned in task 4 will be considered. The work will be done in collaboration with P.-F. Loos.

II. Organisation and implementation of the project

a. Scientific coordinator and its consortium / its team

HYPEDFT is a collaborative project (PRC) composed by two complementary researchers. The scientific coordinator (**Emmanuel Fromager**, University of Strasbourg) is leading the DFT group in the "Lab of Quantum Chemistry" (LCQ) team, which is part of the Institute of Chemistry in Strasbourg. He has already been coordinator of an **ANR young researcher** project [*MCFUNEX* project, October 2014 – March 2019] and scientific leader of a **Lab of excellence program** (LabEx) project [Chemistry of complex systems, University of Strasbourg, October 2013 – October 2016]. The main focus of these two projects was the development of multiconfigurational extensions of DFT based on partially-interacting many-body wavefunctions. In the last five years, E. Fromager has supervised one post-doc (2014-2016) and three PhD students (2015-2018), as well as 5 first-year and 3 second-year master students. His field of research (in connection with *HYPEDFT*) is ensemble DFT for both *ab initio* and model Hamiltonians. His expertise ranges from the derivation of new formalisms, the development of

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approximations (for example for the calculation of excitation energies within ensemble DFT) to the computational implementation and calibration of ensemble DFT methods.

His knowledge in the field will be crucial, in particular, for extending and improving further the DFAs to be designed in task 3 of the proposal (see task 5). E. Fromager, who has the habilitation (HDR) degree, will supervise in collaboration with the partner (see below) the PhD student to be hired with the *HYPEDFT* funds.

The partner (**Pierre-François Loos**, CNRS, University of Toulouse) is co-leader of the "method development" team in the Lab of Quantum Physics and Chemistry (LPCQ) where he holds, since 2017, a CNRS position and he is currently supervising one PhD student. From 2013-2017, Dr Loos was the group leader of the Mathematical and Theoretical Chemistry group as well as senior lecturer at the Australian National University. During this time, he was awarded various grants from the Australian Research Council and supervised several undergraduate students, two postdocs and has been involved in the co-supervision of two PhD students. He has a strong expertise in modeling finite uniform electron gases in ground and excited states but also in the design and implementation of ground-state semi-local functionals based on the latter gases (for both toy and realistic systems). P.-F. Loos will provide all the computational framework (in particular codes that he implemented himself for developing ground-state functionals) that will be extended to ensembles (see tasks 2 and 3). P.-F. Loos is also a contributor to the Quantum Package program in which all the functionals to be developed will be implemented. His contribution will be essential to turn ensemble DFT into a useful computational tool for chemistry.

*At the moment, both the scientific coordinator and the partner are involved in **on-going grant applications** only.*

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b. Implemented and requested resources to reach the objectives

Partner 1: Emmanuel Fromager

Staff expenses

PhD student to be hired for 3 years: 95 k€

HYPEDFT deals with the development of *ab initio* density-functional approximations from first principles. The work includes the derivation of new formalisms, the computational implementation of those as well as their calibration. The project will be successful if all these aspects are covered, which requires at least 3 years. This is the reason why we would like to hire a PhD student who will be the driving force in most of the tasks (**tasks 2-4**). The successful candidate will do his PhD in Strasbourg under the supervision of E. Fromager and in collaboration with P.-F. Loos.

Instruments and material costs

Laptop and external hard disk for the PhD student to be hired: 3000 €

Coding and computing will be the main activity of the PhD student to be hired during the period of the project. He will travel to Toulouse, participate to summer schools and international conferences. He should have a laptop and an external hard disk for backing up his data.

Outsourcing / subcontracting

Mathematica software (personal academic licence for Emmanuel Fromager and the PhD student to be hired): 12000 €

In the past years, P.-F. Loos has written many routines in *Mathematica* for (i) computing the energy levels of ringium and glomium and (ii) constructing density-functional approximations. In order to benefit from his work and extend it to ensembles (see **tasks 2, 3 and 5**), both E. Fromager and the PhD student to be hired will need four- and three-year personal academic licences for *Mathematica,* respectively. A single-year licence costs 1640 €, hence the total amount of 12000€ that is requested. Let us stress that the department of Mathematics at the University of Strasbourg does not have a subscription to *Mathematica* from which we could freely benefit.

General and administrative costs & other operating expenses

Stays in Toulouse (for Emmanuel Fromager and the PhD student to be hired): 4200 €

Funding is requested for *five-day* stays in the partner's group in Toulouse (4 in total for Emmanuel Fromager and 3 for the PhD student to be hired). Both travel and accomodation expenses (600 € for

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one stay and one person) are taken into account in the total amount. The visits are planned as follows (see the Gantt chart).

*Stay 1 (E. Fromager): year 1, period: months 1-3, **task 1***.

purpose of the visit: discussing the various (weight-independent) DFAs to be implemented, agreeing on the atomic and molecular prototypical systems to be studied, starting the implementation in Quantum Package.

*Stay 2 (E. Fromager and the PhD student to be hired): year 2, period: months 1-3, **task 2***.

purpose of the visit: starting the implementation of ensemble DFAs based on ringium, discussing the application of ensemble DFT to quantum dots, fixing practical details about the organization of the first international workshop on ensemble DFT in Strasbourg (planned for June 2021) **[see below]**.

*Stay 3 (E. Fromager and the PhD student to be hired): year 3, period: months 1-3, **tasks 3 and 4***.

purpose of the visit: writing a paper about the newly developed weight-dependent exchange DFAs, discussing the construction of weight- and spin-dependent correlation functionals for glomium.

*Stay 4 (E. Fromager and the PhD student to be hired): year 4, period: months 1-3, **tasks 4 and 5***.

purpose of the visit: writing papers on the calibration of our newly developed ensemble xc DFAs for quantum chemical problems, discussing deviations from uniformity in glomium, fixing practical details about the organization in Toulouse of the second international workshop on ensemble DFT (planned for June 2023) **[see below]**.

Attending conferences *(for Emmanuel Fromager and the PhD student to be hired):* **15 k€**

Funding is requested for covering travel and accomodation expenses as well as registration fees (3000€ per year (4 in total) for Emmanuel Fromager and 3000€ in total for the PhD student to be hired). This is important for promoting our work on ensemble DFT in international conferences like, for example, both Spring and Fall meetings of the *American Chemical Society* to which E. Fromager has been invited four times since 2018.

Participation to summer schools *(for the PhD student to be hired):* **2000 €**

The PhD student to be hired is expected to enlarge his knowledge in quantum chemistry by participating to several international summer schools like, for example, the ISTPC summer school on electron correlation in Physics and Chemistry [51] which is organized by E. Fromager in Aussois, France (the next edition is planned for 2020).

Organizing international workshops *(in Strasbourg and Toulouse) :* **10 k€**

We would like to initiate the organization of bi-annual workshops on density-functional theory for ensembles. Two workshops will be organized over the period of the project, the first one (planned for June 2021) in Strasbourg and the second one (planned for June 2023) in Toulouse. 5000 € are requested for each workshop in order to invite international experts in the field. These workshops will

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give us additional opportunities to promote our work and will hopefully stimulate new developments in the field.

Administrative cost: 11296 €

This additional cost is compulsory. It relates to the fact that the project will be (partly) hosted at the University of Strasbourg and financially managed by its staff.

SUBTOTAL for E. Fromager: 152496 €

Partner 2: Pierre-François Loos

Staff expenses

Master 2 students to be hired: **8100 €**

Funding is requested for hiring second-year master students for a five-month period (2700 € for a single Master 2 student). The three students to be hired (one every year during the first three years of the project) will perform calibration studies of the newly developed ensemble DFT methods according to the work plan (see **tasks 1, 2 and 4**).

General and administrative costs & other operating expenses

Stays in Strasbourg (for Pierre-François Loos and the M2 students to be hired): **4200 €**

Funding is requested for *five-day* stays in the coordinator's group in Strasbourg (4 in total for Pierre-François Loos and 3 in total for the M2 students (one stay for each)). Both travel and accomodation expenses (600 € for one stay and one person) are taken into account in the total amount. The visits are planned as follows (see the Gantt chart).

*Stay 1 (P.-F. Loos and the first M2 student to be hired): year 1, period: months 6-9, **tasks 1 and 2.***

purpose of the visit: writing papers on the weight-independent DFAs implemented in Quantum Package and their performance, discussing the construction of weight-dependent DFAs based on the ringium (with a particular focus on the incorporation of the Fermi hole curvature into the weight-dependent contribution to the xc ensemble energy).

*Stay 2 (P.-F. Loos and the second M2 student to be hired): year 2, period: months 6-9, **tasks 2 and 3**.*

purpose of the visit: writing papers about the ringium-based ensemble DFAs and their application to quantum dots, discussing the construction of ensemble exchange functionals from the glomium (with a particular emphasis on the finite-size effects).

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Stay 3 (P.-F. Loos and the third M2 student to be hired): year 3, period: months 6-9, **tasks 3 and 4.**

purpose of the visit: writing a paper about the newly developed weight-dependent correlation DFAs, starting the implementation in Quantum Package of the functionals developed in task 3, discussing the calibration studies to be performed.

Stay 4 (P.-F. Loos): year 4, period: months 6-9, **task 5.**

purpose of the visit: writing a paper about a more explicit and exact Gould-Pittalis decomposition of the xc energy for the Hubbard dimer, writing papers about the application of the latter decomposition to the design of DFAs for larger ensembles.

Attending conferences *(for Pierre-François Loos):* **12 k€**

Funding is requested for covering travel and accomodation expenses as well as registration fees (3000€ per year (4 in total) for Pierre-François Loos). This is important for promoting our work on ensemble DFT in international conferences.

Administrative cost: 1944 €

This additional cost is compulsory. It relates to the fact that the project will be (partly) hosted at the CNRS (Délégation Régionale Occitanie Ouest) and financially managed by its staff.

SUBTOTAL for P.-F. Loos:	*26244 €*

TOTAL (for the two partners): 178740 €

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Requested means by item of expenditure and by partner*

		Partner 1 E. Fromager	Partner 2 P.-F. Loos	Partner XXX	Partner XXX
Staff expenses		95000	8100		
Instruments and material costs (including the scientific consumables)		3000			
Building and ground costs					
Outsourcing / subcontracting		12000			
General and administrative costs & other operating expenses	Travel costs	31200	16200		
	Administrative management & structure costs**	11296	1944		
Sub-total		152496	26244		
Requested funding	178740				

* The amounts indicated here must be strictly identical to those entered on the website. If both information are not consistent, if they were badly filled in or lacking, the information entered online will prevail on those reported in the submission form / scientific document.

** For marginal cost beneficiaries, these costs will be a package of 8% of the eligible expenses. For full cost beneficiaries, these costs will be a sum of max. 68% of staff expenses and max. 7% of other expenses.

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III. Impact and benefits of the project

HYPEDFT deals with basic science and, more specifically, with electronic structure theory. It aims at developing new computational tools for modeling excited-state properties of complex molecular systems. Various impacts are expected. A first (short-term) one in the DFT community where the ensemble formalism has not attracted as much attention as TD-DFT until now. Another (short/medium-term) impact is expected in the computational chemistry community as all our developments (the newly developed ensemble functionals in particular) will be made freely available in the Quantum Package program. DFT users should therefore be able to apply (and calibrate) ensemble DFT to the complexes they are interested in. If successful, our approach could ultimately have the same impact as DFT in other fields like biochemistry. We should also stress that ensemble DFT (and therefore our developments) can be applied to solids, for example for computing fundamental and optical gaps (within the same formalism [4]). Therefore, we also expect *HYPEDFT to* have a short- or medium-term impact in the condensed matter physics community.

Our theoretical developments and calibration studies will be presented in scientific articles (to be published in rank A journals). We will also communicate about our work when giving talks at international conferences. Funding has been requested for organizing two international workshops on ensemble DFT for that purpose. We also plan to teach our latest developments at the international ISTPC summer school on electron correlation in physics and chemistry (whose founder and organizer is E. Fromager). Most importantly, the implementation of our work in the Quantum Package program will be freely available on GitHub [9].

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