



Theoretical Chemistry Laboratory - Sorbonne University

**INTERNSHIP REPORT**

**DEVELOPMENT AND TEST OF SELF-CONSISTENT  
FIELD EQUATIONS FOR THE RANGE-SEPARATED  
DENSITY FUNCTIONAL THEORY AND THE  
BASIS-SET CORRECTION METHOD**

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## I. INTRODUCTION

### A. Working environment

The Theoretical Chemistry Laboratory (LCT) of Sorbonne University is a joint research unit whose director is Professor Jean-Philip Piquemal. It comprises two research poles : *Methods and tools for quantum chemistry* and *Modelisation of complex systems*. My internship took place in the first one where I worked in the *Theory of electronic structure* group.

Due to the covid-19 crisis, we had to set up "working rituals" such as regular Skype calls and instant chats. The main advantage to work on a theoretical project is that essentially the same work can be done at home. Yet, the lack of a conventional working environment makes it difficult to complete full work days and to create contacts with the research team and the laboratory workers in general. This experience was an opportunity to work on my self-discipline and my autonomy in general by planning reasonable work days and providing persistent efforts to seek for informations before requesting answers from my supervisors.

Finally, I particularly want to thank Julien TOULOUSE and Emmanuel GINER for the time they spent trying to explain and illustrate physical and mathematical concepts through communication tools not adapted to this kind of interactions and for their understanding regarding the time needed to assimilate the new concepts they introduced to me.

I also want to thank the LCT members for their welcome : seminars were the chance to discover a tiny part of the broad field of quantum chemistry that I hope I can continue to explore in the coming years.

### B. Scientific introduction

Under the supervision of Julien TOULOUSE and Emmanuel GINER, I participated in the improvement of the *range-separated density functional theory* (RS-DFT) and *wave-function theory basis-set error correction using density-functional theory* methods which have been the object of a lot of research these recent years.

The purpose of the internship was to implement the self-consistent field equations for the multideterminantal decomposition of the short-range exchange and correlation functionals for the RS-DFT and the basis-set correction methods in the *Quantum package* programming environment. Moreover, we test the use of on-top pair densities obtained from wave functions calculations

to compare with that coming from the *uniform electron gas* (UEG) model. The latter has been widely used by the community due to the relatively good compromise between the accuracy of the results and a cheap computational cost. However, computational chemistry aims to reach *chemical accuracy*,  $1 \text{ kcal/mol} \approx 4 \text{ kJ/mol}$ , required to provide realistic theoretical prediction. Treating realistic chemical systems, with growing sizes, within chemical accuracy motivated the use of hybrid computational methods schemes. Limiting the use of UEG’s on-top pair density is supposed to increase the accuracy but could also permit to extend the range of systems that we are able to study.

The report is organised as follows. In Sec. II, we recall the framework of the different methods used in quantum chemistry. In particular, we introduce both wave-function and density-functional theories. In Sec. III, we present the main hybrid methods used in the field : the *range-separated density functional theory* and the *basis-set correction*. Then, in Sec. IV, we develop the implementation of the self-consistent field equations that will now include the calculations of the multideterminant exchange and correlation functionals. Finally, in Sec. V, we apply the method to the calculation of the Helium atom energy and the determination of the dissociation curve of the  $\text{H}_2$  molecule.

## II. WAVE FUNCTION THEORY AND DENSITY FUNCTIONAL THEORY IN A NUTSHELL<sup>1</sup>

### A. The quantum many-electron problem

We consider here a system of  $N$  electrons and  $N_{\text{nucl}}$  nuclei described with an Hamiltonian  $H$ ,

$$H = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_{\text{nucl}}} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^{N_{\text{nucl}}} \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + \sum_{A=1}^{N_{\text{nucl}}} \sum_{B>A}^{N_{\text{nucl}}} \frac{Z_A Z_B}{R_{AB}}. \quad (1)$$

In this equation, in atomic units, the first term is the kinetic energy operator of the electrons, the second is the kinetic energy operator of the nuclei, the third represents the Coulomb attraction between electrons and nuclei, the fourth is the repulsion between electrons and the fifth is the repulsion between nuclei. Moreover,  $M_A$  is the ratio of the mass of nucleus  $A$  to the mass of an electron, and  $Z_A$  is the atomic number of nucleus  $A$ .

## B. The Born-Oppenheimer approximation

In the Born-Oppenheimer approximation, due to the fact that nuclei are much heavier than electrons (at least 3 orders of magnitude) we neglect the kinetic contribution of the nuclei compare to that of the electrons. Accordingly, we now consider the electronic Hamiltonian :

$$H_{\text{elec}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^{N_{\text{nucl}}} \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}}, \quad (2)$$

with the Schrödinger equation :

$$H_{\text{elec}} \Psi_{\text{elec}} = \mathcal{E}_{\text{elec}} \Psi_{\text{elec}}. \quad (3)$$

In the following, we will not use the “elec“ label.

## C. The antisymmetry of the wave function

To completely describe an electron, we need to specify its spin. To do so, we consider two spin functions  $\alpha(\omega)$  and  $\beta(\omega)$ , corresponding to spin up and down, respectively. The variable  $\omega$  is the spin variable that leads to :

$$\alpha\left(\frac{1}{2}\right) = 1, \quad \alpha\left(-\frac{1}{2}\right) = 0, \quad \beta\left(\frac{1}{2}\right) = 0, \quad \text{and} \quad \beta\left(-\frac{1}{2}\right) = 1. \quad (4)$$

Therefore, the wave function for an  $N$ -electron system depends on  $4N$  coordinates denoted by  $\vec{x}_i = \{\vec{r}_i, \omega_i\}$  for  $i = 1, \dots, N$ . The wave function will thus be designated by  $\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ . It must be antisymmetric with respect to the exchange of two coordinates :

$$\Psi(\vec{x}_1, \dots, \vec{x}_i, \dots, \vec{x}_j, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N), \quad (5)$$

which is well translated into the Slater determinant formalism.

## D. Variational principle

The average energy associated with a given state  $\Psi$  is given by the formula :

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle, \quad (6)$$

where  $\Psi$  is normalized,  $\langle \Psi | \Psi \rangle = 1$ . The variational principle states that this energy is an upper bound to the exact ground-state energy for any approximated wave function  $\Psi$

$$E_0 \leq E[\Psi]. \quad (7)$$

The equality is reached when the function  $\Psi$  is the exact ground-state wave function  $\Psi_0$  which minimizes the energy :

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle. \quad (8)$$

## E. Wave-function theory

Wave-function theory (WFT) aims to approximate  $\Psi_0$  using one of the numerous techniques provided by the analysis of the quantum many-body problem, as for example the variational principle and perturbation theories. We focus on the first one in the entire work presented here. In this work, we only used variational wave functions and therefore for the sake of compactness of the present report, we only introduce two different variational wave function ansatzes : Hartree-Fock (HF) and configuration interaction (CI).

### 1. The Hartree-Fock approximation

In the HF approximation, the exact wave function  $\Psi_0$  is approximated by a unique Slater determinant  $\Phi$  which satisfies the antisymmetry property of any fermionic wave function. Accordingly, the wave function is written as :

$$\Psi_0(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \simeq \Phi_{\mathcal{B}}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix}, \quad (9)$$

where  $\psi_i(\vec{x})$  are orthonormal spin orbitals that are expanded on a one-electron basis set here referred to as  $\mathcal{B}$  :

$$\psi_i(\vec{x}) = \sum_{\mu=1}^M c_{\mu,i} \chi_{\mu}(\vec{x}), \quad (10)$$

where  $M$  is the number of basis functions,  $\chi_{\mu}(\vec{x})$  are Gaussian-type-orbital basis functions and  $c_{\mu,i}$  are coefficients optimized according to some energy minimization of approximated wave function models.

This approximation is also referred to as the independent-electron approximation as the probability of finding two opposite spin electrons is simply the product of the individual probabilities.

The HF approximation for the wave function leads to the following energy :

$$E_{\mathcal{B}}^{\text{HF}} = \min_{\Phi_{\mathcal{B}}} \langle \Phi_{\mathcal{B}} | \hat{H} | \Phi_{\mathcal{B}} \rangle = \langle \Phi_{\mathcal{B}}^{\text{HF}} | \hat{H} | \Phi_{\mathcal{B}}^{\text{HF}} \rangle, \quad (11)$$

where  $\Phi_{\mathcal{B}}^{\text{HF}}$  is the one determinant wave function that minimizes the energy with respect to the spin orbitals  $\psi_i(\vec{x})$ . Therefore, the HF energy depends on the quality of the basis set  $\mathcal{B}$  chosen for a given calculation. Of course, due to the intrinsic approximated nature of the HF wave function, the variational principle applies :

$$E_0 \leq E_{\mathcal{B}}^{\text{HF}}. \quad (12)$$

In order to illustrate a typical HF calculation, we report in Fig. 1 the convergence of the HF energy for the He atom with a sequence of basis sets of Dunning type<sup>2</sup>. As evidenced in Fig. 1, the HF energy converges quite rapidly with respect to the basis set  $\mathcal{B}$ , which is an appealing feature of the HF model. Nevertheless, even when reaching the basis set convergence, an error of about 0.04 Ha is obtained with respect to the estimated exact ground state energy of the He atom. Such an energy difference is defined as the *correlation energy*,

$$E^{\text{corr}} = E_0 - E^{\text{HF}}, \quad (13)$$

which is a fundamental quantity in quantum chemistry. Because of the lack of correlation treatment between electrons, this approximation is insufficient to describe many situations such as bond dissociation of covalent and/or non-covalent nature.

To reduce this error, one might use one of the many post-Hartree-Fock methods available in quantum chemistry which introduces in many different flavours the correlation effects in the wave function and therefore estimates the correlation energy. We present below the *full configuration interaction*.

## 2. The full configuration interaction method

Within a given basis set  $\mathcal{B}$ , in order to improve the description of the correlation effects, the  $N$ -electron wave function is built as a linear combination of *all Slater determinants* that can be generated from the one-electron basis set  $\mathcal{B}$ . Such an approach is referred to as the full configuration interaction (FCI). Usually, we express the FCI wave function as increasing substitution levels with respect to the HF Slater determinant :

$$\Psi_{\mathcal{B}}^{\text{FCI}} = c_{\text{HF}} \Phi_{\mathcal{B}}^{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} c_i^r \Phi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} c_{ij}^{rs} \Phi_{ij}^{rs} + \dots \quad (14)$$



Here  $\Phi^{\text{HF}}$  is the Hartree-Fock determinant,  $\Phi_i^r$  is the Slater determinant where the spin-orbital  $i$  occupied in the HF wave function is replaced by the orbital  $r$  unoccupied in the HF wave function,  $\Phi_{ij}^{rs}$  is the Slater determinant where the spin-orbitals  $i$  and  $j$  occupied in the HF wave function are replaced by the orbitals  $r$  and  $s$  unoccupied in the HF wave function, and so on.

The coefficients of the Slater determinants are optimized using the variational principle of Eq. (6), and the energy of the FCI wave function is formulated as :

$$E_{\mathcal{B}}^{\text{FCI}} = \min_{\Psi_{\mathcal{B}}} \langle \Psi_{\mathcal{B}} | \hat{H} | \Psi_{\mathcal{B}} \rangle = \langle \Psi_{\mathcal{B}}^{\text{FCI}} | \hat{H} | \Psi_{\mathcal{B}}^{\text{FCI}} \rangle. \quad (15)$$

It is important to notice that the FCI is the exact solution of the Schrödinger equation *within a given basis set*  $\mathcal{B}$ . Therefore, at the FCI level, the "only" approximation remaining is the quality of the basis set  $\mathcal{B}$ .

In atomic systems or in organic chemical systems near their equilibrium geometries, the Hartree-Fock determinant dominates the wave function but the contribution of the other Slater determinants improves the energy estimation. Then, we have :

$$E_0 \leq E_{\mathcal{B}}^{\text{FCI}} \leq E_{\mathcal{B}}^{\text{HF}}, \quad (16)$$

and the FCI energy becomes exact only *in the limit of a complete basis set (CBS)*

$$E_0 = \lim_{\mathcal{B} \rightarrow \text{CBS}} E_{\mathcal{B}}^{\text{FCI}}. \quad (17)$$

### 3. One of the main problem of WFT : the basis set convergence

To illustrate the behaviour of the FCI energy we report in Fig. 1 the convergence of the FCI energy for a sequence of Dunning basis sets. From Fig. 1 we observe that, unlike the HF energy, the FCI energy tends towards the exact energy in the limit of a complete basis set. Nevertheless, we also notice that the FCI energy is much more sensitive to the quality of the one-electron basis set than the HF energy.

The reasons of the slow convergence of the FCI energy was initially pointed out by the seminal work of Hylleraas<sup>4</sup> on the He atom where it was shown<sup>4</sup> that the exact wave function exhibits a linear behaviour near the coalescence point (*i.e.* near  $r_{12} = |\vec{r}_1 - \vec{r}_2| = 0$ ) :

$$\Psi(\vec{r}_1, r_{12}) = \Psi(\vec{r}_1, 0) \left( 1 + \frac{1}{2} r_{12} \right) + \mathcal{O}\left( (r_{12})^2 \right), \quad (18)$$

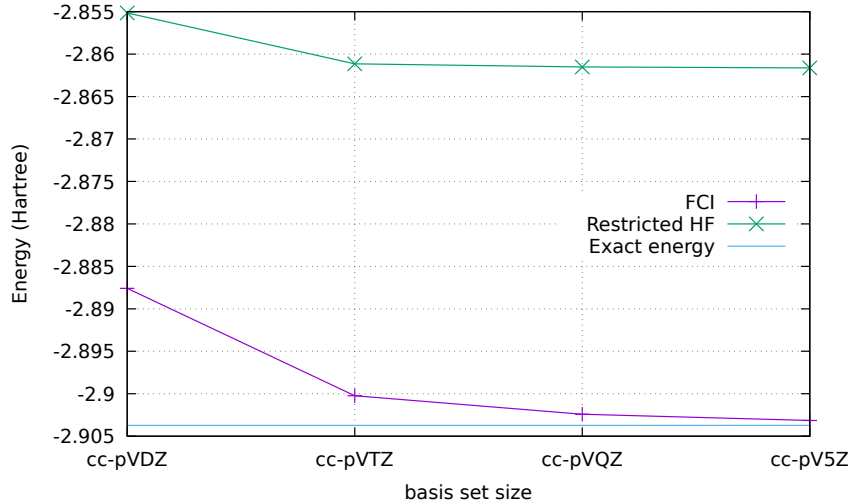


FIG. 1. He ground-state energy with increasing one-electron basis-set size - HF vs FCI calculations ; exact energy from Ref. 3

which is usually referred to as the electron-electron cusp. Therefore, Hylleraas shown that the slow convergence of FCI energies is related to the slow convergence of the wave function in the inter-electronic distance (*i.e.*  $r_{12}$ ) representation, which necessary involves two-body effects. Instead of the wave function, one can have a look at the pair density which contains all necessary information regarding the two-body properties of any wave function.

The pair density,

$$n_2(\vec{r}_1, \vec{r}_2) = N(N-1) \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\omega_1 d\omega_2 d\vec{x}_3 \dots d\vec{x}_N, \quad (19)$$

is the probability density of finding two electrons at positions  $\vec{r}_1$  and  $\vec{r}_2$ .

To give a pictorial illustration of this quantity, we computed the pair density obtained from FCI wave functions in a sequence of Dunning basis sets for the helium atom. As the pair density is function on  $\mathbb{R}^6$  object and therefore quite hard to represent, we represent a section of the pair density when two electrons are on a circle of radius  $0.5 \text{ \AA}$ . The advantage of such section is that the pair density can be represented directly in terms of the angle  $\theta$  between  $\vec{r}_1$  and  $\vec{r}_2$  (see the representation of the Helium atom in Fig. 2). We report in Fig. 2 the variation of the pair density at different levels of calculations as a function of  $\theta$ .

A striking feature appearing in Fig. 2 is that the Hartree-Fock wave function,  $\Psi_{\text{HF}}(\vec{r}_1, \vec{r}_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)$ , leads to a constant pair density with respect to  $\theta$ . This can be easily understood as the pair density, which is the squared modulus of the wave function for a two-electron system, is

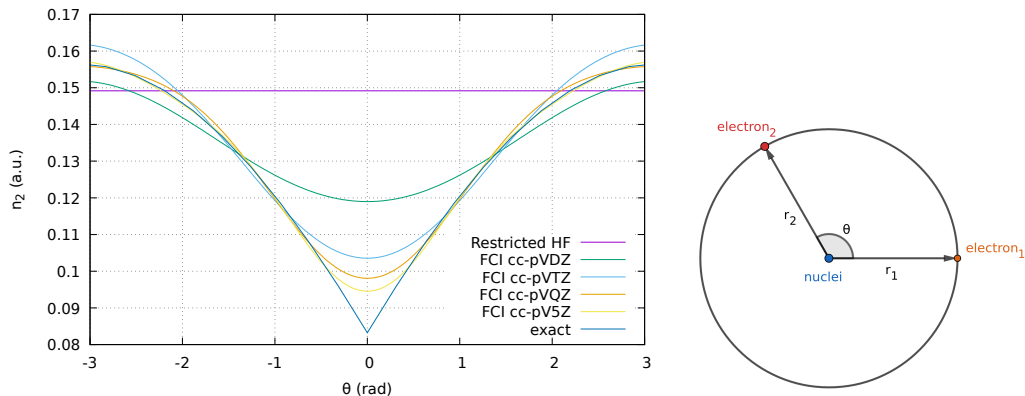


FIG. 2. Left : Pair density of the He atom as a function of  $\theta$  for two electrons on a circle of radius  $0.5 \text{ \AA}$  at different computational levels : HF, FCI for a sequence of Dunning basis sets, and the estimated exact pair density obtained from Ref. 5. Right : Representation of the coordinate system of the He atom

proportional to the squared of  $1s$ -type functions, which only depends on the radial coordinate. On the other hand, the FCI wave functions which are multi-determinantal wave functions present a very different behaviour : the pair density decreases when approaching the coalescence point. This is a signature that the correlation effects brought by the FCI wave function tend to push electrons away from one another, which is often called the Coulomb hole as it lowers the probability of finding electrons at small  $r_{12}$  (or equivalently here at small  $\theta$ ). Another important aspect is the behaviour of the pair density with the size of the basis set : the depth of the Coulomb hole increases with the basis set, and no linear behaviour is obtained near  $\theta = 0$ . When reaching the CBS limit, one obtains the exact wave function which exhibits an electron-electron cusp, i.e a linear dependence of the pair density with respect to  $\theta$ .

The comparison with the exact wave function shows that the probability of finding two electrons at the same point is overestimated using FCI calculations in finite basis sets.

To conclude this section, it should be mentioned that the computational cost of the FCI method rapidly becomes prohibitive as the number of Slater determinant composing the FCI wave function grows exponentially with the number of electrons in the system and basis functions in  $\mathcal{B}$ . Therefore, a wide variety of approximations to the FCI wave function have been developed in order to lower the computational cost of WFT while maintaining its accuracy.

## F. Density-functional theory

### 1. The Levy-Lieb formulation of DFT

Density-functional theory (DFT) states that the energy of an  $N$ -electron system is deducible from its ground-state *one-electron* density  $n(\vec{r})$

$$n(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\omega d\vec{x}_2 d\vec{x}_3 \dots d\vec{x}_N, \quad (20)$$

according to the first Hohenberg-Kohn theorem<sup>6</sup>. Therefore, one can reformulate the variational principle with respect to the density.

Minimizing the energy can be decomposed in two parts :

- Minimizing the energy for a fixed density  $n(\vec{r})$ , which means minimizing over the subset of wave functions  $\Psi$  which yield a given density  $n$  (this is referred to as  $\min_{\Psi \rightarrow n}$ ).
- Minimizing the energy with respect to all possible densities (this is referred to as  $\min_n$ ).

One can have a graphical representation of these two steps in the Fig. 3 from Ref. 7.

Thus, we rewrite the variational principle as :

$$E_0 = \min_n \left( \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{ee} + \hat{V}_{ne} | \Psi \rangle \right), \quad (21)$$

with the kinetic-energy operator  $\hat{T}$ , the electron-electron interaction operator  $\hat{W}_{ee}$ , and the nuclei-electron interaction operator  $\hat{V}_{ne}$ . An important point here is to notice that the electron-nuclei interaction energy is expressed as a very simple linear functional of the density :

$$\langle \Psi | \hat{V}_{ne} | \Psi \rangle = \int v_{ne}(\vec{r}) n(\vec{r}) d\vec{r}, \quad (22)$$

where  $v_{ne}$  is the external potential specific to the system considered. Then we can reformulate the minimization of the energy directly in terms of minimization over the densities,

$$E_0 = \min_n \left( F[n] + \int v_{ne}(\vec{r}) n(\vec{r}) d\vec{r} \right). \quad (23)$$

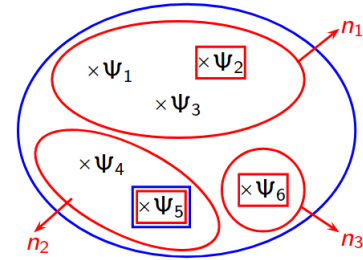


FIG. 3. 1st step : in red, finding the minimum energy state for each value of density  $n_1$ ,  $n_2$  and  $n_3$ ; 2nd step : in blue, finding the minimum energy state between selected states  $\Psi_2$ ,  $\Psi_5$  and  $\Psi_6$

where we have introduced the so-called Levy-Lieb universal density functional  $F[n]$ , independent from the external potential as

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle. \quad (24)$$

The minimizing wave function will be denoted by  $\Psi[n]$ . Therefore, by defining the energy functional  $E[n]$  as

$$E[n] = F[n] + \int v_{\text{nc}}(\vec{r})n(\vec{r}) d\vec{r}, \quad (25)$$

one can rewrite the energy minimization as

$$E_0 = \min_n E[n] \quad (26)$$

and the minimizing density  $n_0$  in Eq. (26)

$$n_0 = \text{argmin} E[n] \quad (27)$$

is of course the exact ground state density.

To conclude this paragraph, it should be mentioned that obtaining reasonable approximations for the functional  $F[n]$  is at the heart of many developments in DFT as will be illustrated in the following paragraphs.

## 2. The Kohn-Sham formulation of DFT

The expression of  $F[n]$  given in Eq. (24) is extremely helpful to formalize DFT, but it is of no use to perform actual calculations. An appealing formulation of  $F[n]$  was given by Kohn and Sham (KS) in Ref. 8:

$$F[n] = T_s[n] + E_{\text{Hxc}}[n]. \quad (28)$$

Here  $T_s[n]$  is the non-interacting kinetic-energy functional which can be defined with a constrained-search formulation :

$$T_s[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle, \quad (29)$$

where  $\Phi$  is a Slater determinant wave function. The Slater determinant minimizing Eq. (29) is referred to as the *Kohn-Sham wave function*  $\Phi[n]$ . The remaining effects from the interaction between electrons are treated in the Hartree-exchange-correlation functional  $E_{\text{Hxc}}[n]$  which is decomposed as :

$$E_{\text{Hxc}}[n] = E_{\text{H}}[n] + E_{\text{xc}}[n], \quad (30)$$

where,

$$E_H[n] = \frac{1}{2} \iint \frac{n(\vec{r}_1)n(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \quad (31)$$

is the Hartree energy representing the electrostatic repulsion of the charge distribution  $n(\vec{r})$ .

The remaining exchange-correlation functional is also decomposed as

$$E_{xc}[n] = E_x[n] + E_c[n], \quad (32)$$

where  $E_x[n]$  is the exchange energy functional evaluated from the Kohn-Sham wave function :

$$E_x[n] = \langle \Phi[n] | \hat{W}_{ec} | \Phi[n] \rangle - E_H[n], \quad (33)$$

and  $E_c[n]$  is the correlation energy functional :

$$E_c[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{ec} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{ec} | \Phi[n] \rangle. \quad (34)$$

Therefore, the KS formulation of DFT can be reformulated as

$$\begin{aligned} E_0 &= \min_n \left( T_s[n] + E_{Hxc}[n] + \int v_{ne}(\vec{r})n(\vec{r}) d\vec{r} \right) \\ &= \min_n \left( \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle + \bar{E}_{Hxc}[n] + \int v_{ne}(\vec{r})n(\vec{r}) d\vec{r} \right), \end{aligned} \quad (35)$$

but as the density  $n$  is the same than that of the Slater determinant  $\Phi$ , one can combine the minimizations over a minimization over  $\Phi$

$$E_0 = \min_{\Phi} \left( \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + E_{Hxc}[n_{\Phi}] \right). \quad (36)$$

Within such a formulation, provided that  $E_{xc}[n]$  is known, the exact energy of a  $N$ -electron system can be obtained by a minimization over a single Slater determinant. Therefore, the computational cost is extremely reduced compared to approximations of WFT where a linear combination of Slater determinants is introduced.

### 3. *Illustration of the Kohn-Sham approach on the He atom and H<sub>2</sub> molecule*

The appealing feature of KS DFT is to provide the exact ground state energy and density using a single Slater determinant formulation. Nevertheless, this scheme is based on an unknown exchange-correlation functional, and therefore depends on the quality of the approximations for this functional. Up to now, a large number of approximated exchange-correlation functionals have

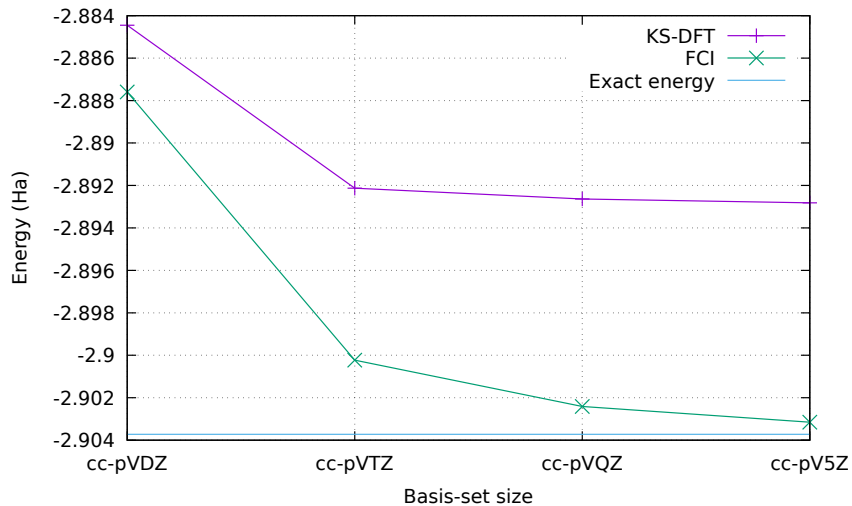


FIG. 4. He ground-state energy with increasing basis sets - KS-DFT vs FCI ; exact energy from Ref. 3

been developed, but throughout our work, we use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>9</sup> to approximate  $E_{xc}[n]$ . This choice is motivated by the fact that the PBE functional was already used in very recent developments of new functionals by Julien TOULOUSE and Emmanuel GINER.

In Fig. 4 below, we compare the convergence of the energy for the ground state of the Helium atom using the FCI and KS PBE schemes. The latter presents a faster convergence with the basis set compared to the FCI scheme. Nevertheless, the PBE approximation leads to a significant error when reaching the converged energy.

To illustrate how PBE is not accurate enough to describe situations such as bond dissociation, we report in Fig. 5 the dissociation curve of the  $H_2$  molecule. As apparent from Fig. 5, we remark an underestimation of the energy at the equilibrium distance (about 10 mHa  $\approx$  0.3 eV) and at long distances (about 73 mHa  $\approx$  1.9 eV).

### III. HYBRID METHODS : THE BEST OF WFT AND KS-DFT

In Secs. II E and II F, we introduced advantages and drawbacks of both WFT and KS-DFT. On the one hand, WFT offers a systematic way to improve the results using better basis sets, but it converges too slowly. On the other hand, KS-DFT offers fast convergence with respect to the basis set, but towards a wrong limit as the universal exchange-correlation functional is not known

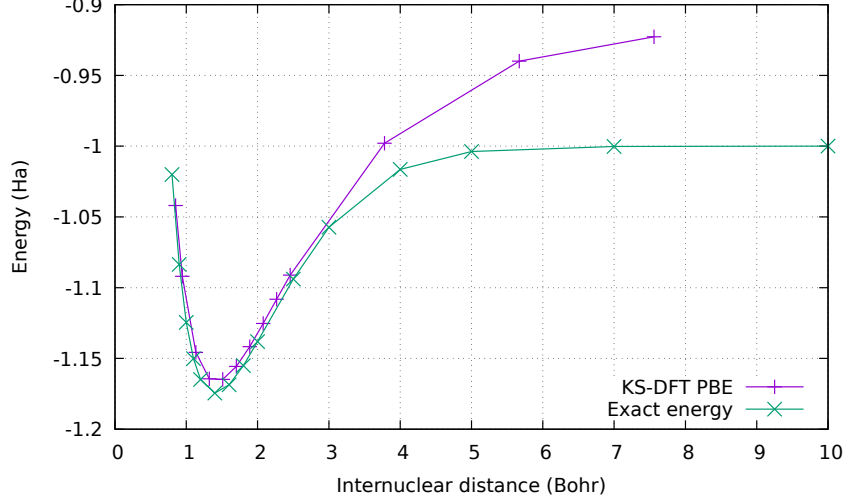


FIG. 5. H<sub>2</sub> dissociation curve - KS-DFT vs accurate energy from Ref. 10 - Basis-set : cc-pVTZ

and therefore approximated in practice. Hybrid methods aim to take advantages of both methods. We present two of them in this section : *range-separated density functional theory* and *basis-set correction*.

### A. Range-separated density functional theory

Range-separated density functional theory has been in development for nearly thirty years (see Ref. 11 and references therein). It aims to take advantage of both KS-DFT and WFT : the semilocal density-functional approximations<sup>12</sup> are accurate at small interelectronic distances while WFT calculations are more appropriate at long-range. As originally proposed by Savin in its seminal paper<sup>13</sup>, the original Levy-Lieb functional of Eq. (28) can be written as follows<sup>11</sup> :

$$F[n] = F^{\text{lr},\mu}[n] + \bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n] \quad (37)$$

where the so-called long-range Levy-Lieb functional is defined as

$$F^{\text{lr},\mu}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \Psi \rangle \quad (38)$$

where  $\hat{W}_{\text{ee}}^{\text{lr},\mu}(r_{12}) = \sum_{i>j} w_{\text{ee}}^{\text{lr},\mu}(\hat{r}_{12})$  and  $w_{\text{ee}}^{\text{lr},\mu}(r_{12}) = \frac{\text{erf}(\mu r_{12})}{r_{12}}$  is the so-called long-range interaction tuned by the *range-separation parameter*  $\mu$ , and the corresponding complementary short-range Hartree-exchange-correlation functional is defined as

$$\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n] = F[n] - F^{\text{lr},\mu}[n]. \quad (39)$$



The advantage of introducing the long-range Levy-Lieb functional  $F^{\text{lr},\mu}[n]$  is that it naturally produces a wave function  $\Psi^{\text{lr},\mu}[n]$  associated to a given density  $n$

$$\Psi^{\text{lr},\mu}[n] = \operatorname{argmin}_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \Psi \rangle, \quad (40)$$

and as the minimization in Eq. (38) contains the two-body operator  $\hat{W}_{\text{ee}}^{\text{lr},\mu}$ ,  $\Psi^{\text{lr},\mu}[n]$  is necessary a multi-determinant wave function as long as  $\mu \neq 0$ . Therefore, this formalism naturally creates a mathematical framework for DFT with a multi-determinant wave function that can take advantage of both WFT and DFT. The complementary short-range Hartree-exchange-correlation part of  $F[n]$  is being treated in a similar framework that the KS-DFT scheme. We decompose  $\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n]$  as in Sec. III F for  $E_{\text{Hxc}}[n]$ , and we get :

$$\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n] = E_{\text{H}}^{\text{sr},\mu}[n] + \bar{E}_{\text{xc}}^{\text{sr},\mu}[n]. \quad (41)$$

Here  $E_{\text{H}}^{\text{sr},\mu}[n]$  is the short-range Hartree energy functional :

$$E_{\text{H}}^{\text{sr},\mu}[n] = \frac{1}{2} \iint n(\vec{r}_1) n(\vec{r}_2) w_{\text{ee}}^{\text{sr},\mu}(r_{12}) d\vec{r}_1 d\vec{r}_2, \quad (42)$$

where the short-range electron-electron interaction is  $w_{\text{ee}}^{\text{sr},\mu}(r_{12}) = 1/r_{12} - w_{\text{ee}}^{\text{lr},\mu}(r_{12})$ .

Similarly to what is done in the Kohn-Sham scheme (see Eq. (35)), one can recombine the different minimization steps over the wave function and the density into a unique minimization over the wave function

$$\begin{aligned} E_0 &= \min_n \left( F[n] + \int v_{\text{ne}}(\vec{r}) n(\vec{r}) \right) \\ &= \min_n \left( \min_{\Psi \rightarrow n} (\langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \Psi \rangle) + \bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n] + \int v_{\text{ne}}(\vec{r}) n(\vec{r}) d\vec{r} \right) \\ &= \min_{\Psi} \left( \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \hat{V}_{\text{ne}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n_{\Psi}] \right). \end{aligned} \quad (43)$$

By introducing the RS-DFT variational energy of  $\Psi$  as

$$E[\Psi] = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \hat{V}_{\text{ne}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n_{\Psi}] \quad (44)$$

one can rewrite the ground state energy as

$$E_0 = \min_{\Psi} E[\Psi]. \quad (45)$$

Of course, as the formulation in terms of minimization over the density of Eq. (26) is equivalent with that where the minimization is performed over wave functions  $\Psi$  (see Eq. (45)), the density

associated with the minimizing wave function of Eq. (45) is necessary the exact ground state density.

The wave function  $\Psi^{\text{lr},\mu}[n_0]$  minimizing Eq. (45) can be obtained by imposing that the functional derivative of  $E[\Psi]$  with respect to  $\Psi$  vanishes, which translates into

$$\left(\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr},\mu}\right)|\Psi^{\text{lr},\mu}[n_0]\rangle + \left.\frac{\delta\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n_\Psi]}{\delta\langle\Psi|}\right|_{\Psi=\Psi^{\text{lr},\mu}[n_0]} = \mathcal{E}|\Psi^{\text{lr},\mu}[n_0]\rangle, \quad (46)$$

where  $\left.\frac{\delta\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n_\Psi]}{\delta\langle\Psi|}\right|_{\Psi=\Psi^{\text{lr},\mu}[n_0]}$  is the functional derivative of  $\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n_\Psi]$  with respect to  $\langle\Psi|$  evaluated at  $\Psi = \Psi^{\text{lr},\mu}[n_0]$ . By introducing the complementary Hartree-exchange-correlation potential operator

$$\hat{V}_{\text{Hxc}}[n] = \int d\vec{r} \hat{n}(\vec{r}) \frac{\delta\bar{E}_{\text{Hxc}}[n]}{\delta n(\vec{r})}, \quad (47)$$

where  $\hat{n}(\vec{r})$  is the density operator, Eq. (46) can be rewritten as an effective non-linear Schrödinger equation

$$\hat{H}^{\text{lr},\mu}[n_0]|\Psi^{\text{lr},\mu}[n_0]\rangle = \mathcal{E}^\mu|\Psi^{\text{lr},\mu}[n_0]\rangle, \quad (48)$$

where the so-called long-range Hamiltonian  $\hat{H}^{\text{lr},\mu}[n]$  is defined as

$$\hat{H}^{\text{lr},\mu}[n] = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hxc}}[n] + \hat{W}_{\text{ee}}^{\text{lr},\mu}. \quad (49)$$

It should be pointed out here that the non-linearity of  $\hat{H}^{\text{lr},\mu}[n]$  comes from its dependence on the density of its solution  $\Psi^{\text{lr},\mu}[n]$  through  $\hat{V}_{\text{Hxc}}[n]$ . Also, Eq. (49) admits two limits :

1. when  $\mu \rightarrow 0$ ,  $\hat{W}_{\text{ee}}^{\text{lr},\mu} \rightarrow 0$  and  $E_{\text{Hxc}}^{\text{lr},\mu}[n] \rightarrow \bar{E}_{\text{Hxc}}[n]$  and the RS-DFT equations become the usual Kohn-Sham equations.
2. when  $\mu \rightarrow \infty$ ,  $\hat{W}_{\text{ee}}^{\text{lr},\mu} \rightarrow \hat{W}_{\text{ee}}$  and  $\bar{E}_{\text{Hxc}}^{\text{lr},\mu}[n] \rightarrow 0$  and the RS-DFT equations become the usual WFT equations.

Of course, provided that full flexibility is given to the wave function  $\Psi$  in the minimization of Eq. (45) and that the complementary functional  $\bar{E}_{\text{Hxc}}^{\text{sr},\mu}[n]$  is known, the results of RS-DFT are independent of  $\mu$  : the density provided by the lowest-energy eigenfunction of  $\hat{H}^{\text{lr},\mu}[n_0]$  remains the exact ground state density  $n_0$  and the associated variational energy associated is the exact ground state energy.

Therefore, as in usual KS-DFT, one needs to have an expression for the unknown  $\bar{E}_{\text{xc}}^{\text{sr},\mu}[n]$ , which can also be decomposed in different ways. In Secs. III B and III C, we introduce two of them : the *standard* and the *multideterminant* decompositions into short-range exchange and correlation energies functionals.

## B. Standard decomposition of $\bar{E}_{xc}^{\text{lr},\mu}[n]$ : the Kohn-Sham determinant as reference

The standard decomposition of  $\bar{E}_{xc}^{\text{sr},\mu}[n]$ , directly modeled on the decomposition of  $\bar{E}_{xc}[n]$  in Sec. III F, is the following :

$$\bar{E}_{xc}^{\text{sr},\mu}[n] = E_x^{\text{sr},\mu}[n] + \bar{E}_c^{\text{sr},\mu}[n], \quad (50)$$

where  $E_x^{\text{sr},\mu}[n]$  is the short-range exchange energy functional taken using the Kohn-Sham wave function  $\Phi[n] = \Psi^{\text{lr},\mu=0}[n]$  as reference :

$$E_x^{\text{sr},\mu}[n] = \langle \Phi[n] | \hat{W}_{ee}^{\text{sr},\mu} | \Phi[n] \rangle - E_{\text{H}}^{\text{sr},\mu}, \quad (51)$$

and  $\bar{E}_c^{\text{sr},\mu}[n]$  is the short-range correlation energy functional :

$$\bar{E}_c^{\text{sr},\mu}[n] = E_c[n] - (\langle \Psi^{\text{lr},\mu}[n] | \hat{T} + \hat{W}_{ee}^{\text{lr},\mu} | \Psi^{\text{lr},\mu}[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{ee}^{\text{lr},\mu} | \Phi[n] \rangle), \quad (52)$$

with the correlation energy functional  $E_c[n]$  defined in Eq. (34). If we define the long-range correlation energy as

$$\bar{E}_c^{\text{lr},\mu}[n] = \langle \Psi^{\text{lr},\mu}[n] | \hat{T} + \hat{W}_{ee}^{\text{lr},\mu} | \Psi^{\text{lr},\mu}[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{ee}^{\text{lr},\mu} | \Phi[n] \rangle, \quad (53)$$

the short-range correlation functional of Eq. (52) can be rewritten as

$$\bar{E}_c^{\text{sr},\mu}[n] = E_c[n] - \bar{E}_c^{\text{lr},\mu}[n], \quad (54)$$

which means that the short-range correlation functional is therefore a smaller quantity (in absolute value) than the usual correlation functional.

In practice, both exchange and correlation terms need to be approximated due to the unknown exchange and correlation pair densities. In the following work, we choose to approximate Eqs. (51) and (52) with the short-range Perdew-Burke-Ernzerhof (srPBE) exchange and correlation functionals defined in Refs. 14, 15 and 16 as :

$$E_x^{\text{sr},\mu,\text{PBE}}[n] = \int e_x^{\text{sr},\mu,\text{PBE}}(n(\vec{r}), \nabla n(\vec{r})) d\vec{r}, \quad (55)$$

and

$$\bar{E}_c^{\text{sr},\mu,\text{PBE}}[n] = \int \bar{e}_c^{\text{sr},\mu,\text{PBE}}(n(\vec{r}), \nabla n(\vec{r})) d\vec{r}, \quad (56)$$

where  $\nabla n(\vec{r})$  is the density gradient,  $e_x^{\text{sr},\mu,\text{PBE}}$  and  $\bar{e}_c^{\text{sr},\mu,\text{PBE}}$  are the energy densities.

## C. Multi-determinant decomposition of $\bar{E}_{xc}^{sr,\mu}[n] : \Psi^{lr,\mu}[n]$ as reference

### 1. The exact equations

Alternatively,  $\bar{E}_{xc}^{sr,\mu}[n]$  can be decomposed into multideterminant short-range exchange and correlation energy functionals as formulated in Ref. 17 :

$$\bar{E}_{xc}^{sr,\mu}[n] = E_{x,\text{md}}^{sr,\mu}[n] + \bar{E}_{c,\text{md}}^{sr,\mu}[n], \quad (57)$$

where the short-range exchange is now defined from the multideterminant wave-function  $\Psi^{lr,\mu}$  in contrast to the standard definition in Eq. (51). Therefore, we define the multi-determinant short-range exchange functional as

$$E_{x,\text{md}}^{sr,\mu}[n] = \langle \Psi^{lr,\mu}[n] | \hat{W}_{ee}^{sr,\mu} | \Psi^{lr,\mu}[n] \rangle - E_H^{sr,\mu}, \quad (58)$$

which is designed such that it recovers the expectation value of the short-range interaction *on the multi-determinant wave function*  $\Psi^{lr,\mu}$  and not on the Kohn-Sham Slater determinant  $\Phi[n]$  as in Eq. (51). The advantage of this decomposition is clearer for the multi-determinant short-range correlation energy which is then

$$\bar{E}_{c,\text{md}}^{sr,\mu}[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{ee} | \Psi[n] \rangle - \langle \Psi^{lr,\mu}[n] | \hat{T} + \hat{W}_{ee}^{lr} | \Psi^{lr,\mu}[n] \rangle. \quad (59)$$

Within these definitions, the Levy-Lieb functional can be rewritten as

$$\begin{aligned} F[n] &= F^{lr,\mu}[n] + E_H^{sr,\mu} + E_{x,\text{md}}^{sr,\mu}[n] + \bar{E}_{c,\text{md}}^{sr,\mu}[n] \\ &= \langle \Psi^{lr,\mu}[n] | \hat{T} + \hat{W}_{ee} | \Psi^{lr,\mu}[n] \rangle + \bar{E}_{c,\text{md}}^{sr,\mu}[n] \end{aligned} \quad (60)$$

and therefore, provided that  $\Psi^{lr,\mu}[n_0]$  is known one can express the exact ground state energy as

$$\begin{aligned} E_0 &= F[n_0] + \int v_{ne}(\vec{r}) n_0(\vec{r}) d\vec{r} \\ &= \langle \Psi^{lr,\mu}[n_0] | \hat{T} + \hat{W}_{ee} | \Psi^{lr,\mu}[n_0] \rangle + \int v_{ne}(\vec{r}) n_0(\vec{r}) d\vec{r} + \bar{E}_{c,\text{md}}^{sr,\mu}[n_0] \\ &= \langle \Psi^{lr,\mu}[n_0] | \hat{H} | \Psi^{lr,\mu}[n_0] \rangle + \bar{E}_{c,\text{md}}^{sr,\mu}[n_0] \end{aligned} \quad (61)$$

which has several advantages. First, as the wave function  $\Psi^{lr,\mu}[n]$  is a multi-determinant wave function, the multi-determinant correlation functional is a smaller quantity (in absolute value) with respect to the usual short-range correlation functional. Second, as an RS-DFT calculation necessary produces the wave function  $\Psi^{lr,\mu}[n]$ , computing the expectation value of the full interaction  $\hat{W}_{ee}$

is usually a quite simple task, and therefore one only needs to compute  $\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n]$  for which an approximation was recently proposed<sup>18</sup>. The following paragraph exposes the main results of this approximation for the  $\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n]$ .

## 2. Current approximation for $\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n]$

In the work of Ref. 18, the authors have introduced an interpolation between the asymptotic large- $\mu$  behaviour of the  $\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n]$  and the usual PBE Kohn-Sham correlation functional at  $\mu = 0$ . The large  $\mu$  behaviour of  $\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n]$  is

$$\bar{E}_{c,\text{md}}^{\text{sr},\mu}[n] \underset{\mu \rightarrow \infty}{=} \frac{c}{\mu^3} \int d\vec{r} n_2(\vec{r}) + \dots \quad (62)$$

where  $c = 2\sqrt{\pi}(1 - \sqrt{\pi})/3$  and  $n_2(\vec{r}) = n_2(\vec{r}, \vec{r})$  is the exact on-top pair density of the system at  $\vec{r}$ , which is nothing but the exact pair-density at coalescence at  $\vec{r}$ . Eq. (62) was obtained by an asymptotic expansion of the RS-DFT equations at large  $\mu$  (See Refs. 18 and 19). The large  $\mu$  behaviour of Eq. (62) naturally introduces the on-top pair density which is a *local* quantity strongly related to the correlation effects, which focusses an increasing attention in the recent development in DFT<sup>20,21</sup>.

The interpolation proposed by the authors in Ref. 18 is :

$$\bar{E}_{c,\text{md}}^{\text{sr},\mu,\text{PBE}}[n, n_2] = \int \bar{e}_{c,\text{md}}^{\text{sr},\mu,\text{PBE}}(n(\vec{r}), \nabla n(\vec{r}), n_2(\vec{r})) d\vec{r} \quad (63)$$

where the correlation energy density  $\bar{e}_{c,\text{md}}^{\text{sr},\mu,\text{PBE}}$  is written as :

$$\bar{e}_{c,\text{md}}^{\text{sr},\mu,\text{PBE}}(n, \nabla n, n_2) = \frac{e_c^{\text{PBE}}(n, \nabla n)}{1 + \beta(n, \nabla n, n_2)\mu^3} \quad (64)$$

$$\beta(n, \nabla n, n_2) = \frac{e_c^{\text{PBE}}(n, \nabla n)}{cn_2}, \quad (65)$$

and  $e_c^{\text{PBE}}$  the correlation PBE energy density from Ref. 16 for  $\mu = 0$ . An advantage of this formulation is that the correlation energy vanishes when  $n_2(\vec{r}) = 0$ . Therefore, the correlation energy is found to be zero for all systems with a vanishing on-top pair density, such as one-electron systems or dissociated H<sub>2</sub>.

As apparent in Eqs. (62) and (64), an important ingredient is the exact on-top pair density, a quantity which is *a priori* unreachable in practice. Nevertheless, based on large- $\mu$  analysis of the effective Schrödinger-like equation<sup>22</sup>, one can derive an estimation of the *exact on-top pair density*

(which corresponds to the  $\mu \rightarrow \infty$  limit) based on the knowledge of the on-top pair density at a finite value  $\mu$  :

$$n_2(\vec{r}) \simeq n_2^{\text{lr},\mu}(\vec{r}) \left( 1 + \frac{2}{\sqrt{\pi}\mu} \right)^{-1}, \quad (66)$$

where  $n_2^{\text{lr},\mu}(\vec{r})$  is the on-top pair density obtained from the wave function  $\Psi^{\text{lr},\mu}$  which is a quantity that can be numerically computed. Such an extrapolation scheme can be qualitatively understood : at a finite value of  $\mu$ , the on-top pair density is obtained from a wave function  $\Psi^{\text{lr},\mu}$  which comes from an effective Hamiltonian with a non divergent interaction, and therefore the exact on-top pair density (which corresponds to the fully interacting system) is necessary lower than  $n_2^{\text{lr},\mu}(\vec{r})$ . Therefore, the authors of Ref. 18 proposed to use the formula of Eq. (66) in the Eqs. (62) and (63) to propose the so-called PBE-OT functional.

### 3. *Open questions with the PBE-OT functional and main direction of the internship*

As no explicit functional form of the exchange counterpart to  $\bar{E}_{\text{c,md}}^{\text{sr},\mu}[n]$  was available, the authors in Ref. 18 could not perform an actual minimization of the energy using the exchange and correlation multi-determinant functionals which use the on-top pair density. Instead they used the formula given by the last right-hand side of Eq. (61) where they approximate the exact long-range wave function  $\Psi^{\text{lr},\mu}[n_0]$  by the lowest-energy eigenfunction of  $\hat{H}^{\text{lr},\mu}[n]$  using the srPBE approximation for the  $\hat{V}_{\text{Hxc}}[n]$ .

One of the main subject of the internship was to develop several approximations of the multi-determinant exchange functional based on the same philosophy than that of the PBE-OT approximation : using the known large- $\mu$  asymptotic behaviour of the multideterminant short-range exchange functional and interpolating it with a usual Kohn-Sham exchange functional at  $\mu = 0$ .

## D. **Basis-set correction**

The basis-set correction (BSC) method aims to correct the basis-set error of wave-function theory with density-functional theory. This approach, very recently introduced by Emmanuel GINER, Julien TOULOUSE and co-authors in Ref. 23, has led to several developments and applications during the last two years<sup>24-27</sup>. One of the main idea of this theory is to map the effect of the basis set incompleteness on the electron-electron interaction operator as a removal of the divergence of the Coulomb interaction. Then, the non-divergent interaction is fitted with the long-range interaction

used in RS-DFT and correlation functionals with multi-determinant reference of RS-DFT are used to recover the missing correlation energy. In the following paragraph, we recall the main equations of such a theory.

We assume that an one-electron basis set  $\mathcal{B}$  is given, and such a basis is used to generate  $N$ -electron wave functions  $\Psi^{\mathcal{B}}$ . Then we re-express the ground-state universal Levy-Lieb functional using the wave functions  $\Psi^{\mathcal{B}}$  which are restricted to the Hilbert space generated by the basis  $\mathcal{B}$ :

$$F[n^{\mathcal{B}}] = \min_{\Psi^{\mathcal{B}} \rightarrow n^{\mathcal{B}}} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle + \bar{E}^{\mathcal{B}}[n^{\mathcal{B}}], \quad (67)$$

where  $n^{\mathcal{B}}$  refers to all the densities that can be obtained from any wave-function  $\Psi^{\mathcal{B}}$  in the Hilbert space generated by  $\mathcal{B}$  and  $\bar{E}^{\mathcal{B}}[n^{\mathcal{B}}]$  is a complementary density functional such as:

$$\bar{E}^{\mathcal{B}}[n^{\mathcal{B}}] = \min_{\Psi \rightarrow n^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \min_{\Psi^{\mathcal{B}} \rightarrow n^{\mathcal{B}}} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle. \quad (68)$$

As originally proposed in Ref. 23, Eqs. (67) and (68) provide a natural path to formalise the basis set incompleteness error as a density functional. As in all DFT frameworks, the explicit form of the complementary functional is not known and the goal is therefore to look for approximations for  $\bar{E}^{\mathcal{B}}[n^{\mathcal{B}}]$ .

In the following, we explain how to link the RS-DFT and BSC methods. To do so, we first focus on the Coulomb electron-electron interaction within a basis set  $\mathcal{B}$ . Then, we develop the use of a local range-separation parameter  $\mu(\vec{r})$  as established in Ref. 23.

### 1. The effective electron-electron interaction

In Eq. 67, the Coulomb expectation value is written as  $\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle$  where, using the projection operator  $P_{\mathcal{B}}$  onto the Hilbert space generated by the basis  $\mathcal{B}$ , we obtain  $\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle$ . Here,  $\hat{W}_{\text{ee}}^{\mathcal{B}}$  is the Coulomb operator projected in the basis  $\mathcal{B}$  which can be written in second-quantized form as

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \frac{1}{2} \sum_{pqrs \in \mathcal{B}} V_{pq}^{rs} \hat{a}_r^{\dagger} \hat{a}_s^{\dagger} \hat{a}_q \hat{a}_p \quad (69)$$

where the summation runs over all the orthonormal spin-orbitals within the basis set  $\mathcal{B}$ ,  $V_{pq}^{rs}$  are the usual two-electron integrals and the  $\hat{a}_p^{\dagger}$  and  $\hat{a}_p$  are the creation and annihilation operators associated to a given spin-orbital  $\psi_p(\vec{r})$ , respectively.

As shown in Ref. 23, one can rewrite the expectation  $\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle$  as an integral in real-space

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iint f_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2, \quad (70)$$

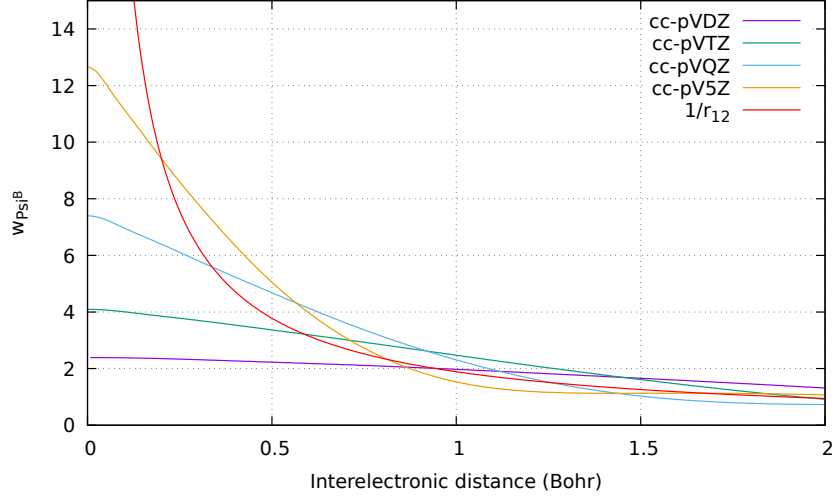


FIG. 6. He effective electron-electron interaction for different basis sets as a function of  $r_{12}$ , where  $f_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2)$  is given in Ref. 23 as

$$f_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) = \sum_{pqrs mn} \psi_p(\vec{r}_1) \psi_q(\vec{r}_2) V_{pq}^{rs} \Gamma_{rs}^{mn} \psi_m(\vec{r}_1) \psi_n(\vec{r}_2) \quad (71)$$

and  $\Gamma_{rs}^{mn}$  is the pair-density tensor given by  $\Gamma_{rs}^{mn} = \langle \Psi^{\mathcal{B}} | \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_n \hat{a}_m | \Psi^{\mathcal{B}} \rangle$ .

The same expectation value can be written also as an integral in real-space

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{ee} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iint \frac{1}{r_{12}} n_{2, \Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (72)$$

where  $n_{2, \Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2)$  is the pair density of the wave function  $\Psi^{\mathcal{B}}$ . From Eqs. (70) and 72, we introduce the effective electron-electron interaction in the basis  $\mathcal{B}$ :

$$w_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) = \frac{f_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2)}{n_{2, \Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2)}, \quad (73)$$

which is not defined when the on-top pair density is zero. Moreover, it has been demonstrated in Ref. 23 that

$$\lim_{\mathcal{B} \rightarrow \text{CBS}} w_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) = \frac{1}{r_{12}}, \quad (74)$$

which guarantees that one recovers the usual Coulomb operator in the complete basis set limit. To illustrate the dependance of the effective electron-electron interaction on the basis-set size, we report in Fig. 6 the variation of  $w_{\Psi^{\mathcal{B}}}(r_{12})$  for different basis-set sizes. There, we notice the non-diverging behaviour of the interaction. In addition to that, the increase of the basis-set size leads to an increase of the interaction value at coalescence.



## 2. Linking RS-DFT and BSC

In RS-DFT, the value of the long-range electron-electron interaction at coalescence is finite and depends on the choice of the range-separation parameter  $\mu$  through  $w_{\text{ee}}^{\text{lr},\mu}(r_{12} = 0) = \frac{2}{\sqrt{\pi}}\mu$ . We have illustrated in the previous section the link between  $w_{\Psi^{\mathcal{B}}}$  and the basis-set quality. As both  $w_{\text{ee}}^{\text{lr},\mu}$  and  $w_{\Psi^{\mathcal{B}}}$  show a non-diverging behaviour at coalescence, we can fit  $w_{\Psi^{\mathcal{B}}}$  using  $w_{\text{ee}}^{\text{lr},\mu}$  and then link RS-DFT and WFT due to the same physical behaviours of the electron-electron interaction they use.

We look at the coalescence point for a given point  $\vec{r}$  and choose  $\mu^{\mathcal{B}}(\vec{r})$  such as  $w_{\Psi^{\mathcal{B}}}(\vec{r}, \vec{r}) = w_{\text{ee}}^{\text{lr},\mu^{\mathcal{B}}(\vec{r})}(r_{12} = 0)$ . Then, the local range-separation parameter is defined as :

$$\mu^{\mathcal{B}}(\vec{r}) = \frac{\sqrt{\pi}}{2} w_{\Psi^{\mathcal{B}}}(\vec{r}, \vec{r}). \quad (75)$$

Finally, we make the following approximation :

$$w_{\Psi^{\mathcal{B}}}(\vec{r}_1, \vec{r}_2) \simeq w_{\Psi^{\mathcal{B}}}^{\text{lr},\mu^{\mathcal{B}}(\vec{r}_1)}(r_{12}) = \frac{\text{erf}(\mu^{\mathcal{B}}(\vec{r}_1)r_{12})}{r_{12}}. \quad (76)$$

Results from Ref. 23 show the validity of this approximation.

## 3. Approximation for $\bar{E}^{\mathcal{B}}$

Once that we can fit the Coulomb interaction within a basis set  $\mathcal{B}$  by a long-range interaction with a range-separation parameter  $\mu^{\mathcal{B}}(\vec{r})$  varying in space, we can approximate the unknown  $\bar{E}^{\mathcal{B}}$  by the correlation functional with multi-determinant reference developed in RS-DFT.

In practice we use the following approximation for the complementary density functional :

$$\bar{E}_{\text{PBE}}^{\mathcal{B}}[n^{\mathcal{B}}, n_2^{\mathcal{B}}] = \int \bar{e}_{\text{c,md}}^{\text{sr},\mu^{\mathcal{B}}(\vec{r}),\text{PBE}}(n^{\mathcal{B}}(\vec{r}), \nabla n^{\mathcal{B}}(\vec{r}), n_2^{\mathcal{B}}(\vec{r})) d\vec{r} \quad (77)$$

where  $n^{\mathcal{B}}(\vec{r})$ ,  $\nabla n^{\mathcal{B}}(\vec{r})$ ,  $n_2^{\mathcal{B}}(\vec{r})$ ,  $\mu^{\mathcal{B}}(\vec{r})$  are respectively the density, density gradient, on-top pair density and range-separation parameter evaluated for the wave-function  $\Psi^{\mathcal{B}}$  restricted to the basis  $\mathcal{B}$  and  $\bar{e}_{\text{c,md}}^{\text{sr},\mu^{\mathcal{B}}(\vec{r}),\text{PBE}}(n^{\mathcal{B}}(\vec{r}), \nabla n^{\mathcal{B}}(\vec{r}), n_2^{\mathcal{B}}(\vec{r}))$  is expressed as in Eq. (64) using a local range-separation parameter.

## IV. IMPLEMENTATION OF RANGE-SEPARATION DENSITY FUNCTIONAL THEORY AND BASIS-SET CORRECTION WITH SELF-CONSISTENT FIELD CALCULATIONS

Now that we have set the framework, we present the work done during this internship. The purpose was to implement the self-consistent calculation of both methods : RS-DFT with multi-determinant exchange/correlation functionals, and BSC. In addition, we allow the iterative calculation of the on-top pair density to compare this effect with the use of the uniform electron gas approximation of the on-top pair density.

### A. The multideterminant short-range exchange functional

Similarly to the developpement of the multideterminant correlation energy, it is possible to know the asymptotic large  $\mu$  behaviour of  $E_{x,\text{md}}^{\text{sr},\mu}[n]$  :

$$E_{x,\text{md}}^{\text{sr},\mu}[n] \underset{\mu \rightarrow \infty}{=} \frac{\pi}{2\mu^2} \int n_{2,\text{xc}}^{\text{lr},\mu}(\vec{r}) d\vec{r} + \frac{g_3}{\mu^3} \int n_2^{\text{lr},\mu}(\vec{r}) d\vec{r} + \frac{g_4}{\mu^4} \int n_2^{\text{lr},\mu}(\vec{r}) d\vec{r} + \dots, \quad (78)$$

where  $n_{2,\text{xc}}^{\text{lr},\mu}$  is the exchange-correlation on-top pair density defined from the on-top pair density defined in Eq. (66) :

$$n_{2,\text{xc}}^{\text{lr},\mu} = n_2^{\text{lr},\mu}(\vec{r}) - n(\vec{r})^2, \quad (79)$$

the coefficient  $g_3$  is :

$$g_3 = \frac{\sqrt{\pi}(4\sqrt{2} - 5)}{3}, \quad (80)$$

and  $g_4$  is expressed as a sign-alternating series that we are not able to solve. Then, we choose to neglect this last term in the present study.

The interpolation between the large  $\mu$  behaviour and the usual KS-PBE exchange functional at  $\mu = 0$  is formulated in a similar way than what was done in Ref. 18 :

$$E_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}[n, n_2] = \int e_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}(n(\vec{r}), \nabla n(\vec{r}), n_2(\vec{r})) d\vec{r}, \quad (81)$$

with the exchange energy density  $e_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}$  expressed as :

$$e_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}(n, \nabla n, n_2) = \frac{e_x^{\text{PBE}}(n, \nabla n)}{1 + \delta(n, \nabla(n), n_2)\mu + \gamma(n, \nabla n, n_2)\mu^2}, \quad (82)$$

where

$$\gamma(n, \nabla n) = \frac{e_x^{\text{PBE}}(n, \nabla n)}{a n_{2,\text{xc}}}, \quad (83)$$

and

$$\delta(n, \nabla n) = -\frac{bn_2(n)\gamma(n, \nabla n)^2}{e_x^{\text{PBE}}(n, \nabla n)}, \quad (84)$$

with  $a = \pi/2$ ,  $b = 2\sqrt{\pi}(2\sqrt{2} - 1)/3$ , and  $e_x^{\text{PBE}}$  the exchange PBE energy density from Ref. 16 for  $\mu = 0$ .

Therefore, similarly to what was done for the multi-determinant correlation functional, the interpolation is done here for the exchange part such that one recovers the known exact large  $\mu$  behaviour of the multi-determinant exchange functional when  $\mu \rightarrow \infty$

$$E_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}[n, n_2] \underset{\mu \rightarrow \infty}{\sim} \frac{\pi}{2\mu^2} \int n_{2,\text{xc}}^{\text{lr},\mu}(\vec{r}) d\vec{r} + \frac{g_3}{\mu^3} \int n_2^{\text{lr},\mu}(\vec{r}) d\vec{r}, \quad (85)$$

and that it tends towards the usual PBE exchange functional when  $\mu \rightarrow 0$

$$\lim_{\mu \rightarrow 0} E_{x,\text{md}}^{\text{sr},\mu,\text{PBE}}[n, n_2] = E_x^{\text{PBE}}[n]. \quad (86)$$

## B. The choice of the on-top pair density

The general formulation of the multi-determinant functionals of Eqs. (64) and (82) provides the opportunity to use different forms for the on-top pair density as the functionals explicitly depend on this variable. We use either the estimated exact on-top pair density  $n_2$  (using Eq. (66)) or the on-top pair density from the uniform electron gas  $n_2^{\text{UEG}}$ . In this section, we provide the formulation of the on-top pair density in the framework of the uniform electron gas model.

The UEG on-top pair density for closed-shell systems is approximated as follows<sup>28</sup> :

$$n_2^{\text{UEG}}(n) \simeq n^2 g_0(n) \quad (87)$$

with  $g_0$ , the on-top pair distribution function of the spin-unpolarized UEG parameterized as :

$$g_0(n) \simeq \frac{1}{2}(1 - Br_s + Cr_s^2 + Dr_s^3 + Er_s^4)e^{-dr_s} \quad (88)$$

with  $C = 0.08193$ ,  $D = -0.01277$ ,  $E = 0.001859$ ,  $d = 0.7524$ ,  $B = -2a_{\text{HD}} - d$ ,  $a_{\text{HD}} \simeq -0.36583$  and the Wigner-Seitz radius  $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$ .

Then, the exchange-correlation on-top pair density is :

$$n_{2,\text{xc}}^{\text{UEG}}(n) = n_2^{\text{UEG}}(n) - n^2. \quad (89)$$

To differentiate both uses we denominate the approximations with the acronyms md-srPBEUEG (*multideterminant short-range PBE using  $n_2^{UEG}$* ) and md-srPBEOT (*multideterminant short-range PBE using  $n_2$* ).

### C. The self-consistent field RS-DFT equation

We give the expression of the energy of the system in the framework of the RS-DFT :

$$E = \min_{\Psi} \left( \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{lr,\mu} | \Psi \rangle + E_H^{sr,\mu} [n_{\Psi}] + E_{x,md}^{sr,\mu} [n_{\Psi}, n_{2,\Psi}] + \bar{E}_{c,md}^{sr,\mu} [n_{\Psi}, n_{2,\Psi}] \right). \quad (90)$$

The minimizing wave function  $\Psi^{lr,\mu}$ , obtained from the Euler-Lagrange equation associated with the latter equation, satisfies the following Schrödinger-like equation<sup>29</sup> :

$$\left( \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{lr,\mu} \right) | \Psi^{lr,\mu} \rangle + \frac{\delta E_H^{sr,\mu}}{\delta \langle \Psi^{lr,\mu} |} + \frac{\delta E_{x,md}^{sr,\mu}}{\delta \langle \Psi^{lr,\mu} |} + \frac{\delta \bar{E}_{c,md}^{sr,\mu}}{\delta \langle \Psi^{lr,\mu} |} = \mathcal{E}^{\mu} | \Psi^{lr,\mu} \rangle \quad (91)$$

the derivative of the Hartree energy functional being known, we focus on the multideterminant exchange and correlation energy functionals. In practice, using the chain rule we get the general form :

$$\frac{\delta \bar{E}_{y,md}^{sr,\mu}}{\delta \langle \Psi^{lr,\mu} |} = \int \left( \frac{\delta \bar{E}_{y,md}^{sr,\mu}}{\delta n(\vec{r})} \frac{\delta n(\vec{r})}{\delta \langle \Psi^{lr,\mu} |} + \frac{\delta \bar{E}_{y,md}^{sr,\mu}}{\delta n_2(\vec{r})} \frac{\delta n_2(\vec{r})}{\delta \langle \Psi^{lr,\mu} |} \right) d\vec{r} \quad (92)$$

where the density, density gradient, and on-top pair density derivatives are formulated as :

$$\frac{\delta n(\vec{r})}{\delta \langle \Psi^{lr,\mu} |} = \hat{n}(\vec{r}) | \Psi^{lr,\mu} \rangle, \quad \text{and} \quad \frac{\delta n_2(\vec{r})}{\delta \langle \Psi^{lr,\mu} |} = \hat{n}_2(\vec{r}) | \Psi^{lr,\mu} \rangle, \quad (93)$$

where  $\hat{n}(\vec{r})$  and  $\hat{n}_2(\vec{r})$  are the density and on-top pair density operators, respectively. Finally, the equation to be solved is the following :

$$\left( \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{lr,\mu} + \hat{V}_H^{sr,\mu} + \hat{V}_{x,md}^{sr,\mu} + \hat{V}_{c,md}^{sr,\mu} \right) | \Psi^{lr,\mu} \rangle = \hat{H}^{\mu} | \Psi^{lr,\mu} \rangle = \mathcal{E}^{\mu} | \Psi^{lr,\mu} \rangle, \quad (94)$$

where  $\hat{V}_H^{sr,\mu}$  is the short-range Hartree potential operator :

$$\hat{V}_H^{sr,\mu} = \int \left( \frac{\delta E_H^{sr,\mu}}{\delta n(\vec{r})} \hat{n}(\vec{r}) \right) d\vec{r}, \quad (95)$$

$\hat{V}_{x,md}^{sr,\mu}$  is the multideterminant short-range energy potential operator that we express from Eq. (82) :

$$\hat{V}_{x,md}^{sr,\mu} = \int \left( \frac{\delta \bar{E}_{x,md}^{sr,\mu}}{\delta n(\vec{r})} \hat{n}(\vec{r}) + \frac{\delta \bar{E}_{x,md}^{sr,\mu}}{\delta n_2(\vec{r})} \hat{n}_2(\vec{r}) \right) d\vec{r} \quad (96)$$

and  $\hat{V}_{c,md}^{sr,\mu}$  is the multideterminant short-range correlation potential operator that we express from Eq. (64) :

$$\hat{V}_{c,md}^{sr,\mu} = \int \left( \frac{\delta \bar{E}_{c,md}^{sr,\mu}}{\delta n(\vec{r})} \hat{n}(\vec{r}) + \frac{\delta \bar{E}_{c,md}^{sr,\mu}}{\delta n_2(\vec{r})} \hat{n}_2(\vec{r}) \right) d\vec{r} \quad (97)$$

#### D. The self-consistent field basis-set correction equation

Similarly, the Schrödinger-like equation to be solved for the basis-set convergence is the following :

$$\left(\hat{T}^{\mathcal{B}} + \hat{V}_{ne}^{\mathcal{B}} + \hat{W}_{ee}^{\mathcal{B}} + \hat{V}^{\mathcal{B}}\right)|\Psi^{\mathcal{B}}\rangle = \hat{H}^{\mathcal{B}}|\Psi^{\mathcal{B}}\rangle = \mathcal{E}^{\mathcal{B}}|\Psi^{\mathcal{B}}\rangle \quad (98)$$

where all the operators are projected in the Hilbert space generated by the basis set  $\mathcal{B}$ , and  $\hat{V}^{\mathcal{B}}$  is the basis-set correction potential operator formulated as following according to Eq. (77) :

$$\hat{V}^{\mathcal{B}} = \int \left( \frac{\delta \bar{E}^{\mathcal{B}}}{\delta n(\vec{r})} \hat{n}(\vec{r}) + \frac{\delta \bar{E}^{\mathcal{B}}}{\delta n_2(\vec{r})} \hat{n}_2(\vec{r}) \right) d\vec{r}. \quad (99)$$

#### E. Implementation

Eqs. (94) and (98) are iterated until the non-linear potentials appearing in the non-linear Hamiltonians  $\hat{H}^{\mu}$  and  $\hat{H}^{\mathcal{B}}$  are such that it fullfil the eigenvalue equation. In practice, we implement this self-consistent field equations in the *Quantum Package* programming environment. Both algorithms can be summarized as follows, taking the exemple of the Helium atom.

**System** : He  $\rightarrow$  By specifying the position(s)/configuration(s) of the nucleus(i)

**One-electron basis-set** : cc-pVTZ  $\rightarrow$  We use the Dunning basis-set.

**Functional** : md-srPBE  $\rightarrow$  Choice of the functional approximation.<sup>30</sup>

**mu** : 0.5 Bohr<sup>-1</sup>  $\rightarrow$  For RS-DFT calculations.

**threshold** : 0.00001 Ha  $\rightarrow$  Convergence threshold on the energy.

1. Calculation of the one determinant wave function  $\Phi$  using the Hartree-Fock self-consistent field equation.
2. Calculation of the full configuration interaction wave function with a self-consistent field calculation.
3. Calculations of the density, density gradient and on-top pair density (the latter, when performing calculations without the UEG approximation).
4. We build the Hamiltonian  $\hat{H}^\mu$  (RS-DFT) or  $\hat{H}^B$  (BSC).
5. We solve Eq. (94) (RS-DFT) or Eq. (98) (BSC).
6. We compare the obtained energy  $E_{\text{Step 6}}$  with the one obtained in Step 2  $E_{\text{Step 2}}$ . If  $|E_{\text{Step 6}} - E_{\text{Step 2}}| > \text{threshold}$ . We restart from Step 3 with the obtained wave function.

In the following, we present our test on the Helium atom and the H<sub>2</sub> molecule using both RS-DFT and BSC methods. We compare the use of the UEG approximation for the on-top pair density with the one estimated from the wave function iteratively.

## V. RESULTS AND DISCUSSION

### A. Study of the RS-DFT energy approximations with the range separation parameter and the basis set : the case of the He atom

In order to illustrate the dependency of the RS-DFT results on the range-separation parameter  $\mu$ , we report in Fig. 7 the variation of the ground state energy with the  $\mu$  parameter. We notice that for  $\mu$  between 0.5 and 2 bohr<sup>-1</sup>, the energy decreases to a minimum. For  $\mu = 1$  bohr<sup>-1</sup>, we remark that we reach a global minimum. For the cc-pVQZ basis set, for which the energies are almost converged with respect to the basis-set size, we remark that this minimum is close to to the exact

energy for the srPBE/lrFCI energy whereas it corresponds to an overestimation of the ground state energy using the md-srPBEUEG approximation developed in the present work.

In view to study the dependency of the RS-DFT results on the basis-set size, we report in Fig. 8, the variation of the estimation of the ground state energy with the basis-set size for two different values of the parameter  $\mu$  : 0.5 and 1 bohr<sup>-1</sup>. We compare the RS-DFT results with the FCI and KS-DFT limits. For both values of  $\mu$ , we notice that the energies converge faster than the FCI energy and converge nearer to the exact energy than the KS-DFT energy. Nevertheless, the important dependency of both approximations to the value of  $\mu$  makes it difficult to chose a value for a given system especially using the md-srPBEUEG approximation for which the minimum for  $\mu = 1$  bohr<sup>-1</sup> leads to an overestimation (in absolute value) of the ground state energy.

### ***1. Understanding the md-srPBEUEG/lrFCI energy overestimation***

In order to understand the overestimation of the total energy using the md-srPBEUEG approximation, we compare the energy components to the exact ones.

To begin with, we report in the first column of Tab. I the ground state energy obtained from the self-consistent field (SCF) equations using both approximations : md-srPBEUEG/lrFCI and srPBE/lrFCI. From Tab. I we observe an error with the SCF calculations using the former functional, of about 7 mHa below the exact ground state energy, whereas the latter gives a very good estimate of the exact ground state energy. Before looking to the energy components, we should ask ourselves whether the eigenfunctions of  $\hat{H}^\mu$  (and therefore the properties that we can obtain from these eigenfunctions) obtained for both approximated functionals are similar.

To do so, we use the self-consistent eigenfunction from the md-srPBEUEG/lrFCI approximation to evaluate the srPBE/lrFCI variational energy : we report the value in the second column of Tab. I. The difference between the obtained energy and the energy self-consistently computed using the srPBE/lrFCI approximation are different from only 0.02 mHa, which is comparable to the threshold of convergence of an SCF calculation. We did the same starting from the srPBE/lrFCI eigenfunction to evaluate the md-srPBEUEG/lrFCI energy and report the result in the third column of Tab. I : the energy difference is of the same order of magnitude. Here we conclude that both

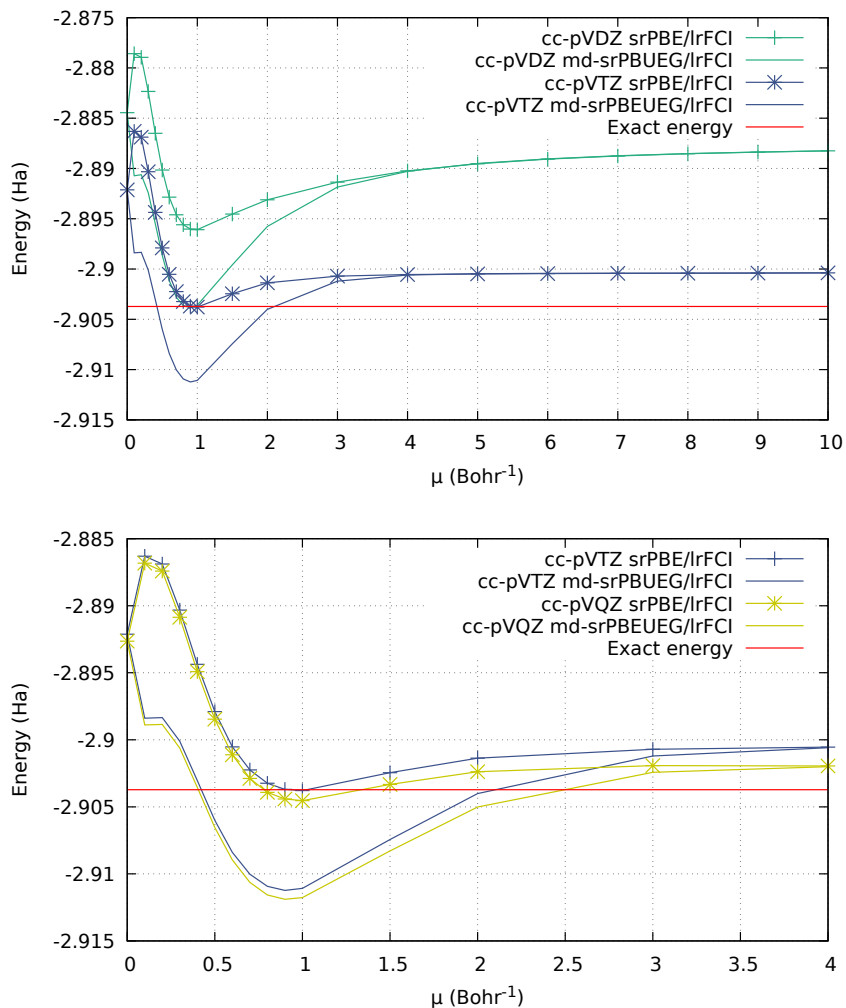


FIG. 7. He ground state energy variation with the range-separation parameter  $\mu$  using the srPBE and md-srPBEUEG approximations for the short range exchange and correlation energy functionals - top : cc-pVDZ and cc-pVTZ ; bottom : cc-pVTZ and cc-pVQZ ; Exact energy from Ref. 3

self consistent calculations lead to very similar self-consistent eigenfunctions, at least in the sense of the variational energy. This implies that both energy functionals have essentially the same energy derivatives as they lead to very similar eigenfunctions. Therefore, the inaccuracy of the md-srPBEUEG functional with respect to the srPBE functional can be seen as an error in the energy rather than the energy derivative.

To further analyze the differences between the energy obtained using the md-srPBEUEG and srPBE functionals, we report the exchange and correlation energies evaluated from one of the



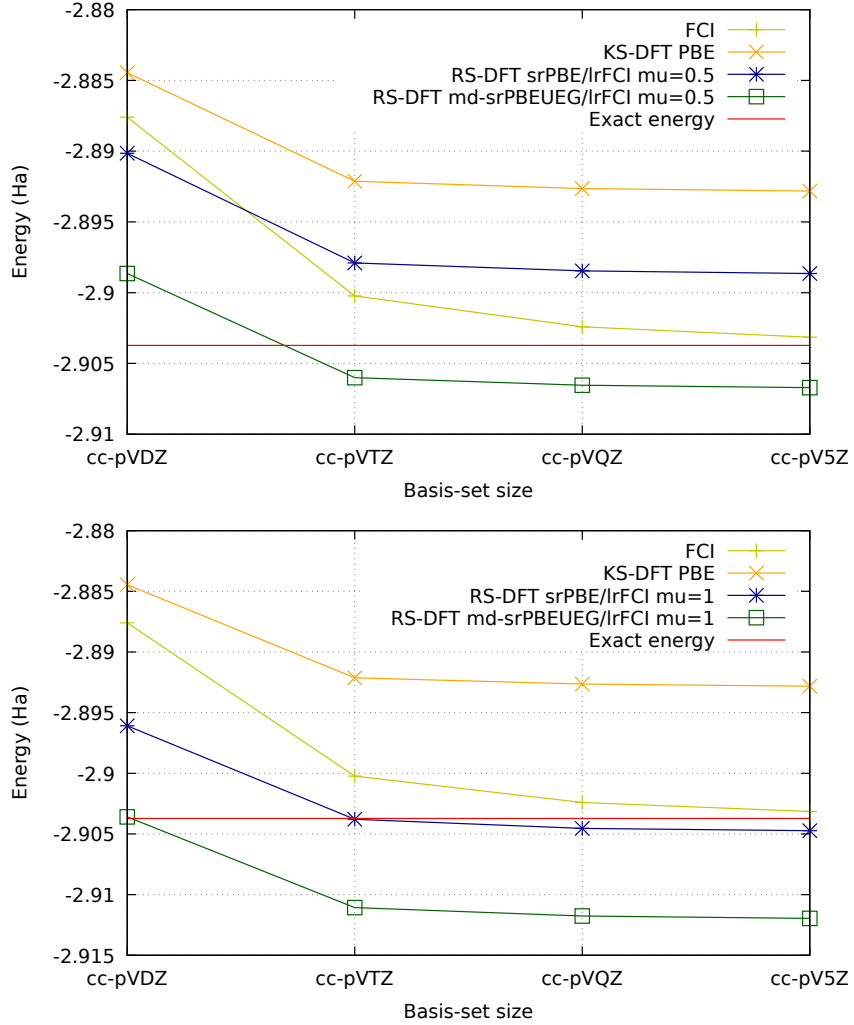


FIG. 8. He ground state energy variation with the basis set size using the srPBE and md-srPBEUEG approximations for the short range exchange and correlation energy functionals : top :  $\mu = 0.5 \text{ bohr}^{-1}$  ; bottom :  $\mu = 1 \text{ bohr}^{-1}$  ; Exact energy from Ref. 3

self-consistent eigenfunctions (here, we choose the md-srPBEUEG/lrFCI one) in Tab. II. We compare this energies with the exact multideterminant exchange and correlation energies according to Eqs. (58) and (61). The exact correlation energy is evaluated from the exact ground state energy that we assume to be  $-2.903724 \text{ Ha}$  according to Ref. 3.

In the framework of the md-srPBEUEG approximation, the exchange energy provides a relative error of 1% whereas the correlation energy provides a relative error of 12%. Therefore one could conclude that the approximation to multi-determinant exchange energy is of better quality than that of the correlation energy. Nevertheless, when one looks at the absolute error one observes that the

md-srPBEUEG exchange energy overestimates the exact exchange energy by 4.7 mH, whereas the correlation counterpart gives an error of 2.9 mH. Therefore, one can conclude that the error is somehow equally distributed in absolute value among the exchange and correlation energy, even if the error coming from the exchange energy is larger probably because of its larger weight on the total energy.

## ***2. Dependence of the short-range exchange energy functional on the choice of the on-top pair density***

From the ground state wave functions obtained from SCF calculations using md-srPBEUEG/IrFCI, we compute the estimation of the short-range exchange and correlation energies using Eq. (64) and (82) and we compare it with the exact formulations for the different on-top pair densities introduced in Sec. IV B. We report the results in Tab. II.

The md-srPBEOTextrap energies (using the extrapolated on-top pair density according to Eq. (66)) lead to relative errors of 15% for the exchange energy and 4% for the correlation energy : the correlation energy is improved using the on-top pair density based on the self-consistent eigenfunction contrary to the exchange energy. It should be notice that an error of 15% on the exchange energy leads to about 50 mHa of error in absolute value, which is one order of magnitude more inaccurate than the multi-determinant exchange energy computed with the on-top pair density coming from the UEG. This results is somehow counterintuitive as one could expect that the on-top pair density coming from the UEG would be less accurate than that coming from a wave function computed for the specific system of study.

Finally, to illustrate the effect of the extrapolation of the on-top pair density, we report in the first column of Tab. II the estimation of the exchange and correlation energy from the on-top pair density  $n_2^{\text{lr},\mu}$ . Clearly, estimating the exchange energy using the extrapolated on-top pair density does not improve the results compare to the non-extrapolated on-top pair density. Nevertheless, the extrapolation slightly improves the estimation of the correlation energy.

To summarize this study on the helium atom, we can conclude that the use of the UEG on-top pair density provides the best estimate for the exchange part of the multi-determinant functionals, and that the on-top pair density coming from the eigenfunctions of  $\hat{H}^\mu$  gives better estimate for the correlation counterpart. These results will lead us to more detailed studies of the exchange and

correlation holes in order to better understand this unexpected discrepancy of behaviour.

	RS-DFT SCF result	$E^{\text{srPBE}}[\Psi^{\text{WF}}]$	$E^{\text{md-srPBEUEG}}[\Psi^{\text{WF}}]$
WF : md-srPBEUEG	-2.911076	-2.903766	
WF : srPBE	-2.903788		-2.911053
$E_0$ : Exact energy	-2.903724		

TABLE I. He ground-state energy (in Hartree, basis-set : cc-pVTZ, mu=1) using different approximations. The first column corresponds to SCF calculations using a given functional, the second and third column correspond to the evaluation of the variational energy with one functional using the self-consistent eigenfunction obtained with the other functional.

$E_{x,\text{md}}^{\text{sr},\mu,\text{PBEOTlr}}$	$E_{x,\text{md}}^{\text{sr},\mu,\text{PBEOTextrap}}$	$E_{x,\text{md}}^{\text{sr},\mu,\text{PBEUEG}}$	$E_{x,\text{md}}^{\text{exact}} = \langle \Psi^{\text{WF}}   \hat{W}_{ee}^{\text{sr},\mu}   \Psi^{\text{WF}} \rangle - E_{\text{H}}^{\text{sr},\mu}$
-0.346554 (R.E. = 12%)	-0.354575 (R.E. = 15%)	-0.311970 (R.E. = 1%)	-0.307603
$\bar{E}_{c,\text{md}}^{\text{sr},\mu,\text{PBEOTlr}}$	$\bar{E}_{c,\text{md}}^{\text{sr},\mu,\text{PBEOTextrap}}$	$\bar{E}_{c,\text{md}}^{\text{sr},\mu,\text{PBEUEG}}$	$\bar{E}_{c,\text{md}}^{\text{exact}} = E_0 - \langle \Psi^{\text{WF}}   \hat{H}   \Psi^{\text{WF}} \rangle$
-0.025840 (R.E. = 6%)	-0.025283 (R.E. = 4%)	-0.027263 (R.E. = 12%)	-0.024279

TABLE II. He multideterminant short-range exchange and correlation energies (in Hartree, basis set : cc-pVTZ, mu=1 bohr<sup>-1</sup>) : comparison between the on-top pair density based on the uniform electron gas approximation and the on-top pair densities from Eq. (66) (OTlr :  $n_2^{\text{lr},\mu}(\vec{r})$ , OTextrap :  $n_2(\vec{r})$ ) - WF = md-srPBEUEG - R.E. = relative error

## B. H<sub>2</sub> dissociation curve

In this section, we compute the H<sub>2</sub> molecule dissociation curve using RS-DFT approximations. We compare the multideterminant self-consistent solutions with the best approximation made until now : the use of the srPBE/lrFCI eigenfunction to evaluate the correlation energy from the extrapolated on-top pair density that we note srPBE/lrFCI+PBEOT.

We report in Fig. 9 the dissociation curve of the H<sub>2</sub> molecule using different approximations. In Fig. 9, we remark that the energies for large internuclear distances are improved using srPBE/lrFCI and md-srPBEUEG/lrFCI approximations compare to the KS-DFT dissociation curve, especially using the multideterminant short-range functionals. Nevertheless, the energies are still to high at dissociation compared to the exact case and the srPBE/lrFCI+PBEOT result.

Around the equilibrium distance, the different approximations provide reasonable energies. However, the md-srPBEUEG/lrFCI approximation still provides too low energies.

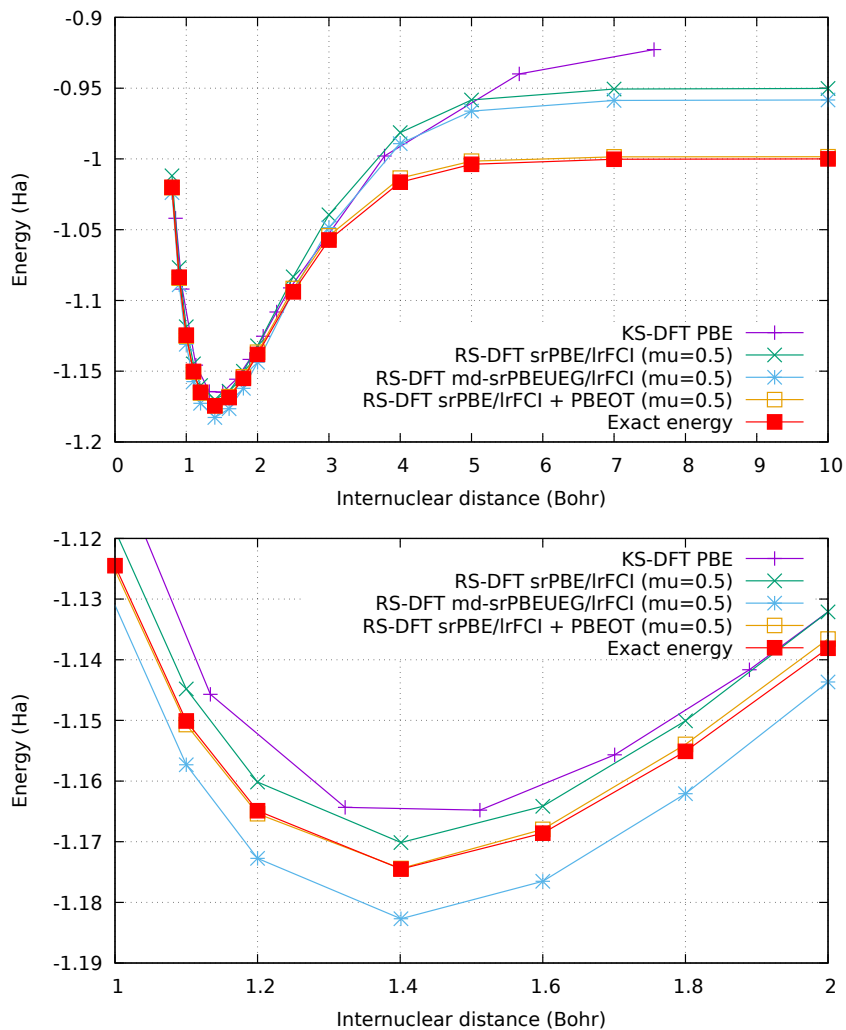


FIG. 9. H<sub>2</sub> dissociation curve (around the equilibrium distance) - Basis-set : cc-pVTZ

## C. The basis-set correction method to overcome the dependence on the range-separation parameter

### 1. Energy convergence with the basis-set size

We compare the convergence in energy in the BSC and RS-DFT methods. As stated in Sec. III D, the BSC method approximates the complementary density functional with the multideterminant short-range correlation energy with a range-separation parameter  $\mu^B(\vec{r})$  estimated for each space

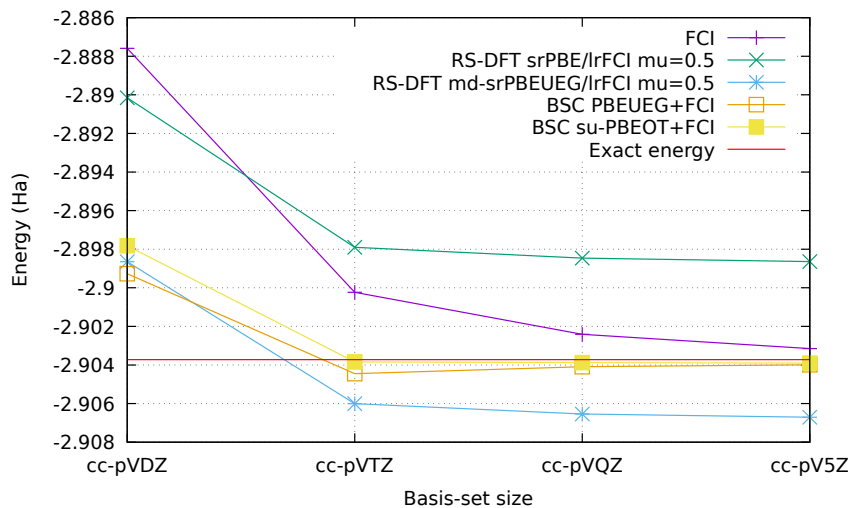


FIG. 10. He energy with increasing basis-set size using different DFT-WFT hybrid methods (SCF calculations).

point.

In Fig. 10, we remark that the BSC method leads to converged energy widely close to the exact energy compared to the RS-DFT approximations. Moreover, we notice a fast convergence with the basis-set size compared to the FCI calculations. Finally, the use of an on-top pair density estimated from the wave function leads to reasonable results.

## 2. $H_2$ dissociation curve

In Fig. 11, we report the difference between the ground state energy evaluated with BSC approximations and the exact energy. The difference with the FCI approximation is also presented. There, we remark that the BSC calculations are more accurate than the FCI calculation. To be more precise, adding self-consistency leads to results relatively more precise as the energy shift at the equilibrium distance (marked with the black vertical line), is about 0.25 mHa. In addition to that, we notice that the use of the exact on-top pair density leads to accurate results which will allow us to consider a wider range of systems using the BSC method.

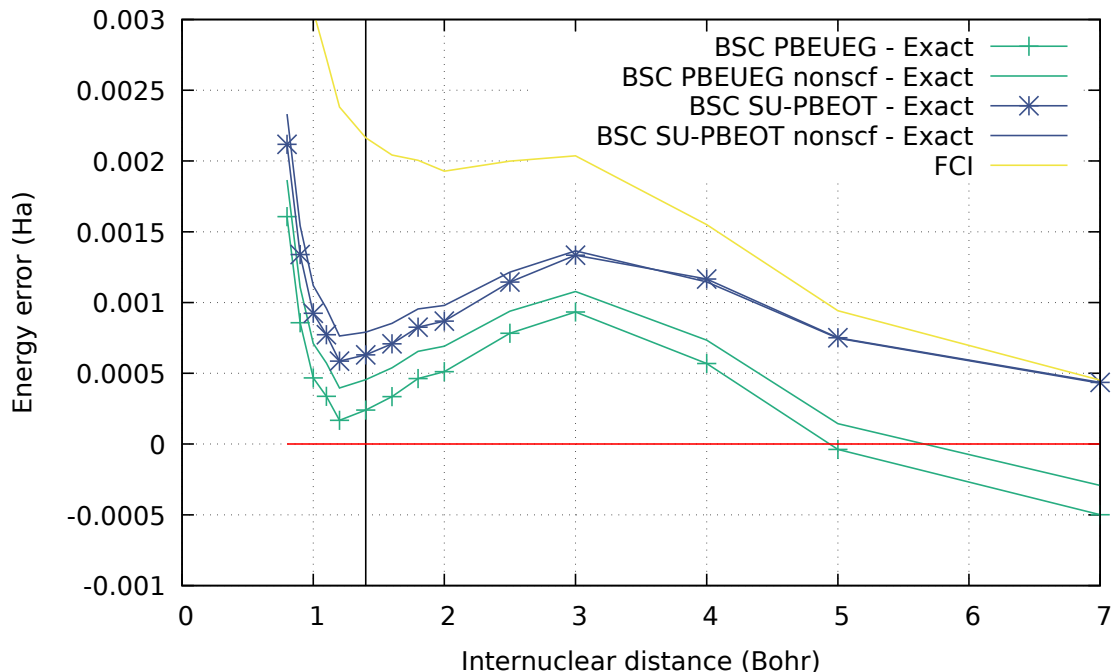


FIG. 11. Difference between the  $H_2$  exact energy and energies from different BSC approximations for different internuclear distances (Basis set : cc-pVTZ).

## VI. CONCLUSION

We have investigated the performance of the self-consistent field calculation of two WFT-DFT hybrid methods : the range-separated DFT and the basis-set correction. The implementation of this schemes needed the development of a multideterminant short-range exchange energy functional, using different flavours of on-top pair densities: the one coming from the UEG, and the one coming from the approximated eigenfunctions for the specific system under study.

Tests of the SCF RS-DFT scheme on the He atom and the  $H_2$  molecule revealed constantly too low energies. Tests on the energy components made us conclude that the multi-determinant short-range exchange functional is the main source of the errors. We noticed that the exchange multi-determinant functional is much better described using the on-top pair density from the UEG than the one coming from  $\Psi^{lr,\mu}$  which was really unexpected. A road to explore would be to extend the large-mu expansion of  $E_{x,md}^{st,\mu}$  to the next term proportional to  $1/\mu^4$ , but further studies are needed to find a way to approximate the  $g_4$  constant.

A major outcome of the work presented here is the good accuracy of the energy obtained using a self-consistent equation with the basis-set correction method. Moreover, the self-consistent

calculations are feasible without the uniform gas electron model which allows us to extend our range of systems to study.

## REFERENCES

- <sup>1</sup>A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Dover, New York, 1996).
- <sup>2</sup>T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>3</sup>S. Chandrasekhar and G. Herzberg, *Physical Review* **98**, 1050–1054 (1955).
- <sup>4</sup>E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929).
- <sup>5</sup>O. Franck, B. Mussard, E. Luppi, and J. Toulouse, *J. Chem. Phys.* **142**, 074107 (2015).
- <sup>6</sup>P. Hohenberg and W. Kohn, *Physical Review* **136**, B864–B871 (1964).
- <sup>7</sup>J. Toulouse, “Introduction to density-functional theory (slides) - european summerschool in quantum chemistry,” <https://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/> (2019).
- <sup>8</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133–A1138 (1965).
- <sup>9</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>10</sup>G. C. Lie and E. Clementi, *J. Chem. Phys.* **60**, 1288 (1974).
- <sup>11</sup>J. Toulouse, F. Colonna, and A. Savin, *Phys. Rev. A* **70**, 062505 (2004).
- <sup>12</sup>E.g. LDA, GGA.
- <sup>13</sup>A. Savin, “On degeneracy, near degeneracy and density functional theory,” in *Recent Developments of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996) pp. 327–357.
- <sup>14</sup>J. Toulouse, F. Colonna, and A. Savin, *J. Chem. Phys.* **122**, 014110 (2005).
- <sup>15</sup>E. Goll, H.-J. Werner, and H. Stoll, “A short-range gradient-corrected density functional in long-range coupled-cluster calculations for rare gas dimers,” *Phys. Chem. Phys.* **7**, 3917 (2005).
- <sup>16</sup>E. Goll, H.-J. Werner, H. Stoll, T. Leininger, P. Gori-Giorgi, and A. Savin, *Chem. Phys.* **329**, 276 (2006).
- <sup>17</sup>J. Toulouse, P. Gori-Giorgi, and A. Savin, *Theor. Chem. Acc.* **114**, 305 (2005).
- <sup>18</sup>A. Ferté, E. Giner, and J. Toulouse, *J. Chem. Phys.* **150**, 084103 (2019).
- <sup>19</sup>S. Pazziani, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, *Phys. Rev. B* **73**, 155111 (2006).
- <sup>20</sup>R. K. Carlson, D. G. Truhlar, and L. Gagliardi, *J. Phys. Chem. A* **121**, 5540 (2017).
- <sup>21</sup>O. V. Gritsenko, R. van Meer, and K. Pernal, *Phys. Rev. A* **98**, 062510 (2018).
- <sup>22</sup>P. Gori-Giorgi and A. Savin, *Phys. Rev. A* **73**, 032506 (2006).

- <sup>23</sup>E. Giner, B. Pradines, A. Ferté, R. Assaraf, A. Savin, and J. Toulouse, *J. Chem. Phys.* **149**, 194301 (2018).
- <sup>24</sup>P.-F. Loos, B. Pradines, A. Scemama, J. Toulouse, and E. Giner, *J. Phys. Chem. Lett.* **10**, 2931–2937 (2019).
- <sup>25</sup>E. Giner, A. Scemama, J. Toulouse, and P.-F. Loos, *J. Chem. Phys.* **151**, 144118 (2019).
- <sup>26</sup>P.-F. Loos, B. Pradines, A. Scemama, E. Giner, and J. Toulouse, *J. Chem. Theory Comput.* , 1018–1028 (2020).
- <sup>27</sup>E. Giner, A. Scemama, P.-F. Loos, and J. Toulouse, *The Journal of Chemical Physics* **152**, 174104 (2020).
- <sup>28</sup>P. Gori-Giorgi and J. P. Perdew, *Phys. Rev. B* **64**, 155102 (2001).
- <sup>29</sup>Where, for requirement of clarity, we do not mention the functionals dependence of the functional on the density and on-top pair density of  $\Psi^{lr,\mu}$ .
- <sup>30</sup>SrPBE : short-range PBE ; md-srPBE : multideterminant short-range PBE ; PBEUEG : PBE with  $n_2^{\text{UEG}}$  ; suPBEOT : spin unrestricted PBE using  $n_2$  from the wave function.