Generalization of internal density-functional theory and Kohn-Sham scheme to multicomponent self-bound systems, and link with traditional density-functional theory

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We generalize the recently developed "internal" density-functional theory (DFT) and Kohn-Sham scheme to multicomponent systems. We obtain a general formalism, applicable for the description of multicomponent self-bound systems (such as molecular systems where the nuclei are treated explicitly, atomic nuclei and mixtures of ^{3}He and ^{4}He droplets), where the fundamental translational symmetry has been treated correctly. The main difference with traditional DFT is the explicit inclusion of center-of-mass correlations in the functional. A large part of the paper is dedicated to the application to molecular systems, which permits us to clarify the approximations that underly traditional DFT.

I. INTRODUCTION

Density-functional theory (DFT) [1–3] is a tool widely used in condensed-matter physics and quantum chemistry to calculate properties of many-electron systems. It is based on the simple local density instead of the less tractable N-body wave function. One of the pillars of DFT is the Hohenberg-Kohn (HK) theorem [4], which, in its original form, proves that for any nondegenerate system of fermions or bosons [1] put into a local external potential $v_{ext}(\mathbf{r})$ there exists a unique functional of the local one-body density $\rho(\mathbf{r})$ that gives the exact ground-state energy when $\rho(\mathbf{r})$ corresponds to the exact ground-state density. The Kohn-Sham (KS) scheme provides a practical method to compute self-consistently the ground-state density in a quantum framework, defining the local single-particle potential (i.e., an auxiliary noninteracting system) which reproduces the exact ground-state density [5].

Traditional DFT is particularly well suited to describe the electrons in a molecule, but not for the description of self-bound systems, such as atomic nuclei, He droplets, or molecular systems where the nuclei are treated explicitly. Indeed, in those systems external fields are not required to obtain bound states. As a consequence, isolated self-bound systems are plagued by a center-of-mass (c.m.) problem: for any stationary state, the c.m. is delocalized in the whole space (because of the translational invariance of the Hamiltonian) and the laboratory wave function is consequently not normalizable. This prevents us from using traditional DFT methods, formulated in terms of the laboratory density, when $v_{ext}(\mathbf{r}) = 0$ [6]. Indeed, the laboratory density is then an indeterminate constant [6–8], which prevents us from constructing from it a universal functional. Moreover, it is internal properties (measured in the c.m. frame) and not laboratory properties that are of experimental interest. Experimentalists always deduce internal properties using the c.m. observables (position, momentum, or kinetic energy of the c.m.) and Galilean invariance to transform all the other observables into the c.m. frame.

It is thus a question of interest to formulate a rigorous DFT formalism and KS scheme in terms of the internal density ρ_{int}, having achieved the correct separation of internal properties from the c.m. motion. Efforts in that direction have been made recently in Refs. [7,9], but the question of a rigorous "internal" KS scheme remained open (see the corresponding discussion

of Ref. [6] for more details). The different approach found in Refs. [10,11] results in a rigorous KS scheme, but that is not "internal" (i.e., formulated within the c.m. frame of reference), so that it is not directly comparable to self-consistent mean-field-like calculations with effective interactions formulated in the c.m. frame of reference.

In Ref. [6] it was proposed to use Jacobi coordinates to decouple the c.m. properties from internal ones in self-bound systems, which permits one to separate the non-normalizable part of the wave function from the normalizable part which describes internal properties. Moreover, an arbitrary translationally invariant potential of the form $\sum_{i=1}^{N} v_{int}(\mathbf{r}_i - \mathbf{R})$, where $\mathbf{R} = \frac{1}{N}\sum_{j=1}^{N} \mathbf{r}_j$ is the total c.m. of the particles, was added to the Hamiltonian of a self-bound system. This potential is an "internal" potential, i.e., it acts in the c.m. frame, and is the only form that satisfies all the key formal properties [6]. Of course v_{int} should be zero in the stationary isolated self-bound case. This is why in Ref. [6] the authors presented it as a mathematical auxiliary to reach the desired goal and showed that it can be dropped properly at the end, preserving all the conclusions (because the internal ground state should by definition remain bound at this limit). Nevertheless, its form is suitable to model the internal effects of fields used in experiments. Through it and using Jacobi coordinates it was shown, by a different way than those found in Refs. [7,9], the stationary "internal" DFT theorem for identical particles: the internal many-body ground state can be written as a functional of the internal density ρ_{int}. Then, the corresponding "internal" KS scheme was formulated rigorously in the c.m. frame. This work provided a first step toward a fundamental justification for the use of internal density functionals for stationary mean-field-like calculations of nuclei [12] or He droplets [13] with effective interactions, showing that there exists an ultimate functional which permits one to reproduce the exact internal density. The major difference with traditional DFT is that the c.m. correlations (which appear due to the redundant coordinate problem) are explicitly included in the functional.

The aim of the present article is to generalize the internal DFT formalism and KS scheme to self-bound systems composed of different kinds of particles (i.e., multicomponent systems). This is crucial to obtain a fundamental justification to the use of density functionals for the description of:

(i) *Molecular systems where the nuclei are treated explicitly and quantum mechanically.* Taking into account the quantum nature of the nuclei is important for describing small molecules [14] and solid hydrogen [15], for instance, and explicit treatment of the nuclei is necessary to describe nonadiabatic phenomena. Moreover, taking into account the electron-nuclei correlations can be important for the description of some physical properties [16]. For those reasons, various multicomponent DFT formalisms have been developed [8,16–20], but in none of them has the c.m. motion been separated properly from the beginning, leading to formal difficulties (that will be detailed in Sec. III D). Here we propose a general formulation that overcomes those difficulties and is suited for the description of all self-bound systems. We show that the application to molecular systems is particularly interesting for understanding the approximations inherent to traditional DFT and thus how to eventually improve its results for molecular systems.

(ii) *Atomic nuclei.* The application of multicomponent internal DFT to protons and neutrons gives a further step toward the use of mean-field-like calculations with effective interactions, as currently done in nuclear physics [12], and shows that the c.m. correlations can be included in the functional. It thus opens the way to an alternative to the numerically very costly projection techniques used in nuclear physics to restore Galilean invariance [12,21–23]: they would not be necessary if the ultimate functional were known.

(iii) *Mixtures of ^{3}He and ^{4}He droplets.* Mean-field-like calculations with effective interactions are also used to describe those systems [13] and can be justified more fundamentally by the multicomponent internal DFT formalism.

The article is organized as follows. We first give the foundations of the multicomponent internal DFT formalism and make explicit the link with the previously developed formalisms. Then we apply the formalism to molecular systems where the nuclei are treated explicitly. This application clearly shows the link between multicomponent internal DFT and "one kind of particle" standard and internal DFT. Finally, we mention some features of the application to atomic nuclei and mixtures of ^{3}He and ^{4}He droplets.

II. MANY-BODY FORMULATION

A. General formulation

For the sake of simplicity and to underline more clearly the physics, we assume the following:

(i) *Two different kinds of particles.* This is sufficient to describe atomic nuclei, mixtures of ^{3}He and ^{4}He droplets, and molecular systems with only one kind of nuclei. The generalization to more kinds of different particles, for the description of molecular systems with more than one kind of nuclei, is easy.

(ii) *Two-body particle-particle interactions.* The generalization to three-body, etc., interactions is straightforward.

(iii) *Particles without spin.* Generalization to spin-polarized systems can be obtained by introduction of an arbitrary internal magnetic field $\sum_i \mathbf{B}_{int}(\mathbf{r}_i - \mathbf{R})$, which models the effect on internal properties of magnetic fields used in experiments, and adapting the standard derivation [1,24].

We thus consider

(i) $N^{(1)}$ particles (1) of mass $m^{(1)}$ and laboratory coordinates $\{\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}\}$,

(ii) $N^{(2)}$ particles (2) of mass $m^{(2)}$ and laboratory coordinates $\{\mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}\}$,

and start from a general translationally invariant many-body Hamiltonian,[1]

$$
\begin{aligned}
H = {} & \sum_{i=1}^{N^{(1)}} \frac{\mathbf{p}_i^{(1)2}}{2m^{(1)}} + \sum_{i=1}^{N^{(2)}} \frac{\mathbf{p}_i^{(2)2}}{2m^{(2)}} + \sum_{\substack{i,j=1 \\ i>j}}^{N^{(1)}} u^{(1)}\big(\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(1)}\big) \\
& + \sum_{\substack{i,j=1 \\ i>j}}^{N^{(2)}} u^{(2)}\big(\mathbf{r}_i^{(2)} - \mathbf{r}_j^{(2)}\big) + \sum_{i=1}^{N^{(1)}} \sum_{j=1}^{N^{(2)}} u^{(12)}\big(\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}\big) \\
& + \sum_{i=1}^{N^{(1)}} v_{int}^{(1)}\big(\mathbf{r}_i^{(1)} - \mathbf{R}\big) + \sum_{i=1}^{N^{(2)}} v_{int}^{(2)}\big(\mathbf{r}_i^{(2)} - \mathbf{R}\big), \quad (1)
\end{aligned}
$$

composed of

(i) the usual kinetic energy terms,

(ii) translationally invariant two-body potentials $u^{(1)}$, $u^{(2)}$, and $u^{(12)}$, which describe the particle-particle interactions,

(iii) arbitrary translationally invariant internal potentials $v_{int}^{(1)}$ and $v_{int}^{(2)}$, which act on each species in the c.m. frame and can model internal effects of potentials used in experiments (such as electric fields in the molecular case), or can be safely dropped at the end in the case of an isolated self-bound system.

The total c.m. coordinate $\mathbf{R}$, i.e., of particles (1) and (2), is defined as

$$
\begin{aligned}
\mathbf{R} &= \frac{1}{N^{(1)}m^{(1)} + N^{(2)}m^{(2)}} \left[m^{(1)} \sum_{i=1}^{N^{(1)}} \mathbf{r}_i^{(1)} + m^{(2)} \sum_{i=1}^{N^{(2)}} \mathbf{r}_i^{(2)} \right] \\
&= \frac{M^{(1)}\mathbf{R}^{(1)} + M^{(2)}\mathbf{R}^{(2)}}{M^{(1)} + M^{(2)}}, \quad (2)
\end{aligned}
$$

where $M^{(l)} = N^{(l)}m^{(l)}$ is the total mass of the particles (l), and $\mathbf{R}^{(l)} = \frac{1}{N^{(l)}} \sum_{i=1}^{N^{(l)}} \mathbf{r}_i^{(l)}$ is the center of mass of the particles (l). The $(N^{(1)} + N^{(2)} - 1)$ Jacobi coordinates $\{\xi_\alpha\}$ are defined as (see Appendix A for some reminders)

$$
\text{for} \quad \alpha \in [1; N^{(1)} - 1]: \quad \xi_\alpha = \mathbf{r}_{\alpha+1}^{(1)} - \frac{1}{\alpha} \sum_{i=1}^{\alpha} \mathbf{r}_i^{(1)},
$$

$$
\text{for} \quad \alpha = N^{(1)}: \quad \xi_{N^{(1)}} = \mathbf{r}_1^{(2)} - \mathbf{R}^{(1)},
$$

$$
\text{for} \quad \alpha \in [N^{(1)} + 1; N^{(1)} + N^{(2)} - 1]:
$$

$$
\xi_\alpha = \mathbf{r}_{\alpha-N^{(1)}+1}^{(2)} - \frac{m^{(2)} \sum_{i=1}^{\alpha-N^{(1)}} \mathbf{r}_i^{(2)} + M^{(1)}\mathbf{R}^{(1)}}{(\alpha - N^{(1)})m^{(2)} + M^{(1)}}. \quad (3)
$$

---

[1]In a Hamiltonian and wave-function-based description of an isolated self-bound system, the Hamiltonian should be explicitly translationally invariant to ensure Galilean invariance of the wave function. Translational invariance, which states that the observables do not depend on the position of the c.m., is a necessary but not sufficient condition for the more fundamental Galilean invariance, which ensures that scalar observables are the same in all inertial frames.

The ξ_α are relative to the c.m. of the other $1, \ldots, \alpha - 1$ particles and are independent of $\mathbf{R}$. They are to be distinguished from the $(N^{(1)} + N^{(2)})$ laboratory coordinates $\mathbf{r}_i^{(l)}$ and the $(N^{(1)} + N^{(2)})$ c.m. frame coordinates $(\mathbf{r}_i^{(l)} - \mathbf{R})$ relative to the total c.m.

Note that for multicomponent systems, those "standard" Jacobi coordinates cannot be associated to one specific kind of particle, in contrary to the laboratory or c.m. frame coordinates. More precisely, even if the $\{\xi_\alpha ; \alpha \in [1; N^{(1)} - 1]\}$ are the Jacobi coordinates associated to particles (1) only, the $\{\xi_\alpha ; \alpha \in [N^{(1)}; N^{(1)} + N^{(2)} - 1]\}$ mix the laboratory coordinates of particles (1) and (2).

We mention that the "standard" Jacobi coordinates used in this paper do not constitute the unique set of coordinates which permit separation of the c.m. contribution from the internal contribution in the Hamiltonian, as we do thereafter. Another possible decomposition is [instead of (3)]

$$\text{for} \quad l = 1,2 \quad \text{and} \quad \alpha \in [1; N^{(l)} - 1]:$$
$$\xi_\alpha^{(l)} = \mathbf{r}_{\alpha+1}^{(l)} - \frac{1}{\alpha} \sum_{i=1}^{\alpha} \mathbf{r}_i^{(l)}, \qquad (4)$$
$$\text{and} \quad \mathbf{R}^{(12)} = \mathbf{R}^{(2)} - \mathbf{R}^{(1)},$$

in addition to the total c.m. coordinate $\mathbf{R}$ defined in Eq. (2). $\mathbf{R}^{(12)}$ is the relative motion of the c.m. of each species. The use of this set of coordinates permits one to introduce the Jacobi coordinates $\xi_\alpha^{(l)}$ reduced to a given kind of particles (l), which is more symmetric. In this article we decided to use the set defined in Eq. (3) because it permits us to obtain more directly the results of Appendix B and Sec. IV A in the limit when one kind of particle has a much larger mass than the other kind, and does not change the final results nor the way to obtain them [the formulation in terms of the set (4) is straightforward].

Since the $\{\mathbf{r}_i^{(l)} - \mathbf{r}_{j \neq i}^{(l)}\}$, $\{\mathbf{r}_i^{(l)} - \mathbf{r}_j^{(m \neq l)}\}$ and $\{\mathbf{r}_i^{(l)} - \mathbf{R}\}$ can be rewritten as functions of the ξ_α, the interaction potentials $u^{(1)}$, $u^{(2)}$, $u^{(12)}$, and the internal potentials $v_{\text{int}}^{(1)}$ and $v_{\text{int}}^{(2)}$ can be rewritten as functions of the ξ_α. We denote

$$\sum_{\substack{i,j=1 \\ i>j}}^{N^{(l)}} u^{(l)}\left(\mathbf{r}_i^{(l)} - \mathbf{r}_j^{(l)}\right) \to U^{(l)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}),$$

$$\sum_{i=1}^{N^{(1)}} \sum_{j=1}^{N^{(2)}} u^{(12)}\left(\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}\right) \to U^{(12)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}), \qquad (5)$$

$$\sum_{i=1}^{N^{(l)}} v_{\text{int}}^{(l)}\left(\mathbf{r}_i^{(l)} - \mathbf{R}\right) \to V_{\text{int}}^{(l)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}).$$

After having defined the conjugate momenta of $\mathbf{R}$ and ξ_α (see Appendix A), we can separate (1) into $H = H_{\text{CM}} + H_{\text{int}}$, where the c.m. Hamiltonian ($M = N^{(1)}m^{(1)} + N^{(2)}m^{(2)}$ is the total mass)

$$H_{\text{CM}} = -\frac{\hbar^2 \Delta_{\mathbf{R}}}{2M} \qquad (6)$$

is a one-body operator acting in $\mathbf{R}$ space only, and the internal Hamiltonian

$$H_{\text{int}} = \sum_{\alpha=1}^{N^{(1)}+N^{(2)}-1} \frac{\tau_\alpha^2}{2\mu_\alpha} + U^{(1)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})$$
$$+ U^{(2)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}) + U^{(12)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})$$
$$+ V_{\text{int}}^{(1)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}) + V_{\text{int}}^{(2)}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})$$

is a $(N^{(1)} + N^{(2)} - 1)$ body operator in the $\{\xi_\alpha\}$ space. It contains the particle-particle interaction potentials and the internal potentials. τ_α is the conjugate momentum of ξ_α and μ_α the corresponding reduced mass, defined as

$$\text{for} \quad \alpha \in [1; N^{(1)} - 1]: \quad \mu_\alpha = \frac{\alpha}{\alpha+1}m^{(1)},$$
$$\text{for} \quad \alpha \in [N^{(1)}; N^{(1)} + N^{(2)} - 1]: \qquad (7)$$
$$\mu_\alpha = \frac{[M^{(1)} + (\alpha - N^{(1)})m^{(2)}]m^{(2)}}{M^{(1)} + (\alpha - N^{(1)} + 1)m^{(2)}}.$$

Hence the $(N^{(1)} + N^{(2)})$-body laboratory wave function $\psi(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})$ can be separated into a wave function Γ that is an eigenstate of H_{CM} and depends on the c.m. coordinate $\mathbf{R}$ only, and an internal wave function ψ_{int} that is an eigenstate of H_{int} and depends on the remaining $(N^{(1)} + N^{(2)} - 1)$ Jacobi coordinates ξ_α:

$$\psi\left(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}\right)$$
$$= \Gamma(\mathbf{R}) \, \psi_{\text{int}}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}). \qquad (8)$$

The $\Gamma(\mathbf{R})$ describes the motion of the c.m. of the isolated system in any chosen inertial frame of reference (such as the laboratory). The ψ_{int} describes the internal properties and is a function of the $(N^{(1)} + N^{(2)} - 1)$ Jacobi coordinates. Of course it could also be written as a function of the $N^{(1)}$ coordinates $\mathbf{r}_i^{(1)}$ and $N^{(2)}$ coordinates $\mathbf{r}_i^{(2)}$, i.e., $\psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})$, but one of them would be redundant [25].

Thus c.m. properties and internal properties are fully decoupled and the total energy splits into $E = E_{\text{CM}} + E_{\text{int}}$. Since Γ is solution of the free Schrödinger equation, $\Gamma(\mathbf{R})$ should be an arbitrary stationary plane wave, i.e., infinitely spread and thus not normalizable. This leads to delocalization of $\mathbf{R}$ and arbitrary c.m. energy $E_{\text{CM}} = \hbar^2 \mathbf{K}^2/(2M)$. This does not correspond to experimental situations, where the system is no longer isolated: interactions with other systems of the experimental apparatus localize the c.m.. But the formal decoupling between c.m. motion and internal properties permits us to leave the c.m. motion to the choice of experimental conditions, internal properties being comparable to the experimental ones. If ψ_{int} is normalizable, which is by definition always the case for the ground state of a self-bound system, the internal energy can be written

$$E_{\text{int}}[\psi_{\text{int}}] = (\psi_{\text{int}}|H_{\text{int}}|\psi_{\text{int}}). \qquad (9)$$

B. Some useful definitions

Before we address the generalization of internal DFT to many kinds of particles, we define some quantities and relations that are useful for subsequent considerations. Following Refs. [6,10,26], we define the internal one-body densities for

each species

$$\rho_{\text{int}}^{(l)}(\mathbf{r}) = N^{(l)} \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})$$
$$\times \left| \psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \right|^2$$
$$\times \delta(\mathbf{r} - (\mathbf{r}_i^{(l)} - \mathbf{R})). \tag{10}$$

They are normalized to $N^{(l)}$. The laboratory densities $\rho^{(l)}(\mathbf{r})$ are obtained by convolution of $\rho_{\text{int}}^{(l)}$ with the c.m. wave function (following Refs. [10,26]): $\rho^{(l)}(\mathbf{r}) = \int d\mathbf{R} |\Gamma(\mathbf{R})|^2 \rho_{\text{int}}^{(l)}(\mathbf{r} - \mathbf{R})$.

Following the considerations of Refs. [6] and [26], we define the local parts of the two-body internal density matrices for each species

$$\gamma_{\text{int}}^{(l)}(\mathbf{r},\mathbf{r}') = N^{(l)}(N^{(l)} - 1) \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})$$
$$\times \left| \psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \right|^2$$
$$\times \delta(\mathbf{r} - (\mathbf{r}_i^{(l)} - \mathbf{R})) \delta(\mathbf{r}' - (\mathbf{r}_{j \neq i}^{(l)} - \mathbf{R})). \tag{11}$$

These have the required normalization to $N^{(l)}(N^{(l)} - 1)$. Following similar steps to those in Refs. [10] and [26], we can show that the local part of the two-body laboratory density matrices $\gamma^{(l)}(\mathbf{r},\mathbf{r}')$ are obtained by convolution of $\gamma_{\text{int}}^{(l)}$ with the c.m. wave function: $\gamma^{(l)}(\mathbf{r},\mathbf{r}') = \int d\mathbf{R} |\Gamma(\mathbf{R})|^2 \gamma_{\text{int}}^{(l)}(\mathbf{r} - \mathbf{R},\mathbf{r}' - \mathbf{R})$.

Finally, we introduce the local part of the two-body internal coupling density matrix,

$$\gamma_{\text{int}}^{(12)}(\mathbf{r},\mathbf{r}') = N^{(1)} N^{(2)} \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})$$
$$\times \left| \psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \right|^2$$
$$\times \delta(\mathbf{r} - (\mathbf{r}_i^{(1)} - \mathbf{R})) \delta(\mathbf{r}' - (\mathbf{r}_j^{(2)} - \mathbf{R})), \tag{12}$$

where $\mathbf{r}$ acts in the particle (1) space and $\mathbf{r}'$ acts in the particle (2) space.

The definitions of $\rho_{\text{int}}^{(l)}(\mathbf{r})$, $\gamma_{\text{int}}^{(l)}(\mathbf{r},\mathbf{r}')$, and $\gamma_{\text{int}}^{(12)}(\mathbf{r},\mathbf{r}')$ show clearly that they are defined in the c.m. frame, i.e., that the positions $\mathbf{r}$ and $\mathbf{r}'$ are measured in the c.m. frame [see the δ relations in Eqs. (10)–(12)]. Compared to the traditional definitions, a $\delta(\mathbf{R})$ appears in the definition of the internal densities calculated with ψ_{int} written in terms of the $\{\mathbf{r}_i^{(l)}\}$ coordinates. Since one of them is redundant, the $\delta(\mathbf{R})$ represents the dependence of the redundant coordinate on the others.[2] Note that, following steps similar to those in Ref. [6], one can rewrite $\rho_{\text{int}}^{(l)}$, $\gamma_{\text{int}}^{(l)}$, and $\gamma_{\text{int}}^{(12)}$ as functions of Jacobi coordinates $\{\xi_\alpha\}$.

We establish a useful relation. For any function $f(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})$ of laboratory coordinates expressible in terms of Jacobi coordinates [we denote $F(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})$ and $\hat{F}$ the associated operator] we have

$$(\psi_{\text{int}} | \hat{F} | \psi_{\text{int}}) = \int d\xi_1 \cdots d\xi_{N^{(1)}+N^{(2)}-1} F(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}) |\psi_{\text{int}}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})|^2$$

$$= \int d\mathbf{R} d\xi_1 \cdots d\xi_{N^{(1)}+N^{(2)}-1} \delta(\mathbf{R}) F(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1}) |\psi_{\text{int}}(\xi_1, \ldots, \xi_{N^{(1)}+N^{(2)}-1})|^2$$

$$= \int d\mathbf{r}_{N^{(1)}}^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R}) f(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) |\psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})|^2. \tag{13}$$

We see that the internal mean values calculated with ψ_{int} expressed as a function of the $(N^{(1)} + N^{(2)} - 1)$ coordinates ξ_α can also be calculated with ψ_{int} expressed as a function of the $(N^{(1)} + N^{(2)})$ coordinates $\mathbf{r}_i^{(l)}$. Then, as above, a $\delta(\mathbf{R})$ that represents the dependence of the redundant coordinate on the others appears.

III. GENERALIZATION OF INTERNAL DFT AND KOHN-SHAM SCHEME TO MANY KINDS OF PARTICLES

A. Hohenberg-Kohn theorem

We show that ψ_{int} can be written as a functional of the internal densities $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$. The relation (13) leads to [$\hat{V}_{\text{int}}^{(l)}$

is defined with (5)]

$$(\psi_{\text{int}} | \hat{V}_{\text{int}}^{(l)} | \psi_{\text{int}}) \tag{14}$$
$$= \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})$$
$$\times \sum_{i=1}^{N^{(l)}} v_{\text{int}}^{(l)}(\mathbf{r}_i^{(l)} - \mathbf{R}) |\psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_N^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})|^2$$
$$= \sum_{i=1}^{N^{(l)}} \int d\mathbf{r} \, v_{\text{int}}^{(l)}(\mathbf{r}) \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \, \delta(\mathbf{R})$$
$$\times |\psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_N^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})|^2 \delta(\mathbf{r} - (\mathbf{r}_i^{(l)} - \mathbf{R}))$$
$$= \sum_{i=1}^{N^{(l)}} \int d\mathbf{r} \, v_{\text{int}}^{(l)}(\mathbf{r}) \frac{\rho_{\text{int}}^{(l)}(\mathbf{r})}{N^{(l)}} = \int d\mathbf{r} \, v_{\text{int}}^{(l)}(\mathbf{r}) \, \rho_{\text{int}}^{(l)}(\mathbf{r}), \tag{15}$$

where we used (10) to obtain the penultimate equality. We see that the potential $v_{\text{int}}^{(l)}(\mathbf{r}_i^{(l)} - \mathbf{R})$ that is $N^{(l)}$ body with respect to the laboratory coordinates becomes one body (and local) when expressed with the c.m. frame coordinates (remember that the $\rho_{\text{int}}^{(l)}$ are defined in the c.m. frame, cf. Sec. II B).

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[2]More generally, we should introduce a $\delta(\mathbf{R} - \mathbf{a})$, where $\mathbf{a}$ is an arbitrary translation vector, instead of the $\delta(\mathbf{R})$. This is linked to the translational invariance. In this paper we chose $\mathbf{a} = \mathbf{0}$, which leads to perfectly equivalent results and permits lightening of the notations.

The internal energy $E_{\text{int}}[\psi_{\text{int}}]$ (9) can be rewritten

$$
E_{\text{int}}[\psi_{\text{int}}] = \left(\psi_{\text{int}} \left| \sum_{\alpha=1}^{N^{(1)}+N^{(2)}-1} \frac{\tau_\alpha^2}{2\mu_\alpha} \right| \psi_{\text{int}} \right)
$$
$$
+ (\psi_{\text{int}} | \hat{U}^{(1)} + \hat{U}^{(2)} + \hat{U}^{(12)} | \psi_{\text{int}})
$$
$$
+ \int d\mathbf{r}\, v_{\text{int}}^{(1)}(\mathbf{r}) \rho_{\text{int}}^{(1)}(\mathbf{r}) + \int d\mathbf{r}\, v_{\text{int}}^{(2)}(\mathbf{r}) \rho_{\text{int}}^{(2)}(\mathbf{r}). \quad (16)
$$

As in its definition enter two arbitrary one-body potentials in the c.m. frame of the form $\int d\mathbf{r}\, v_{\text{int}}^{(l)}(\mathbf{r})\, \rho_{\text{int}}^{(l)}(\mathbf{r})$, and as the ground state ψ_{int} of H_{int} is obtained by minimization of E_{int}, we can directly apply the usual proof of the standard HK theorem [1,4], generalized to many kinds of particles [17,20]. We thus can claim that for a nondegenerate ground state ψ_{int} and given kinds of particles (1) and (2) (i.e., given interactions $u^{(1)}$, $u^{(2)}$, and $u^{(12)}$), the ground state ψ_{int} can be expressed as a unique functional of $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$, i.e., $\psi_{\text{int}}[\rho_{\text{int}}^{(1)}, \rho_{\text{int}}^{(2)}]$, and therefore

also the corresponding internal energy of a self-bound system, i.e., $E_{\text{int}}[\rho_{\text{int}}^{(1)}, \rho_{\text{int}}^{(2)}]$.

As emphasized in Refs. [6,27], the HK theorem is valid only for arbitrary one-body potentials that lead to *bound* ground states. As a direct consequence, the internal DFT formalism is valid only for potentials $v_{\text{int}}^{(1)}$ and $v_{\text{int}}^{(2)}$ that lead to *bound* internal ground states ψ_{int}. For pure self-bound systems, described by our formalism in the limit $v_{\text{int}}^{(1)} = v_{\text{int}}^{(2)} = 0$, ψ_{int} should by definition be a bound ground state so that the previous conclusions still hold.

B. Internal Kohn-Sham scheme

Following similar steps as in Eq. (13), we rewrite the interacting kinetic energy as (we note $(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(1)}}^{(1)}; \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \rightarrow (\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})$ and $d\mathbf{r}_1^{(1)} \ldots d\mathbf{r}_{N^{(1)}}^{(1)} d\mathbf{r}_1^{(2)} \ldots d\mathbf{r}_{N^{(2)}}^{(2)} \rightarrow d\mathbf{r}_1^{(1)} \ldots d\mathbf{r}_{N^{(2)}}^{(2)}$ for simplicity)

$$
\left(\psi_{\text{int}} \left| \sum_{\alpha=1}^{N^{(1)}+N^{(2)}-1} \frac{\tau_\alpha^2}{2\mu_\alpha} \right| \psi_{\text{int}} \right) = \int d\xi_1 \cdots \xi_{N^{(1)}+N^{(2)}-1} \psi_{\text{int}}^*(\{\xi_\alpha\}) \left(-\frac{\hbar^2 \Delta_{\mathbf{R}}}{2M} + \sum_{\alpha=1}^{N^{(1)}+N^{(2)}-1} \frac{\tau_\alpha^2}{2\mu_\alpha} \right) \psi_{\text{int}}(\{\xi_\alpha\})
$$
$$
= \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})\, \psi_{\text{int}}^*(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \left(\sum_{i=1}^{N^{(1)}} \frac{\mathbf{p}_i^{(1)2}}{2m^{(1)}} + \sum_{i=1}^{N^{(2)}} \frac{\mathbf{p}_i^{(2)2}}{2m^{(2)}} \right) \psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}), \quad (17)
$$

which permits recovery of an interpretation in terms of particles (1) and (2) and makes it clear that the major difference with the standard kinetic energy comes from the c.m. correlations, i.e., the $\delta(\mathbf{R})$ term in the previous expression.

Using relation (17) and the notations introduced in Sec. II B, we can rewrite the internal energy as

$$
E_{\text{int}}[\rho_{\text{int}}^{(1)}, \rho_{\text{int}}^{(2)}] = \int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})\, \psi_{\text{int}}^*(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)}) \left(\sum_{i=1}^{N^{(1)}} \frac{\mathbf{p}_i^{(1)2}}{2m^{(1)}} + \sum_{i=1}^{N^{(2)}} \frac{\mathbf{p}_i^{(2)2}}{2m^{(2)}} \right) \psi_{\text{int}}(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_{N^{(2)}}^{(2)})
$$
$$
+ \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \gamma_{\text{int}}^{(1)}(\mathbf{r}, \mathbf{r}')\, u^{(1)}(\mathbf{r} - \mathbf{r}') + \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \gamma_{\text{int}}^{(2)}(\mathbf{r}, \mathbf{r}')\, u^{(2)}(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}\, d\mathbf{r}'\, \gamma_{\text{int}}^{(12)}(\mathbf{r}, \mathbf{r}')\, u^{(12)}(\mathbf{r} - \mathbf{r}')
$$
$$
+ \int d\mathbf{r}\, v_{\text{int}}^{(1)}(\mathbf{r}) \rho_{\text{int}}^{(1)}(\mathbf{r}) + \int d\mathbf{r}\, v_{\text{int}}^{(2)}(\mathbf{r}) \rho_{\text{int}}^{(2)}(\mathbf{r}). \quad (18)
$$

To recover the internal KS scheme, we assume, as in the traditional KS scheme, that there exist, *in the c.m. frame* (the $\rho_{\text{int}}^{(l)}$ being defined in the c.m. frame, see Sec. II B), two noninteracting systems (i.e., two local single-particle potentials $v_S^{(l)}$):

$$
\left(\frac{\mathbf{p}^2}{2m^{(l)}} + v_S^{(l)}(\mathbf{r}) \right) \varphi_{\text{int}}^{(l)i}(\mathbf{r}) = \epsilon_i^{(l)} \varphi_{\text{int}}^{(l)i}(\mathbf{r}),
$$
$$
l = 1, 2, \quad i = 1 \ldots N^{(l)}, \quad (19)
$$

which reproduce *exactly* the densities $\rho_{\text{int}}^{(l)}$ of the interacting system:

$$
\rho_{\text{int}}^{(l)}(\mathbf{r}) = \sum_{i=1}^{N^{(l)}} \left| \varphi_{\text{int}}^{(l)i}(\mathbf{r}) \right|^2. \quad (20)
$$

Note that even if only $(N^{(1)} + N^{(2)} - 1)$ coordinates are sufficient to describe internal properties, we introduce in the KS scheme $(N^{(1)} + N^{(2)})$ orbitals, i.e., the same number as the number of particles. The reason is discussed in Sec. III C.

In Eq. (19) we implicitly supposed that the particles are fermions (i.e., that the $\{\varphi_{\text{int}}^{(l)i}\}$ are orthonormal). A KS scheme to describe boson condensates can be defined similarly by choosing identical $\varphi_{\text{int}}^{(l)i}$ for a given kind of particles (l). Uniqueness of the potential $v_S^{(l)}(\mathbf{r})$ for a given density $\rho_{\text{int}}^{(l)}(\mathbf{r})$ is ensured by a direct application of traditional DFT formalism to each KS equation (19). Of course, the question of the validity of the KS hypothesis, known as the "noninteracting v-representability" problem, remains, at least qualitatively, the same as it is in traditional DFT [1] (but can quantitatively be different).

To use notation similar to the traditional notation, we add and subtract from the internal energy (18) the internal Hartree

energies

$$E_H^{(l)}\big[\rho_{\text{int}}^{(l)}\big] = \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_{\text{int}}^{(l)}(\mathbf{r})\, \rho_{\text{int}}^{(l)}(\mathbf{r}')\, u^{(l)}(\mathbf{r}-\mathbf{r}'),$$

the "coupling" Hartree term

$$E_H^{(12)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] = \int d\mathbf{r} d\mathbf{r}'\, \rho_{\text{int}}^{(1)}(\mathbf{r})\rho_{\text{int}}^{(2)}(\mathbf{r}')u^{(12)}(\mathbf{r}-\mathbf{r}')$$

and the noninteracting kinetic energy terms

$$\sum_{i=1}^{N^{(l)}} \left(\varphi_{\text{int}}^{(l)i} \left| \frac{\mathbf{p}^2}{2m^{(l)}} \right| \varphi_{\text{int}}^{(l)i} \right).$$

This permits us to rewrite the internal energy (18) as

$$
\begin{aligned}
&E_{\text{int}}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] \\
&= \sum_{i=1}^{N^{(1)}} \left(\varphi_{\text{int}}^{(1)i} \left| \frac{\mathbf{p}^2}{2m^{(1)}} \right| \varphi_{\text{int}}^{(1)i} \right) + \sum_{i=1}^{N^{(2)}} \left(\varphi_{\text{int}}^{(2)i} \left| \frac{\mathbf{p}^2}{2m^{(2)}} \right| \varphi_{\text{int}}^{(2)i} \right) \\
&\quad + E_H^{(1)}\big[\rho_{\text{int}}^{(1)}\big] + E_H^{(2)}\big[\rho_{\text{int}}^{(2)}\big] + E_H^{(12)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] \\
&\quad + E_{XC}^{(1)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] + E_{XC}^{(2)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] + E_C^{(12)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] \\
&\quad + \int d\mathbf{r} v_{\text{int}}^{(1)}(\mathbf{r})\rho_{\text{int}}^{(1)}(\mathbf{r}) + \int d\mathbf{r} v_{\text{int}}^{(2)}(\mathbf{r})\rho_{\text{int}}^{(2)}(\mathbf{r}).
\end{aligned} \tag{21}
$$

The internal exchange-correlation energy for the identical particles of kind (l) is defined as

$$
\begin{aligned}
E_{XC}^{(l)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] &= \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \left[\gamma_{\text{int}}^{(l)}(\mathbf{r},\mathbf{r}') - \rho_{\text{int}}^{(l)}(\mathbf{r})\, \rho_{\text{int}}^{(l)}(\mathbf{r}') \right] u^{(l)}(\mathbf{r}-\mathbf{r}') \\
&\quad + \sum_{i=1}^{N^{(l)}} \left[\int d\mathbf{r}_1^{(1)} \cdots d\mathbf{r}_{N^{(2)}}^{(2)} \delta(\mathbf{R})\, \psi_{\text{int}}^*\big(\mathbf{r}_1^{(1)} \cdots \mathbf{r}_{N^{(2)}}^{(2)}\big) \frac{\mathbf{p}_i^{(l)2}}{2m^{(l)}} \psi_{\text{int}}\big(\mathbf{r}_1^{(1)} \cdots \mathbf{r}_{N^{(2)}}^{(2)}\big) - \left(\varphi_{\text{int}}^{(l)i} \left| \frac{\mathbf{p}^2}{2m^{(l)}} \right| \varphi_{\text{int}}^{(l)i} \right) \right].
\end{aligned} \tag{22}
$$

Note that since the KS assumption implies $\varphi_{\text{int}}^{(l)i}[\rho_{\text{int}}^{(l)}]$ [1], $E_{XC}^{(l)}$ can well be written as a functional of $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$.

We see that $E_{XC}^{(l)}$ contains the exchange correlations that come from the interaction $u^{(l)}$ [first line of (22)], but also the correlations contained in the interacting kinetic energy [second line of (22)]. Concerning these correlations, it is clear that they come, on the one hand, from the correlations neglected in the traditional independent-particle framework, but also from the c.m. correlations (the $\delta(\mathbf{R})$ term in the previous expression). The kinetic energy term is the only one that *explicitly* contains those correlations because they directly affect the motions of the particles in the c.m. frame. Indeed, in this frame, if one particle moves in one direction, the other particles will tend to move in the opposite direction. As quantum particles are described by wave functions, they always have associated zero-point motions. Those zero-point motions are coupled by the c.m. correlations, which is specific to quantum systems; the corresponding quantum part of the c.m. correlations is included in $E_{XC}^{(l)}$.[3]

The inclusion of the c.m. correlations in the exchange-correlation functional is the major difference with traditional DFT [4,5] and previously developed multicomponent DFT formalisms [8,16–20], and opens the way to the search for a local c.m. correlations potential, which would *a priori* be computationally much less costly than the projection techniques used, for instance, in nuclear physics [12,21–23]. Note also that the inclusion of the c.m. correlations explains why $E_{XC}^{(l)}$ is a functional of both $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$, and not only of $\rho_{\text{int}}^{(l)}$ as one might have expected: those correlations necessarily couple the particles (1) and (2), and thus their densities. (This is underscored from another point of view in Sec. III D.)

We emphasize the fact that a part of the total c.m. correlations is contained in $E_{XC}^{(1)}$ and another part in $E_{XC}^{(2)}$. Indeed, it is the interacting kinetic energy term as a whole that contains explicitly the c.m. correlations, and this term is split in both $E_{XC}^{(1)}$ and $E_{XC}^{(2)}$. The decomposition we choose for the energy functional is of course not unique. But even if it does not include all the c.m. correlations in one specific functional, its advantage is that the meaning of the obtained functionals is clear and that it permits us to recover the functional forms of "one kind of particle" traditional and internal DFT, in the limits that are discussed in Sec. IV.

The internal coupling correlation energy between particles of kinds (1) and (2) is defined as

$$
\begin{aligned}
E_C^{(12)}\big[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}\big] &= \int d\mathbf{r}\, d\mathbf{r}' \left[\gamma_{\text{int}}^{(12)}(\mathbf{r},\mathbf{r}') - \rho_{\text{int}}^{(1)}(\mathbf{r})\, \rho_{\text{int}}^{(2)}(\mathbf{r}') \right] \\
&\quad \times u^{(12)}(\mathbf{r}-\mathbf{r}').
\end{aligned} \tag{23}
$$

------

[3]We take the opportunity to underline a key difference between the classical and quantum separation of the c.m. motion. In classical mechanics, as particles are pointlike, this separation is done simply by a coordinate change. It can be done using Jacobi coordinates (the redundant coordinate is then treated explicitly) or the c.m. frame coordinates (which lead to a similar final result because the redundant coordinate is implicitly taken into account through the translational symmetry of the Hamiltonian). In quantum mechanics, particles are described by wave functions. Then one has to separate the non-normalizable part of the laboratory wave function, which can be done using Jacobi coordinates. Another consequence is that, in the c.m. frame, all points of space that satisfy $m^{(1)} \sum_{i=1}^{N^{(1)}} \mathbf{r}_j^{(1)} + m^{(2)} \sum_{i=1}^{N^{(2)}} \mathbf{r}_i^{(2)} = 0$ (and only those points) are allowed. This couples

------

the zero-point motions and produces a purely quantum contribution to the c.m. correlations.

There is of course no exchange energy in Eq. (23) because particles (1) and (2) are not identical. As this term does not contain *explicitly* the c.m. correlations, the spirit of the already developed approximations found in Refs. [8,16,20] remains suitable within the formalism presented here, at least for molecular systems, especially that of [16], which is directly applicable to a coupling correlation energy written in the form of Eq. (23).

The remaining task is to minimize the internal energy (21) so as obtain the equations of motion (which define $\rho_{\text{int}}^{(l)}$).

Varying $E_{\text{int}}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]$ with respect to $\varphi_{\text{int}}^{(l)i*}$ and imposing the (ortho-)normality of the $\{\varphi_{\text{int}}^{(l)i}\}$,

$$\frac{\delta}{\delta\varphi_{\text{int}}^{(l)i*}(\mathbf{r})}\left(E_{\text{int}}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]-\sum_{m=1}^{2}\sum_{i=1}^{N^{(m)}}\epsilon_i^{(m)}\left(\varphi_{\text{int}}^{(m)i}\big|\varphi_{\text{int}}^{(m)i}\right)\right)=0$$

leads to "internal" Kohn-Sham equations (19) for the $\{\varphi_{\text{int}}^{(l)i}\}$ with

$$v_S^{(l)}(\mathbf{r})=\int d\mathbf{r}'\rho_{\text{int}}^{(l)}(\mathbf{r}')u^{(l)}(\mathbf{r}-\mathbf{r}')+U_{XC}^{(l/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r})+v_{\text{int}}^{(l)}(\mathbf{r})+\int d\mathbf{r}'\rho_{\text{int}}^{(m)}(\mathbf{r}')u^{(12)}(\mathbf{r}-\mathbf{r}')$$
$$+U_C^{(m/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r})+U_C^{(12/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r}),\quad\text{for}\quad m\neq l. \tag{24}$$

We keep $v_{\text{int}}^{(l)}$ for generality but recall that it can be set to zero in the case of an isolated self-bound system. In addition to the classical parts of the interaction [the Hartree potentials for the $(l)-(l)$ and (1)–(2) interactions, and the optional external potentials] appear purely quantum potentials, which are defined as follows.

The exchange-correlation potential for the particles of kind (l) is

$$U_{XC}^{(l/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r})=\frac{\delta E_{XC}^{(l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]}{\delta\rho_{\text{int}}^{(l)}(\mathbf{r})}. \tag{25}$$

It is a functional of $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$, and not only of $\rho_{\text{int}}^{(l)}$, for the reasons discussed above and linked to the c.m. correlations. This potential contains the "standard" exchange-correlation for the $(l)-(l)$ interaction and the part of the c.m. correlations that is contained in $E_{XC}^{(l)}$.

The other part of the c.m. correlations is included in $E_{XC}^{(m\neq l)}$ (because of the decomposition we choose). Thus there also appear complementary pure c.m. correlation potentials

$$U_C^{(m/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r})=\frac{\delta E_{XC}^{(m)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]}{\delta\rho_{\text{int}}^{(l)}(\mathbf{r})},\quad\text{for}\quad m\neq l.$$

Finally, the coupling correlation potential is

$$U_C^{(12/l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}](\mathbf{r})=\frac{\delta E_C^{(12)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]}{\delta\rho_{\text{int}}^{(l)}(\mathbf{r})}. \tag{26}$$

All those potentials are local, as expected, which is the computational power of DFT. One can note that Eqs. (19) and (24) are symmetrical under the exchange (1) $\leftrightarrow$ (2).

Note that the first line of Eq. (24) contains the terms that describe the interaction between the identical particles of kind (l), which are close to those found in the "one kind of particle" KS scheme [5]. The second line of Eq. (24) contains terms that are specific to the KS equations for two kinds of particles. They describe the interaction of the particles of kind (l) with the particles of kind $(m\neq l)$.

C. Why do we introduce a number of orbitals equal to the number of particles in the KS scheme?

The internal DFT formalism raises the following question (we consider only one kind of fermion in this section to simplify the discussion): since for a self-bound system composed of N particles, only $(N-1)$ coordinates are sufficient to describe internal properties, why do we introduce N orbitals in the internal KS scheme? We mention that the question of the number of orbitals to introduce in the KS scheme also occurs in traditional DFT. Indeed, this number is not imposed by the theory; it has been fixed "by hand" to N orthonormal orbitals (introducing an auxiliary system of N noninteracting particles). From now on, nothing would fundamentally forbid us from introducing another number of orbitals (eventually nonorthogonal with effective masses). This would, of course, change the form of the KS energy functional, which will "adapt" to the change of the number of orbitals. More precisely, since to a chosen number M of orbitals corresponds a specific definition of the noninteracting "kinetic energy," it would change the part of $E_{XC}[\rho]$ that corresponds to the difference between the interacting kinetic energy and the noninteracting "kinetic energy" [i.e., the second line of (22)], that we note $E_{\Delta\text{kin}}[\rho]$. For instance, in the case where only one KS orbital would be introduced, $E_{\Delta\text{kin}}^{(M=1)}[\rho]$ would be drastically different from $E_{\Delta\text{kin}}^{(M=N)}[\rho]$, but it is easy to show that the corresponding single KS equation would lead to the exact interacting ground-state density, i.e., to the same result as the one obtained by direct variation of the HK functional by ρ, so that the noninteracting v-representability is perfectly achieved (since the KS noninteracting "kinetic energy" can then trivially be written as an explicit functional of ρ ($\varphi_1=\sqrt{\rho}$) and thus its variation is defined for all densities for which $\sqrt{\rho}$ is differentiable, including the interacting v-representable ones).

Purely formally speaking, the question of the optimum number of orbitals to introduce in the KS scheme can be reformulated as follows: Is the noninteracting v-representability better achieved with a certain number of orbitals M (>1)? This question is still open in traditional (and internal) DFT.

But practically speaking, many advantages justify the introduction of N orbitals:

(i) Even if only $(N-1)$ coordinates are sufficient to describe the internal properties of a self-bound system, they still describe a system of N particles. We thus have to introduce N orthonormal orbitals if we want them to be interpreted (to first order only) as single-particle orbitals and obtain a scheme comparable to actual mean-field-like calculations with effective interactions. In particular, the highest KS eigenvalue ϵ_N is then the negative of the ionization (or the separation) energy with the exact functional [28,29].

(ii) The antisymmetrization is explicit in terms of the N particle coordinates only. Introduction of N orbitals permits us to explicitly take into account the antisymmetrization in the definition of ρ, while the antisymmetrization would be implicit if another number of orbitals was introduced and thus more difficult to obtain because it would have to be more precisely taken into account in parametrizations of $E_{XC}[\rho]$.

(iii) It leads straightforwardly to the classical (pointlike) limit (see Appendix D).

(iv) It *a priori* permits one to obtain, in the general case, the noninteracting kinetic energy that is the closest to the interacting kinetic energy (i.e., the smallest $E_{\Delta\mathrm{kin}}^{(M)}[\rho]$). Indeed, $E_{\Delta\mathrm{kin}}^{(M=N)}[\rho]$ contains only the correlations energy part of the interacting kinetic energy, which is generally a correction. It is essentially for quite small self-bound systems and within the

internal DFT formalism that $E_{\Delta\mathrm{kin}}^{(M=N)}[\rho]$ can be more than a correction, because it contains the c.m. correlations, which can be large for those systems. Then, one track is to conserve N orbitals and to develop precise parametrizations for $E_{\Delta\mathrm{kin}}^{(M=N)}[\rho]$ (which is not achieved by actual functionals); this would permit us to preserve the advantages listed above. But the previous discussion also opened the door to another possible track: study whether the introduction of a number of orbitals $M \neq N$ (for instance $M = N-1$ with effective masses) would permit us to obtain a smaller $E_{\Delta\mathrm{kin}}^{(M)}[\rho]$, so that difficulties in parametrizing $E_{\Delta\mathrm{kin}}^{(M)}[\rho]$ would affect the result as little as possible. This goes beyond the scope of this paper.

D. Link with previous multicomponent DFT formalisms

The previous multicomponent DFT formalisms found in Refs. [16–19] have been developed without separation of the c.m. motion, as already underlined in Ref. [18]. The definitions of the energy functionals were based on the *laboratory* wave function ψ and densities $\rho^{(l)}$. To understand the key differences with those previous formalisms, we switch to the Levy-Lieb constrained search formulation [27,30], within which they have been developed. The corresponding energy can be decomposed in a form similar to Eq. (21), where only the definitions of $E_{XC}^{(l)}$ and $E_C^{(12)}$ change [i.e., the fourth line of Eq. (21)] [16,18,19]:

$$E_{XC}^{(l)}\big[\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}\big] \to E_{XC}^{(l)}[\rho^{(l)}] = \min_{\psi^{(l)}\to\rho^{(l)}}(\psi^{(l)}|\hat{T}^{(l)}+\hat{U}^{(l)}|\psi^{(l)}) - \min_{\psi_{SD}^{(l)}\to\rho^{(l)}}\big(\psi_{SD}^{(l)}|\hat{T}^{(l)}|\psi_{SD}^{(l)}\big) - E_H^{(l)}[\rho^{(l)}],$$

$$E_C^{(12)}\big[\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}\big] \to E_C^{(12)}[\rho^{(1)},\rho^{(2)}] = \min_{\psi\to\rho^{(1)},\rho^{(2)}}(\psi|\hat{T}^{(1)}+\hat{T}^{(2)}+\hat{U}^{(1)}+\hat{U}^{(2)}+\hat{U}^{(12)}|\psi) - \min_{\psi^{(1)}\to\rho^{(1)}}(\psi^{(1)}|\hat{T}^{(1)}+\hat{U}^{(1)}|\psi^{(1)})$$

$$- \min_{\psi^{(2)}\to\rho^{(2)}}(\psi^{(2)}|\hat{T}^{(2)}+\hat{U}^{(2)}|\psi^{(2)}) - E_H^{(12)}[\rho^{(1)},\rho^{(2)}]. \tag{27}$$

The ψ are the interacting $(N^{(1)}+N^{(2)})$-particle states, the $\psi_{SD}^{(l)}$ are the noninteracting $N^{(l)}$-particle states (Slater determinants), the $\psi^{(l)}$ are the interacting $N^{(l)}$-particle states, and $\hat{T}^{(l)} = \sum_{i=1}^{N^{(l)}} \frac{\hat{p}_i^{(l)2}}{2m^{(l)}}$ is the kinetic energy operator for particles of kind (l). The interest of the introduction of the $\psi^{(l)}$ (and of the constrained search formulation) is that it permits us to define $E_{XC}^{(l)}$ as a functional of $\rho^{(l)}$ only (and not of both $\rho^{(1)}$ and $\rho^{(2)}$). The constrained search formulation is by definition restricted to densities and thus states that are normalizable (the variational principle being defined only for systems for which the wave function is normalizable [27,31]). However, as the functionals are formulated in terms of the laboratory density (i.e., the c.m. motion is not separated), the equations obtained after minimization of the energy functional should lead to full delocalization of the density. Moreover, as the theory is not formulated in terms of internal properties, the c.m. correlations do not appear explicitly in the functional.

Internal DFT overcomes those problems because it is based on the ground state internal wave function, which is by definition always normalizable for self-bound systems, and is the one which defines the observables of experimental interest [6]. For better comparison with the previous multicomponent DFT formalisms, we reformulate the energies $E_{XC}^{(l)}$ and $E_C^{(12)}$ defined in Sec. III B within the constrained search formulation:

$$E_{XC}^{(l)}\big[\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}\big] = \min_{\psi_{\mathrm{int}}\to\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}}(\psi_{\mathrm{int}}|\hat{T}^{(l)}+\hat{U}^{(l)}|\psi_{\mathrm{int}}) - \min_{\psi_{SD}^{(l)}\to\rho_{\mathrm{int}}^{(l)}}\big(\psi_{SD}^{(l)}|\hat{T}^{(l)}|\psi_{SD}^{(l)}\big) - E_H^{(l)}\big[\rho_{\mathrm{int}}^{(l)}\big],$$

$$E_C^{(12)}\big[\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}\big] = \min_{\psi_{\mathrm{int}}\to\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}}(\psi_{\mathrm{int}}|\hat{T}^{(1)}+\hat{T}^{(2)}+\hat{U}^{(1)}+\hat{U}^{(2)}+\hat{U}^{(12)}|\psi_{\mathrm{int}})$$

$$- \min_{\psi_{\mathrm{int}}\to\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}}(\psi_{\mathrm{int}}|\hat{T}^{(1)}+\hat{U}^{(1)}|\psi_{\mathrm{int}}) - \min_{\psi_{\mathrm{int}}\to\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}}(\psi_{\mathrm{int}}|\hat{T}^{(2)}+\hat{U}^{(2)}|\psi_{\mathrm{int}}) - E_H^{(12)}\big[\rho_{\mathrm{int}}^{(1)},\rho_{\mathrm{int}}^{(2)}\big]. \tag{28}$$

The ψ_{int} are the interacting internal states which can be expressed with $(N^{(1)} + N^{(2)} - 1)$ Jacobi coordinates.[4] The $\psi_{SD}^{(l)}$ are the noninteracting $N^{(l)}$-particle states.

Note that the choice we made in Eq. (28) for the $\tilde{\psi}$ used in the minimization of $(\tilde{\psi}|\hat{T}^{(l)} + \hat{U}^{(l)}|\tilde{\psi})$ is not unique (because there is a cancellation between $E_{XC}^{(l)}$ and $E_C^{(12)}$). One could, for instance, use interacting states $\psi_{\text{int}}^{(l)}$ expressible with $(N^{(l)} - 1)$ Jacobi coordinates which lead to $\rho_{\text{int}}^{(l)}$, instead of the $(N^{(1)} + N^{(2)} - 1)$ Jacobi coordinate state leading to $\rho_{\text{int}}^{(1)}$ and $\rho_{\text{int}}^{(2)}$.[5] Even if formally correct, this is not the choice used in Eq. (28), mainly because it would lead to interpretation difficulties. Indeed, it amounts to considering that the particles of kinds (1) and (2) have independent c.m. motions,[6] while the c.m. motion is common for the system as a whole. Moreover, this would bring no gain because it would move the explicit inclusion of total c.m. correlations to $E_C^{(12)}$, so that previously developed approximations for this term [8,16,20] would not be fully usable, contrary to the formulation proposed in this paper. Another advantage of the decomposition we choose in this paper is that it permits a clear link with "one kind of particle" standard and internal DFT, which is discussed in Sec. IV.

We now discuss the link with the slightly different work found in Refs. [8,20]. First of all, this work is by its very nature essentially suited for the description of molecular systems, since the electronic coordinates are transformed to the body-fixed frame *independently* from the nuclear coordinates. [This "decoupling" is possible in molecular systems due to the large difference of masses between electrons and nuclei (see Appendix B); independent transformations are no longer possible for a self-bound system where there is no large difference of masses between the different kinds of particles constituting it.] Second, this work treats the breaking of rotational symmetry, which goes further than the other multicomponent DFT formalisms. (We don't treat rotational symmetry in this article, but we are working on the problem.) Third, the nuclear $N^{(n)}$-body density is used as a basic variable instead of the nuclear one-body density, for easier description of collective phenomena, but it is of course less easy to handle numerically for quite large systems.

The difficulty discussed above remains: Even if the electronic coordinates are transformed to the body-fixed frame, since the c.m. wave function is not *separated* from the beginning, all the densities are defined through a fully delocalized wave function (for a ground state). But numerically speaking this does not cause a real problem because:

(i) The KS step breaks by essence the translational symmetry, so that it forces the densities to become localized.

---

[4]Note that when the integrals involving ψ_{int} are written in the $(N^{(1)} + N^{(2)})$ particle coordinates representation, following similar steps as in Eq. (13), $\delta(\mathbf{R})$ appears explicitly.

[5]Since the c.m. motion is "subtracted" in our formalism, the most pertinent interacting states to use are of course internal ones, i.e., expressible in terms of Jacobi coordinates.

[6]Indeed, following similar steps as in Eq. (13), the integral $(\psi_{\text{int}}^{(l)}|\hat{T}^{(l)} + \hat{U}^{(l)}|\psi_{\text{int}}^{(l)})$ can be written in terms of the $N^{(l)}$ coordinates of particles (l). Then $\delta(\mathbf{R}^{(l)})$ appears explicitly.

(ii) In Refs. [8,20], the KS scheme is formulated in terms of the $N^{(n)}$-body nuclear density and, in the presented practical calculations, the nuclear c.m. has been separated at a second step, leading to the inclusion of the c.m. correlations in the corresponding $N^{(n)}$-body auxiliary nuclear wave function.

In the formalism presented in the present article, the c.m. motion has been separated from the beginning, leading to a proper formulation of the HK theorem in terms of the internal densities and the explicit inclusion of the c.m. correlations in the functional. This formalism is suited to study all self-bound systems.

We now study thoroughly the application to molecular systems, which permits us to make explicit the link between this formalism and traditional DFT, and then detail the application to atomic nuclei and mixtures of ^{3}He and ^{4}He droplets.

IV. APPLICATION TO MOLECULAR SYSTEMS AND LIMIT OF TRADITIONAL DFT

Electrons (we note $l = e$) are fermions, so that exchange and correlations are included in the functional $E_{XC}^{(e)}$. Nuclei (we note $l = n$) are approximated as pointlike and can be fermions or bosons (in the latter case, the functional $E_{XC}^{(n)}$ contains only correlations and all the $\varphi_{\text{int}}^{(n)i}$ are identical). The internal potentials $v_{\text{int}}^{(l)}$ can then describe internal effects of a polarization potential (i.e., a voltage applied to the system), for instance in the stationary case, or internal effects of lasers used in molecular irradiation experiments, for instance in the time-dependent case [32].

A. Simplification of the formalism due to the large difference of masses

In molecular systems the nuclei are much heavier than the electrons, i.e., $m^{(n)} \gg m^{(e)}$. It thus should be a very good approximation to consider $\mathbf{R} = \mathbf{R}^{(n)}$ and apply Jacobi coordinates to the nuclear coordinates only, so that the nuclei will be described by $(N^{(n)} - 1)$ Jacobi coordinates and will carry all the c.m. correlations. As a consequence, the electrons are not concerned by the redundant coordinates problem (i.e., the c.m. correlations) and remain described by $N^{(e)}$ coordinates in the frame attached to the c.m. of the nuclei. See Appendix B for better understanding of this mechanism from the point of view of Jacobi coordinates and Appendix C from the point of view of the functionals.

As a direct consequence, the electronic exchange-correlation functional $E_{XC}^{(e)}$ no longer contains explicitly the c.m. correlations and its form becomes comparable to that of the exchange-correlation functional of "one kind of particle" traditional DFT [1] [see Eq. (C3)]. All the c.m. correlations are explicitly included in the nuclear exchange-correlation functional $E_{XC}^{(n)}$ only and its form becomes comparable to the form of the exchange-correlation functional of "one kind of particle" internal DFT [6] [see Eq. (C4)]. Since it is only the c.m. coupling between the particles (l) and (m ≠ l) that produces a $\rho_{\text{int}}^{(m \neq l)}$ dependence in $E_{XC}^{(l)}$ [see discussion

following Eq. (22)], we have

$$\frac{\delta E_{XC}^{(l)}[\rho_{\text{int}}^{(1)},\rho_{\text{int}}^{(2)}]}{\delta\rho_{\text{int}}^{(m)}(\mathbf{r})} = 0, \quad \text{for} \quad m \neq l \Rightarrow E_{XC}^{(l)}[\rho_{\text{int}}^{(l)}].$$

The internal energy (21) thus becomes

$$
\begin{aligned}
&E_{\text{int}}\big[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}\big] \\
&= \sum_{i=1}^{N^{(n)}}\left(\varphi_{\text{int}}^{(n)i}\left|\frac{\mathbf{p}^2}{2m^{(n)}}\right|\varphi_{\text{int}}^{(n)i}\right) + \sum_{i=1}^{N^{(e)}}\left(\varphi_{\text{int}}^{(e)i}\left|\frac{\mathbf{p}^2}{2m^{(e)}}\right|\varphi_{\text{int}}^{(e)i}\right) \\
&\quad + E_H^{(n)}\big[\rho_{\text{int}}^{(n)}\big] + E_H^{(e)}\big[\rho_{\text{int}}^{(e)}\big] + E_H^{(ne)}\big[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}\big] \\
&\quad + E_{XC}^{(n)}\big[\rho_{\text{int}}^{(n)}\big] + E_{XC}^{(e)}\big[\rho_{\text{int}}^{(e)}\big] + E_C^{(ne)}\big[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}\big] \\
&\quad + \int d\mathbf{r}\, v_{\text{int}}^{(n)}(\mathbf{r})\rho_{\text{int}}^{(n)}(\mathbf{r}) + \int d\mathbf{r}\, v_{\text{int}}^{(e)}(\mathbf{r})\rho_{\text{int}}^{(e)}(\mathbf{r}), \quad (29)
\end{aligned}
$$

and the KS potentials (24) for the electrons and nuclei become

$$
\begin{aligned}
v_S^{(e)}(\mathbf{r}) &= \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(e)}(\mathbf{r}-\mathbf{r}') + U_{XC}^{(e/e)}[\rho_{\text{int}}^{(e)}](\mathbf{r}) + v_{\text{int}}^{(e)}(\mathbf{r}) \\
&\quad + \int d\mathbf{r}'\rho_{\text{int}}^{(n)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}') + U_C^{(en/e)}[\rho_{\text{int}}^{(e)},\rho_{\text{int}}^{(n)}](\mathbf{r}), \\
v_S^{(n)}(\mathbf{r}) &= \int d\mathbf{r}'\rho_{\text{int}}^{(n)}(\mathbf{r}')u^{(n)}(\mathbf{r}-\mathbf{r}') + U_{XC}^{(n/n)}[\rho_{\text{int}}^{(n)}](\mathbf{r}) + v_{\text{int}}^{(n)}(\mathbf{r}) \\
&\quad + \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}') + U_C^{(en/n)}[\rho_{\text{int}}^{(e)},\rho_{\text{int}}^{(n)}](\mathbf{r}).
\end{aligned}
$$
$$(30)$$

Since $E_{XC}^{(e)}[\rho_{\text{int}}^{(e)}]$ is comparable to the exchange-correlation functional of traditional DFT, standard approximations remain pertinent, for example, the widely used local density approximation (LDA)[7] (see, e.g., Ref. [33]) or its extension to the generalized gradient approximation (GGA) [34].

It remains an open problem to find satisfying numerically manageable approximations for $E_{XC}^{(n)}[\rho_{\text{int}}^{(n)}]$, which among others would contain the c.m. correlation energy. It would permit us to study molecular systems where the quantum nature of the nuclei plays an important role (for example, small molecules [14] and solid hydrogen [15]). The LDA could not be used *a priori* to approximate it because the nuclei are generally localized. It would probably be more pertinent to start from an approximation which exploits localization (and not delocalization as LDA does). A crude approximation would be to do the maximum localization approximation and replace, in the obtained functional, the corresponding classical density by the true density of the system. Appendix D details how to make properly the classical (pointlike) approximation for self-bound systems, which is not completely trivial because of the translational symmetry. Then, the "kinetic energy correlations" part of $E_{XC}^{(n)}$ (which contains explicitly the c.m. correlations) disappears and $\gamma_{\text{int}}^{(n)}(\mathbf{r},\mathbf{r}') - \rho_{\text{int}}^{(n)}(\mathbf{r})\rho_{\text{int}}^{(n)}(\mathbf{r}') \rightarrow \sum_{i=1}^{N^{(n)}}\rho_{\text{int}}^{(n)i}(\mathbf{r})\rho_{\text{int}}^{(n)i}(\mathbf{r}')$, where $\rho_{\text{int}}^{(n)i} = |\varphi_{\text{int}}^{(n)i}|^2$

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[7]That is, the maximum delocalization approximation (Fermi gas) and replacement, in the obtained functional, of the Fermi gas density by the true density of the system.

(see Appendix D). We thus obtain $E_{XC}^{(n)} = -\sum_{i=1}^{N^{(n)}} E_H^{(n)}[\rho_{\text{int}}^{(n)i}]$, which corresponds to the self-interaction correction to the (n)-(n) Hartree energy, as noticed in Refs. [18,35] for the standard case, and leads to the potential $U_{XC}^{(n/n)} = -\int d\mathbf{r}'\rho_{\text{int}}^{(n)i}(\mathbf{r}')u^{(n)}(\mathbf{r}-\mathbf{r}')$ when applied to the state $\varphi_{\text{int}}^{(n)i}$. This approximation gives a single density dependence and not an explicit total density dependence. (This dependence is nevertheless implicit as soon as a local KS potential is imposed, which is the aim of the optimized effective potential method [36–38], because it implies $\varphi_{\text{int}}^{(n)i}[\rho_{\text{int}}^{(n)}]$.) This necessitates extra (numerically more costly) caution to ensure the orthonormality of the $\{\varphi_{\text{int}}^{(n)i}\}$ (see, for example, Refs. [39–41]).

Even if this "maximally localized" approximation should be used as *a minima* in the absence of other approximations, its range of validity is not clear. Indeed, the width of the nuclear single densities is not systematically very small [18,42]. Moreover, this approximation does not permit us to evaluate the c.m. correlations contained in $E_{XC}^{(n)}$ (because they disappear in the classical limit, see Appendix D and footnote 3). Thus, the question of a suitable approximation for $E_{XC}^{(n)}$ as a functional of the one-body total nuclear density, including the c.m. correlations, remains open. A possible approach would be to use the semiclassical approximation [43] instead of the crude classical (pointlike) approximation.

Concerning $E_C^{(ne)}[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}]$, we recall that the spirit of the already developed approximations found in Refs. [8,16,20] remain suitable within the formalism presented here, especially that of Ref. [16], but further developments are certainly desirable.

Finally, one can note that the KS equations (19) and (30) still remain symmetric under the exchange $(e) \leftrightarrow (n)$, but the forms of $E_{XC}^{(n)}$ and $E_{XC}^{(e)}$ (thus of $U_{XC}^{(n/n)}$ and $U_{XC}^{(e/e)}$) are different: one contains explicitly the c.m. correlations whereas the other one does not.

We now make further approximations that permit us to recover traditional DFT and thus to understand better the approximations inherent to this formalism and how to eventually improve its results.

B. Further approximations that enable us to recover traditional DFT

1. Electron-nuclear correlation energy neglected

We suppose that in the total internal energy (29), the electron-nuclear correlation energy $E_{XC}^{(en)}$ is negligible compared to the other energies. This in particular implies that $|E_C^{(ne)}|$ is much smaller than $|E_{XC}^{(n)}|$. It is likely that this is a fair approximation for a certain class of molecular systems, since

(i) $E_{XC}^{(n)}$ should at least contain the (n)-(n) Hartree self-interaction (as discussed above),

(ii) electrons and nuclei are different kinds of particles, and

(iii) nuclei are generally localized (thus not too far from classical particles).

However, the range of validity of this approximation is not presently perfectly clear. Indeed, there exist molecular systems for which the electron-nuclei correlations are important for the description of some physical properties [16]. Then one has to remain at the previous step.

Within this approximation the total internal energy becomes

$$E_{\text{int}}\big[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}\big]$$

$$= \sum_{i=1}^{N^{(n)}} \left(\varphi_{\text{int}}^{(n)i}\left|\frac{\mathbf{p}^2}{2m^{(n)}}\right|\varphi_{\text{int}}^{(n)i}\right) + \sum_{i=1}^{N^{(e)}} \left(\varphi_{\text{int}}^{(e)i}\left|\frac{\mathbf{p}^2}{2m^{(e)}}\right|\varphi_{\text{int}}^{(e)i}\right)$$

$$+ E_H^{(n)}\big[\rho_{\text{int}}^{(n)}\big] + E_H^{(e)}\big[\rho_{\text{int}}^{(e)}\big] + E_H^{(ne)}\big[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}\big]$$

$$+ E_{XC}^{(n)}\big[\rho_{\text{int}}^{(n)}\big] + E_{XC}^{(e)}\big[\rho_{\text{int}}^{(e)}\big]$$

$$+ \int d\mathbf{r}\, v_{\text{int}}^{(n)}(\mathbf{r})\rho_{\text{int}}^{(n)}(\mathbf{r}) + \int d\mathbf{r}\, v_{\text{int}}^{(e)}(\mathbf{r})\rho_{\text{int}}^{(e)}(\mathbf{r}), \qquad (31)$$

and the KS potentials (30) become

$$v_S^{(e)}(\mathbf{r}) = \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(e)}(\mathbf{r}-\mathbf{r}') + U_{XC}^{(e/e)}\big[\rho_{\text{int}}^{(e)}\big](\mathbf{r})$$

$$+ v_{\text{int}}^{(e)}(\mathbf{r}) + \int d\mathbf{r}'\rho_{\text{int}}^{(n)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}'),$$

$$v_S^{(n)}(\mathbf{r}) = \int d\mathbf{r}'\rho_{\text{int}}^{(n)}(\mathbf{r}')u^{(n)}(\mathbf{r}-\mathbf{r}') + U_{XC}^{(n/n)}\big[\rho_{\text{int}}^{(n)}\big](\mathbf{r})$$

$$+ v_{\text{int}}^{(n)}(\mathbf{r}) + \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}'). \qquad (32)$$

We see that for the electrons we have recovered the traditional "one kind of particle" KS potential (as $U_{XC}^{(e/e)}$ does not contain the c.m. correlations), with, in standard notation [1–5],

$$v^{\text{ext}}(\mathbf{r}) = v_{\text{int}}^{(e)}(\mathbf{r}) + \int d\mathbf{r}'\rho_{\text{int}}^{(n)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}'). \qquad (33)$$

The potential v^{ext} contains the arbitrary one-body internal potential $v_{\text{int}}^{(e)}$ and the Hartree part of the electron-nuclear interaction (which is a functional of the nuclear one-body density $\rho_{\text{int}}^{(n)}$), and v^{ext} is thus a functional of $v_{\text{int}}^{(e)}$ and $\rho_{\text{int}}^{(n)}$, which is allowed by traditional DFT. (Traditional DFT is valid for any v^{ext} that is not a functional of the electronic wave function, thus density, and that leads to a bound state.) The potential v^{ext}, which is *internal* for (self-bound) molecular systems, becomes *external* for the pure electronic problem. This permits us to understand why traditional DFT is particularly well suited for the description of the electrons (only) in a molecular system, in the frame attached to the c.m. of the nuclei.

Note that contrary to what is sometimes thought, traditional DFT does not, strictly speaking, involve the a clamped nuclei approximation (and thus not the Born-Oppenheimer approximation either). Indeed, traditional KS equations (from which follow the $\varphi_{\text{int}}^{(e)i}$) do not necessarily depend parametrically on the nuclear positions. One is allowed to use an external potential of the form (33), so that the nuclei are described with a spatial width (i.e., quantum-mechanically), and to specify another equation that defines $\rho_{\text{int}}^{(n)}$. It is when this last equation is not specified (for instance, if we simply impose that each nuclei is represented by a Gaussian of fixed width) or when the nuclei are treated classically (see next section) that the total molecular energy should be calculated for various nuclear configurations (various mean positions of the Gaussians in the first case) to deduce the configuration of minimum energy. In the most general case, the considerations of this section permit one to understand that, from the point of view of the KS potential, traditional DFT fundamentally requires that the electron-nuclear correlation energy $E_{XC}^{(ne)}[\rho_{\text{int}}^{(n)},\rho_{\text{int}}^{(e)}]$

is neglected but not necessarily the clamped nuclei approximation.

Concerning the nuclear potential $v_S^{(n)}$, note that it is similar to the "one kind of particle" *internal* KS potential (as c.m. correlations are included in $E_{XC}^{(n)}$), with (using the notations of [6])

$$v^{\text{int}}(\mathbf{r}) = v_{\text{int}}^{(n)}(\mathbf{r}) + \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(en)}(\mathbf{r}-\mathbf{r}').$$

2. Classical (pointlike) nuclei

A quantum treatment of the nuclei may be necessary for an accurate description of small molecules [14] and certain molecular systems of intermediate size. For larger molecular systems, a classical treatment of the nuclei is generally sufficient because the nuclei become more and more localized in $\{\mathbf{r}\}$ and $\{\mathbf{p}\}$ spaces. A further approximation is to suppose that the nuclei are perfectly localized in both spaces. The Appendix D shows how to make this approximation properly in the case of self-bound systems. We note $\{\mathbf{r}_i^{(ncl)},\mathbf{p}_i^{(ncl)}\}$, the positions and momenta of the classical nuclei in the c.m. frame, i.e., satisfying $\sum_{i=1}^{N^{(n)}}\mathbf{r}_i^{(ncl)} = 0$ and $\sum_{i=1}^{N^{(n)}}\mathbf{p}_i^{(ncl)} = 0$. We pose $|\varphi_{\text{int}}^{(n)i}(\mathbf{r})|^2 \to \delta(\mathbf{r}-\mathbf{r}_i^{(ncl)})$ and $|\varphi_{\text{int}}^{(n)i}(\mathbf{p})|^2 \to \delta(\mathbf{p}-\mathbf{p}_i^{(ncl)})$, so that $\rho_{\text{int}}^{(n)}(\mathbf{r}) \to \sum_{i=1}^{N^{(n)}}\delta(\mathbf{r}-\mathbf{r}_i^{(ncl)})$ and $\rho_{\text{int}}^{(n)}(\mathbf{p}) \to \sum_{i=1}^{N^{(n)}}\delta(\mathbf{p}-\mathbf{p}_i^{(ncl)})$. The total internal energy (31) becomes (remember that only a Hartree self-interaction correction remains in $E_{XC}^{(n)}$ at the classical pointlike limit, see Sec. IV A, and that in the stationary case each $\mathbf{p}_i^{(ncl)}$ should be null)

$$E_{\text{int}}\big[\rho_{\text{int}}^{(e)},\{\mathbf{r}_i^{(ncl)}\}\big]$$

$$= \sum_{i=1}^{N^{(e)}} \left(\varphi_{\text{int}}^{(e)i}\left|\frac{\mathbf{p}^2}{2m^{(e)}}\right|\varphi_{\text{int}}^{(e)i}\right) + E_H^{(e)}\big[\rho_{\text{int}}^{(e)}\big] + E_{XC}^{(e)}\big[\rho_{\text{int}}^{(e)}\big]$$

$$+ \int d\mathbf{r}\, v_{\text{int}}^{(e)}(\mathbf{r})\rho_{\text{int}}^{(e)}(\mathbf{r}) + \sum_{i=1}^{N^{(n)}}\int d\mathbf{r}\rho_{\text{int}}^{(e)}(\mathbf{r})u^{(en)}\big(\mathbf{r}-\mathbf{r}_i^{(ncl)}\big)$$

$$+ \sum_{i>j=1}^{N^{(n)}} u^{(n)}\big(\mathbf{r}_i^{(ncl)}-\mathbf{r}_j^{(ncl)}\big) + \sum_{i=1}^{N^{(n)}} v_{\text{int}}^{(n)}\big(\mathbf{r}_i^{(ncl)}\big), \qquad (34)$$

and the electronic KS potential (32) becomes

$$v_S^{(e)}(\mathbf{r}) = \int d\mathbf{r}'\rho_{\text{int}}^{(e)}(\mathbf{r}')u^{(e)}(\mathbf{r}-\mathbf{r}') + U_{XC}^{(e/e)}\big[\rho_{\text{int}}^{(e)}\big](\mathbf{r})$$

$$+ v_{\text{int}}^{(e)}(\mathbf{r}) + \sum_{i=1}^{N^{(n)}} u^{(en)}\big(\mathbf{r}-\mathbf{r}_i^{(ncl)}\big), \qquad (35)$$

which now depends parametrically on the nuclear positions $\{\mathbf{r}_i^{(ncl)}\}$. Thus the $\{\varphi_{\text{int}}^{(e)i}\}$ and $\rho_{\text{int}}^{(e)}$ also depend parametrically on the $\{\mathbf{r}_i^{(ncl)}\}$. We recover a traditional "one kind of particle" DFT equation [1–5] with a classical nuclear background:

$$v^{\text{ext}}(\mathbf{r}) = v_{\text{int}}^{(e)}(\mathbf{r}) + \sum_{i=1}^{N^{(n)}} u^{(en)}\big(\mathbf{r}-\mathbf{r}_i^{(ncl)}\big).$$

The nuclear KS equations become obsolete in the stationary case. Indeed, classical pointlike nuclei have no zero point

motions, so that they fall to the bottom of the potential well, and the ground state of the whole molecule can be found by minimization of the total internal energy (34) for various nuclear configurations $\{\mathbf{r}_i^{(ncl)}\}$.

3. A method to improve the results of traditional DFT

The previous considerations permit us to set up a method to improve the results of traditional DFT in the molecular case:

(i) Start from the classical nuclei approximation described in Sec. IV B 2, with electrons described by "one kind of particle" DFT and parametrized by the nuclear positions. This is what is done in most of the practical calculations. This is essentially suited for molecular systems whose nuclei are very localized, i.e., quite large molecular systems.

(ii) If this is not enough, for instance, in the case of relatively small molecules where quantum effects associated with the nuclei play a role, skip to the approximation described in Sec. IV B 1. The nuclei are then treated quantum mechanically but the electron-nuclear correlation energy is neglected. There remain the (n)-(n) Hartree interaction with at least a self-interaction correction, until other more satisfactory nuclear exchange-correlation functionals (including the c.m. correlations) are available. The electrons still satisfy "one kind of particle" traditional KS equations, but the corresponding orbitals are no longer parametrized by the nuclear positions.

(iii) If this is still not enough, for instance, in cases where the electron-nuclei correlations play an important role, add the electron-nuclear correlation energy as described in Sec. IV A, using, for instance, the approximation proposed in Ref. [16] (but further developments appear desirable). The obtained equations go beyond "one kind of particle" traditional and internal KS equations because of the coupling correlation term $E_C^{(ne)}[\rho_{\rm int}^{(n)},\rho_{\rm int}^{(e)}]$.

V. ON THE APPLICATION TO ATOMIC NUCLEI AND MIXTURES OF ³He AND ⁴He DROPLETS

When the masses of each species constituting the self-bound system are not very different (for instance, in the case of protons and neutrons in an atomic nucleus or mixtures of ³He and ⁴He droplets), one cannot do the approximations presented in the previous section, because the c.m. correlations couple all the particles, and the complete formalism presented in Sec. III B has to be used.

One interest of the application of multicomponent internal DFT formalism to protons and neutrons is to give a fundamental justification to the use of internal density functionals for stationary mean-field-like calculations of nuclei with effective interactions [12], showing that there exists an ultimate *local* potential which contains the c.m. correlations and permits one to reproduce the exact internal densities of the protons and neutrons.[8] It gives a more fundamental justification than the Hartree-Fock (HF) framework to the stationary nuclear mean-field-like calculations. Indeed, HF does not contain quantum correlations, nor does it treat correctly the redundant

coordinate problem, which introduces a spurious coupling between internal properties and c.m. motion [21,44]. A way to overcome this problem in the stationary case is to perform projected HF (projection before variation on c.m. momentum), which permits restoration of Galilean invariance, but at the price of abandoning the independent-particle description [12,21–23] and at a large numerical cost. The internal DFT formalism demonstrates that the c.m. correlations can be taken into account through a local potential, *a priori* numerically much less costly than the projection techniques.

We emphasize that for nuclear systems, the $v_{\rm int}^{(l)}$ are generally zero. It is the dependence on the initial state that allows, in the time-dependent case, a description of, for instance, the collision of two nuclei in the frame attached to the total c.m. of the nuclei [32].

We mention that the point of view often adopted in nuclear physics is that the protons and neutrons are the same kinds of particles, leading to isospin considerations [44]. From this point of view, it is rather the inclusion of the isospin in "one kind of particle" internal DFT that would give KS equations comparable to nuclear mean-field-like calculations.

The application of multicomponent internal DFT to mixtures of ³He and ⁴He droplets[9] also permits us to give a fundamental justification to the mean-field-like calculations done to describe those systems [13]. Since the c.m. correlations are, to our knowledge, still not treated in existing calculations of helium droplets, this work opens the way to their inclusion.

VI. CONCLUSION

We have generalized the internal DFT formalism and Kohn-Sham scheme to multicomponent self-bound systems, treating correctly their fundamental translational symmetry. The formalism we obtained applies to the description of molecular systems where the nuclei are treated explicitly, atomic nuclei and mixtures of ³He and ⁴He droplets. The main difference with traditional DFT is the explicit inclusion of the quantum center-of-mass correlations (due to the zero-point motion) in the functional.

The application to molecular systems where the nuclei are treated explicitly permits us to clarify the approximations that underly traditional "one kind of particle" DFT and KS scheme (i.e., electron-nuclei correlation energy neglected) and why this formalism is essentially suited for the description of the electrons (only) in the frame attached to the c.m. of the nuclei. We also set up a method to improve the results of traditional DFT in the case of molecular systems.

The application to atomic nuclei and mixtures of ³He and ⁴He droplets provides a step toward a fundamental justification to the use of effective interactions that are functionals of the one-body densities of each species in mean-field-like calculations.

Finally, we mention the questions that remain open:

_____

[8]Protons and neutrons are both fermions, so that the two functionals $E_{XC}^{(l)}$ should contain *exchange* and correlations.

[9]³He are fermions, so that the corresponding $E_{XC}^{(l)}$ functional should contain *exchange* and correlations. ⁴He are bosons, so that the corresponding $E_{XC}^{(l)}$ functional should contain only correlations and the corresponding orbitals $\varphi_{\rm int}^{(l)i}$ should be identical (for condensates).

(i) The search for a general functional that describes the c.m. correlations and leads to a local KS potential is continuing. It would give a numerically advantageous alternative to the projection techniques used in nuclear physics to restore Galilean invariance. It could also be used to improve the description of helium droplets and nuclei in molecular systems.

(ii) In the case of molecular systems, it appears desirable to find more satisfactory functional forms for the nucleus-nucleus correlation energy $E_{XC}^{(n)}[\rho_{\text{int}}^{(n)}]$ than the simple self-interaction correction to the Hartree energy obtained through the crude classical (pointlike) approximation. One way could be to use semiclassical approximations. It also appears desirable to pursue the search of functionals for the electron-nuclear correlation energy $E_C^{(ne)}[\rho_{\text{int}}^{(n)}, \rho_{\text{int}}^{(e)}]$.

(iii) The generalization of this work to the time-dependent case is not completely trivial and is under investigation, following the considerations of Refs. [32,45].

(iv) The question of the noninteracting v-representability according to the number of orbitals introduced in the KS scheme merits further study.

(v) It would be interesting to apply the same reasoning to rotational invariance to formulate the theory in terms of the internal density with respect to the body-fixed frame (sometimes also called "intrinsic" one-body density [46]). Indeed, even if this density is not directly observable experimentally, there is some indirect experimental evidence for the existence of rotational symmetry-breaking states in nuclear rotational bands. Such a work would certainly shed some light on the symmetry-breaking question.

APPENDIX A: JACOBI COORDINATES FOR PARTICLES OF DIFFERENT KINDS

We consider a system of N particles of different kinds. We start from the set of conjugate laboratory coordinates $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$, associated to the masses $\{m_i\}$, with $i = 1, \ldots, N$. The Jacobi coordinates are ($\alpha = 1, \ldots, N - 1$)

(i) the c.m. position $\mathbf{R} = \frac{1}{\sum_{i=1}^{N} m_i} \sum_{i=1}^{N} m_i \mathbf{r}_i$, conjugated to the total momentum $\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$,

(ii) the relative positions (relative to the c.m. of the $i - 1$ other particles) $\xi_\alpha = \mathbf{r}_{\alpha+1} - \frac{1}{\sum_{i=1}^{\alpha} m_i} \sum_{i=1}^{\alpha} m_i \mathbf{r}_i$, conjugate to the relative momenta $\tau_\alpha = \frac{1}{\sum_{i=1}^{\alpha+1} m_i} (\mathbf{p}_{\alpha+1} \sum_{i=1}^{\alpha} m_i - m_{\alpha+1} \sum_{i=1}^{\alpha} \mathbf{p}_i)$. If we note $\sum_{i=1}^{N} m_i = M$ the total mass and $\mu_\alpha = \frac{m_{\alpha+1} \sum_{i=1}^{\alpha} m_i}{\sum_{i=1}^{\alpha+1} m_i}$ the relative mass, we can decompose the kinetic energy as $\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} = \frac{\mathbf{P}^2}{2M} + \sum_{\alpha=1}^{N-1} \frac{\tau_\alpha^2}{2\mu_\alpha}$.

APPENDIX B: SIMPLIFICATION OF THE JACOBI COORDINATES WHEN ONE KIND OF PARTICLE IS MUCH HEAVIER THAN THE OTHER

We suppose that $m^{(1)} \gg m^{(2)}$. Then if $N^{(2)}$ is not much larger than $N^{(1)}$ and/or $\mathbf{R}^{(2)}$ is not very far away from $\mathbf{R}^{(1)}$, which is the case for molecular systems, one can simplify (2) in

$$\mathbf{R} = \frac{1}{N^{(1)}} \sum_{i=1}^{N^{(1)}} \mathbf{r}_j^{(1)} = \mathbf{R}^{(1)}, \tag{B1}$$

so that the c.m. of the whole system coincides with the c.m. $\mathbf{R}^{(1)}$ of the particles (1) only. Moreover, Jacobi coordinates (3) and reduced masses (7) can be simplified in

for $\alpha \in [1; N^{(1)} - 1]$:

$$\xi_\alpha = \mathbf{r}_{\alpha+1}^{(1)} - \frac{1}{\alpha} \sum_{i=1}^{\alpha} \mathbf{r}_i^{(1)} = \xi_\alpha^{(1)} \quad \text{and} \quad \mu_\alpha = \frac{\alpha}{\alpha+1} m^{(1)},$$

for $i \in [1; N^{(2)}]$:

$$\xi_{N^{(1)}-1+i} = \mathbf{r}_i^{(2)} - \mathbf{R}^{(1)} = \mathbf{r}_i'^{(2)} \quad \text{and} \quad \mu_{N^{(1)}-1+i} = m^{(2)},$$

where the $(N^{(1)} - 1)$ coordinates $\xi_\alpha^{(1)}$ appear as Jacobi coordinates specific to the particles of kind (1) only, and the remaining $N^{(2)}$ coordinates $\mathbf{r}_i'^{(2)}$ appear naturally as the coordinates of each $N^{(2)}$ single particles (2) in the c.m. frame. Thus we see that we obtain an equivalent result if we apply Jacobi coordinates to the heavy particles only and if we describe each light particle by its coordinates in the frame attached to the c.m. of the heavy particles. As a consequence, the redundant coordinate problem, and thus the c.m. correlations, concerns only the heavy particles. This explains why those correlations should not appear in the exchange-correlation energy functional of the light particles (for instance, the electrons in a molecule).

APPENDIX C: EXCHANGE-CORRELATION FUNCTIONALS WHEN ONE KIND OF PARTICLE IS MUCH HEAVIER THAN THE OTHER

In the molecular case, as $\mathbf{R} = \mathbf{R}^{(n)}$, for any function $f(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)})$ that depends on the electronic coordinates only, we have

$$\begin{aligned} I_f = &\int d\mathbf{r}_1^{(n)} \cdots d\mathbf{r}_{N^{(n)}}^{(n)} d\mathbf{r}_1^{(e)} \cdots d\mathbf{r}_{N^{(e)}}^{(e)} \delta(\mathbf{R}) \\ &\times \left| \psi_{\text{int}}(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \right|^2 \\ &\times f(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \\ = &\int d\mathbf{r}_1^{(e)} \cdots d\mathbf{r}_{N^{(e)}}^{(e)} f(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \left| \psi_{\text{int}}^{(e)}(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \right|^2, \end{aligned}$$

where we have defined the local part of the $N^{(e)}$-body electronic density as

$$\begin{aligned} \left| \psi_{\text{int}}^{(e)}(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \right|^2 = &\int d\mathbf{r}_1^{(n)} \cdots d\mathbf{r}_{N^{(n)}}^{(n)} \delta(\mathbf{R}^{(n)}) \\ &\times \left| \psi_{\text{int}}(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}) \right|^2. \end{aligned} \tag{C1}$$

This makes it clear that I_f is no longer explicitly affected by (or no longer contains explicitly) the c.m. correlations. Indeed, the

$\delta(\mathbf{R}^{(n)})$ does not directly affect the integral over the electronic coordinates. The c.m. correlations are included only implicitly through $|\psi_{\text{int}}^{(e)}|^2$.

More generally, we consider an operator $\hat{F}$ that acts on the electronic coordinates only (we write $\hat{F}(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)})$ in $\{\mathbf{r}\}$ representation). We find

$$
\begin{aligned}
I_{\hat{F}} &= \int d\mathbf{r}_1^{(n)} \cdots d\mathbf{r}_{N^{(n)}}^{(n)} d\mathbf{r}_1^{(e)} \cdots d\mathbf{r}_{N^{(e)}}^{(e)} \delta(\mathbf{R}) \\
&\quad \times \psi_{\text{int}}^*\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \hat{F}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \\
&\quad \times \psi_{\text{int}}\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \\
&= \int d\mathbf{r}_1^{(e)} \cdots d\mathbf{r}_{N^{(e)}}^{(e)} \psi_{\text{int}}^{(e)*}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \hat{F}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \\
&\quad \times \psi_{\text{int}}^{(e)}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right),
\end{aligned}
\tag{C2}
$$

where $\psi_{\text{int}}^{(e)}$ is defined such as

$$
\begin{aligned}
&\psi_{\text{int}}^{(e)*}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \hat{F}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \psi_{\text{int}}^{(e)}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \\
&= \int d\mathbf{r}_1^{(n)} \cdots d\mathbf{r}_{N^{(n)}}^{(n)} \delta(\mathbf{R}^{(n)}) \psi_{\text{int}}^*\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \\
&\quad \times \hat{F}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \psi_{\text{int}}\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}; \mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right).
\end{aligned}
$$

This definition complies with (C1) (when $\hat{F} \to f$). As above, we see that $I_{\hat{F}}$ is not explicitly affected by the c.m. correlations. (Those correlations are included only implicitly through the "electronic wave function" $\psi_{\text{int}}^{(e)}$.)

All this makes it clear, from a complementary point of view of that presented in Appendix B, that the c.m. correlations should no longer appear explicitly in the electronic exchange-correlation functional (22). Indeed, it can be rewritten with the previous notation,

$$
\begin{aligned}
E_{XC}^{(e)} &= \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \left[\gamma_{\text{int}}^{(e)}(\mathbf{r}, \mathbf{r}') - \rho_{\text{int}}^{(e)}(\mathbf{r}) \rho_{\text{int}}^{(e)}(\mathbf{r}') \right] u^{(e)}(\mathbf{r} - \mathbf{r}') \\
&\quad + \sum_{i=1}^{N^{(e)}} \left[\int d\mathbf{r}_1^{(e)} \cdots d\mathbf{r}_{N^{(e)}}^{(e)} \psi_{\text{int}}^{(e)*}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) \right. \\
&\quad \left. \times \frac{\mathbf{p}_i^{(e)2}}{2m^{(e)}} \psi_{\text{int}}^{(e)}\left(\mathbf{r}_1^{(e)}, \ldots, \mathbf{r}_{N^{(e)}}^{(e)}\right) - \left(\varphi_{\text{int}}^{(e)i} \left| \frac{\mathbf{p}^2}{2m^{(e)}} \right| \varphi_{\text{int}}^{(e)i} \right) \right],
\end{aligned}
\tag{C3}
$$

whose form is similar to that of traditional DFT [1]. Using the same kind of reasoning for the nuclei, we obtain

$$
\begin{aligned}
E_{XC}^{(n)} &= \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \left[\gamma_{\text{int}}^{(n)}(\mathbf{r}, \mathbf{r}') - \rho_{\text{int}}^{(n)}(\mathbf{r}) \rho_{\text{int}}^{(n)}(\mathbf{r}') \right] u^{(n)}(\mathbf{r} - \mathbf{r}') \\
&\quad + \sum_{i=1}^{N^{(n)}} \left[\int d\mathbf{r}_1^{(n)} \cdots d\mathbf{r}_{N^{(n)}}^{(n)} \delta(\mathbf{R}^{(n)}) \psi_{\text{int}}^{(n)*}\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}\right) \right. \\
&\quad \left. \times \frac{\mathbf{p}_i^{(n)2}}{2m^{(n)}} \psi_{\text{int}}^{(n)}\left(\mathbf{r}_1^{(n)}, \ldots, \mathbf{r}_{N^{(n)}}^{(n)}\right) - \left(\varphi_{\text{int}}^{(n)i} \left| \frac{\mathbf{p}^2}{2m^{(n)}} \right| \varphi_{\text{int}}^{(n)i} \right) \right],
\end{aligned}
\tag{C4}
$$

which explicitly contains all the c.m. correlations and whose form is similar to that of internal DFT [6].

APPENDIX D: THE CLASSICAL (POINTLIKE) LIMIT IN THE INTERNAL DFT FORMALISM

To lighten the notation and since it is sufficient for the considerations of this paper, we consider only one kind of particle in this section. The generalization to many kinds of particles is straightforward.

1. Classical limit for the densities

The classical (pointlike) limit for a N-body density $|\tilde{\psi}|^2$ is usually obtained by assuming

$$
|\tilde{\psi}(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 \to \frac{1}{N!} \sum_P \Pi_{i=1}^N \rho^{(cl)i}(\mathbf{r}_{P(i)}), \tag{D1}
$$

where the $\{\mathbf{r}_i\}$ are the coordinates of the N particles, P the possible permutations of those coordinates, and

$$
\rho^{(cl)i}(\mathbf{r}) = \delta\left(\mathbf{r} - \mathbf{r}_i^{(cl)}\right) \tag{D2}
$$

are the classical densities of each particle i (the $\mathbf{r}_i^{(cl)}$ being their classical positions). Of course, this approximation breaks the translational invariance so that it can be fundamentally justified only for densities $|\tilde{\psi}|^2$ that are *not* translationally invariant (and are symmetric under the exchange of two particles, of course). It thus *cannot* be fundamentally justified for the laboratory N-body density $|\psi|^2$ of a self-bound system, nor for its internal N-body density $|\psi_{\text{int}}|^2$ expressed with the particle coordinates $\{\mathbf{r}_i\}$, because they are both translationally invariant.

For self-bound systems, it is in fact for the c.m. frame N-body "density" $\delta(\mathbf{R})|\psi_{\text{int}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2$ that the classical approximation can fundamentally be justified. Indeed, this "density" is obviously not translationally invariant (the $\delta(\mathbf{R})$ fixes the c.m. in position space and amounts to move in the c.m. frame) and is symmetric under the exchange of two particles (as $|\psi_{\text{int}}|^2$ satisfies this symmetry). It is non-null only for the $\{\mathbf{r}_i\}$ that satisfy $\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i = 0$ (i.e., the $\{\mathbf{r}_i\}$ become the c.m. frame coordinates).

In the same way, for a classical system described in the c.m. frame, $\frac{1}{N!} \sum_P \Pi_{i=1}^N \rho_i^{(cl)}(\mathbf{r}_{P(i)})$ is non-null only for the $\{\mathbf{r}_i^{(cl)}\}$ that satisfy $\sum_{i=1}^N \mathbf{r}_i^{(cl)} = 0$. Thus, for self-bound systems the proper way to do the classical approximation is to replace

$$
\delta(\mathbf{R})|\psi_{\text{int}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 \to \frac{1}{N!} \sum_P \Pi_{i=1}^N \rho_{\text{int}}^{(cl)i}(\mathbf{r}_{P(i)}) \tag{D3}
$$

with

$$
\sum_{i=1}^N \mathbf{r}_i^{(cl)} = 0 \quad \text{and} \quad \rho_{\text{int}}^{(cl)i}(\mathbf{r}) = \delta\left(\mathbf{r} - \mathbf{r}_i^{(cl)}\right). \tag{D4}
$$

Inserting this approximation in the definitions of Sec. II B, we obtain the classical (pointlike) limits of the one- and two-body internal densities

$$
\begin{aligned}
\rho_{\text{int}}^{(cl)}(\mathbf{r}) &= \sum_{i=1}^N \rho_{\text{int}}^{(cl)i}(\mathbf{r}), \\
\gamma_{\text{int}}^{(cl)}(\mathbf{r}, \mathbf{r}') &= \rho_{\text{int}}^{(cl)}(\mathbf{r}) \rho_{\text{int}}^{(cl)}(\mathbf{r}') - \sum_{i=1}^N \rho_{\text{int}}^{(cl)i}(\mathbf{r}) \rho_{\text{int}}^{(cl)i}(\mathbf{r}').
\end{aligned}
\tag{D5}
$$

2. Classical limit for the kinetic energy terms

We define the one-body density in $\{\mathbf{p}\}$ space of the interacting system as

$$\rho_{\text{int}}(\mathbf{p}) = N \int d\mathbf{p}_1 \ldots d\mathbf{p}_N \delta(\mathbf{P}) \, |\psi_{\text{int}}(\mathbf{p}_1,\ldots,\mathbf{p}_N)|^2 \, \delta(\mathbf{p}_i - \mathbf{p}),$$

where $\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$ is fixed to zero, so that ρ_{int} is defined in the c.m. frame. The interacting internal kinetic energy can then be written

$$\left(\psi_{\text{int}} \left| \sum_{\alpha=1}^{N-1} \frac{\tau_\alpha^2}{2\mu_\alpha} \right| \psi_{\text{int}} \right) = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \rho_{\text{int}}(\mathbf{p}).$$

The one-body density in $\{\mathbf{p}\}$ space of the noninteracting (KS) system is defined as [1]

$$\rho_{\text{int}}^S(\mathbf{p}) = \int d\mathbf{r} d\mathbf{r}' \exp^{i\mathbf{p}(\mathbf{r}-\mathbf{r}')/\hbar} \sum_{i=1}^{N} \varphi_{\text{int}}^i(\mathbf{r}) \varphi_{\text{int}}^{i*}(\mathbf{r}'),$$

so that the kinetic energy of the noninteracting system can be written

$$\sum_{i=1}^{N} \left(\varphi_{\text{int}}^i \left| \frac{\mathbf{p}^2}{2m} \right| \varphi_{\text{int}}^i \right) = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} \rho_{\text{int}}^S(\mathbf{p}).$$

Even if the one-body densities in the $\{\mathbf{r}\}$ space of the interacting and noninteracting systems are the same, it is not the case for the one-body densities in the $\{\mathbf{p}\}$ space, i.e., $\rho_{\text{int}}(\mathbf{p}) \neq \rho_{\text{int}}^S(\mathbf{p})$ (the difference is due to the quantum correlations). Thus in the general case, the difference between interacting and noninteracting internal kinetic energies that appear in E_{XC} [see second line of Eq. (22)] is not null:

$$\left(\psi_{\text{int}} \left| \sum_{\alpha=1}^{N-1} \frac{\tau_\alpha^2}{2\mu_\alpha} \right| \psi_{\text{int}} \right) - \sum_{i=1}^{N} \left(\varphi_{\text{int}}^i \left| \frac{\mathbf{p}^2}{2m} \right| \varphi_{\text{int}}^i \right)$$

$$= \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} (\rho_{\text{int}}(\mathbf{p}) - \rho_{\text{int}}^S(\mathbf{p})) \neq 0. \qquad \text{(D6)}$$

But since the mean total momenta of the interacting and noninteracting systems should be equal, the classical (pointlike) limit (obtained supposing that the system is perfectly localized in both $\{\mathbf{r}\}$ and $\{\mathbf{p}\}$ spaces) gives

$$\rho_{\text{int}}(\mathbf{p}) = \rho_{\text{int}}^S(\mathbf{p}) = \sum_{i=1}^{N} \delta\big(\mathbf{p} - \mathbf{p}_i^{(cl)}\big),$$

where the $\mathbf{p}_i^{(cl)}$ are the classical momenta of the particles in the c.m. frame, which satisfy $\sum_{i=1}^{N} \mathbf{p}_i^{cl} = 0$ (in the stationary case, $\mathbf{p}_i^{cl} = 0$ of course). Thus, in the classical limit, the "kinetic energy-exchange correlations" part of E_{XC} [i.e., the second line of Eq. (22)], which contains explicitly the c.m. correlations in $\{\mathbf{r}\}$ representation, disappears.

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