

Utilization of Deformations in Molecular Quantum Chemistry and Application to Density Functional Theory

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Abstract. The aim of this paper is to present in a way accessible to most quantum chemists a general mathematical method which consists in deforming wave-functions and density functions (in the spirit of the Local Scaling Transformation). This deformation method allows us to obtain several new results including a characterization of the set of wave-functions that have the same given density function (which gives a new insight on a result of G. Zumbach and K. Maschke) and an N -representability result where symmetry is taken into account. We also propose new theoretical ways to generate approximations of the exact density functional, and give a numerical example.

Keywords. Density functional theory, approximation of density functionals, deformations of wave functions, N -representability in a given symmetry class, Jacobian problem.

I Introduction

We are interested in the calculation of the ground-state energy E_0 of an N -electron system. In the molecular case, we have

$$E_0 = \inf \{ \langle \Psi, \mathcal{H}\Psi \rangle, \int |\Psi|^2 = 1 \}$$

where

$$\mathcal{H} = - \sum_{i=1}^N \Delta_i + \sum_{i=1}^N v(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

and

$$v(\mathbf{r}) = \sum_{j=1}^P \frac{-Z_j}{|\mathbf{r} - \mathbf{R}_j|}$$

($(\mathbf{R}_j)_{j=1,\dots,P}$ are the P nuclei positions and Z_j their charge). Following the point of view of density functional theory, we try to obtain an approximation of E_0 by minimization of functionals that explicitly depend of the density function ρ , and eventually, other parameters. In order to do this, we deform a given wave-function in such a way that we are able to control the corresponding density function.

In their article [1], I. Petkov, M. Stoitsov and E.S. Kryachko developed the Local Scaling Transformation Theory (see also [2] and [3]). They essentially consider radial deformations in the atomic case. In this case, several numerical and theoretical results have been obtained (see [4, 5, 6, 7, 8]).

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We have generalized these transformations to the non-radial case and in a more systematic approach in a series of mathematically-oriented papers [9, 10, 11, 12]. Here we present the main results with only formal proofs and discuss some possible applications in quantum chemistry.

In Section 2, we develop our general deformation method. We will see that this method uses the resolution of a classical mathematical problem, namely the Jacobian problem.

Thus in section 3 (which summarizes [9]), we develop a first method in order to solve this Jacobian problem, and we give a new insight on the decomposition result of G. Zumbach and K. Maschke [14].

Symmetry problems in DFT are important (see Görling [13]). In Section 4, in order to deal with symmetry problems associated with the structure of the molecules, we develop and adapt another method due to J. Moser [15] for solving the Jacobian problem. In particular, we propose density functionals for the calculation of the minimal energy in a given symmetry class. In this section, we also give a new N-representability result for totally symmetric density functions (this part was not included in [10]).

Finally in section 5, we discuss the applied view point and give some numericals calculus on the Helium atom that show how the deformation method can be used in order to improve the energy (we use a Variational Monte Carlo Method to calculate the energies).

In general, the method we propose give a way to deform explicitly a wave function to improve its density function. But we do not propose a method to calculate the associated energy. In particular the difficulty of the calculation of the correlation energy is not solved.

II The general deformation method

Let \mathbf{f} be a one-to-one and regular function from \mathbb{R}^3 onto \mathbb{R}^3 . (In [9] we also consider non-regular deformations.) Let $\Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)$ be an N -electron wave-function, where $\mathbf{r}_i \in \mathbb{R}^3$ are the space variables, and σ_i the spin variables. We assume that Ψ is antisymmetric and square integrable. We define:

$$(\mathbf{T}_{\mathbf{f}}\Psi)(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) := \left(\prod_{i=1}^N J_{\mathbf{f}}(\mathbf{r}_i) \right)^{1/2} \Psi(\mathbf{f}(\mathbf{r}_1), \sigma_1; \dots; \mathbf{f}(\mathbf{r}_N), \sigma_N).$$

where $J_{\mathbf{f}} = |\det(\partial f_i / \partial x_j)|$ is the absolute value of the Jacobian determinant of \mathbf{f} . Notice that this transformation does not change the spin variables. Therefore, in order to simplify the presentation, we shall drop the spin variables. Thus we shall consider Ψ as a function that depends only on space variables, $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$. We assume that Ψ belongs to $L_a^2(\mathbb{R}^{3N})$, the space of square-integrable functions on \mathbb{R}^{3N} that are antisymmetric (other symmetries could be considered) with respect to the variables $(\mathbf{r}_1, \dots, \mathbf{r}_N)$. In this case our transformation becomes

$$(\mathbf{T}_{\mathbf{f}}\Psi)(\mathbf{r}_1, \dots, \mathbf{r}_N) := \left(\prod_{i=1}^N J_{\mathbf{f}}(\mathbf{r}_i) \right)^{1/2} \Psi(\mathbf{f}(\mathbf{r}_1), \dots, \mathbf{f}(\mathbf{r}_N)). \quad (1)$$

Using the change of variable formula note that $\int |\mathbf{T}_{\mathbf{f}}\Psi|^2 = \int |\Psi|^2$, so $\mathbf{T}_{\mathbf{f}}$ defines a unitary operator from $L_a^2(\mathbb{R}^{3N})$ onto $L_a^2(\mathbb{R}^{3N})$.

The wave-function $\mathbf{T}_f\Psi$ represents a deformation of the initial wave-function Ψ . The function \mathbf{f} will be called the deformation. For instance, if $\mathbf{f}(\mathbf{r}) = \lambda \mathbf{r}$, then $J_f(\mathbf{r}) = \lambda^3$ and \mathbf{T}_f is the usual uniform scaling transformation.

We have the following fundamental property. If we denote ρ_Ψ the density function of Ψ , that is:

$$\rho_\Psi(\mathbf{r}) := N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N,$$

then the following holds:

$$\text{if } \Psi_2 = \mathbf{T}_f\Psi_1 \text{ then } \rho_{\Psi_2}(\mathbf{r}) = J_f(\mathbf{r}) \rho_{\Psi_1}(\mathbf{f}(\mathbf{r})). \quad (2)$$

This is a simple consequence of the use of the change of variable $\mathbf{r} \rightarrow \mathbf{f}(\mathbf{r})$ for the variables $\mathbf{r} = \mathbf{r}_2$ to $\mathbf{r} = \mathbf{r}_N$.

Let us introduce the notation

$$J_f(\mathbf{r}) \rho(\mathbf{f}(\mathbf{r})) := (\mathbf{f} * \rho)(\mathbf{r}). \quad (3)$$

In (3), $\mathbf{f} * \rho$ represents the deformed density function. So (2) means that the deformed wave-function has the deformed density function.

Different authors have considered linear decomposition of wave-function in particular basis orbitals, and then have used deformations in order to optimize the basis orbitals [1, 3, 14, 16]. In our presentation, we deform directly the wave-function instead of the orbitals. However, since the transformation \mathbf{T}_f is linear, the two approaches become equivalent when we use a representation of the wave-function in a given basis of orbitals (and Slater determinants).

The aim of this deformation method is to generate explicit wave-functions Ψ of given density ρ . In fact we are able to parameterize all the set of wave-functions which have density ρ (see Section III).

More precisely, if Ψ_0 is a wave-function of density ρ_0 , for any density function ρ , we construct a deformed wave-function Ψ issued from Ψ_0 , as $\Psi = \mathbf{T}_f\Psi_0$ where we assume that \mathbf{f} deforms ρ_0 into ρ (i.e., $\rho = \mathbf{f} * \rho_0$). Then, we have by construction $\rho_\Psi = \rho$. Thus in order to generate explicit Ψ 's we have to obtain explicit solutions \mathbf{f} of the equation $\rho = \mathbf{f} * \rho_0$. This equation is known as the *Jacobian problem* [15, 17].

The use of deformations allows to construct a new type of density functionals. Actually, the energy $E[\Psi] := \langle \Psi, \mathcal{H}\Psi \rangle$ of the above Ψ may be written as follows:

$$E[\Psi] = E[\mathbf{T}_f\Psi_0] = F[\rho, \Psi_0]. \quad (4)$$

In (4), one must understand that \mathbf{f} is a function which depends only on ρ and ρ_0 . Note that this formula shows explicitly the dependence of the energy of the wave-function Ψ with respect to its associated density ρ . This can be compared with the work of J.E. Harriman [16, 18] where the kinetic energy is decomposed in terms that depend or do not depend on the density function.

Now, for a given normalized Ψ_0 , $\rho \rightarrow F[\rho, \Psi_0]$ is a density functional and we have

$$E_0 \leq \inf_{\rho} F[\rho, \Psi_0] \leq E[\Psi_0]. \quad (5)$$

Thus, in particular, it satisfies the variational principle.

The philosophy behind the formula (5) is to improve an initial wave-function Ψ_0 by deformation.

III First method for solving the Jacobian problem

In this section, in order to deform a density function ρ_1 into another density function ρ_2 , we use an auxiliary density function, with a constant value N on the unit cube $(0, 1)^3$. In fact for every ρ , following Zumbach and Maschke, we construct a deformation \mathbf{f} from \mathbb{R}^3 onto $(0, 1)^3$ such that

$$\rho = \mathbf{f} * \rho_c$$

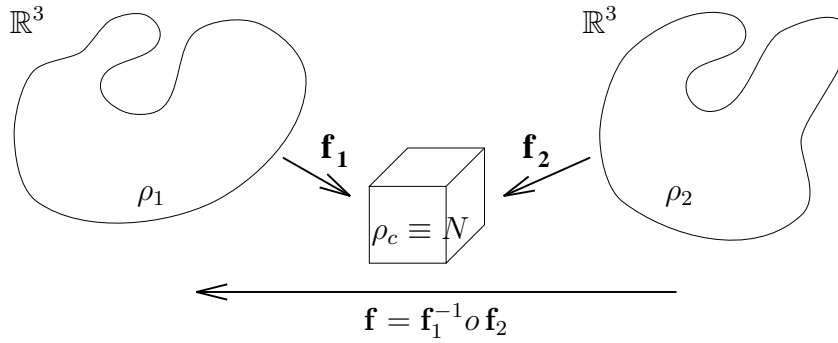
where $\rho_c(\mathbf{r}) = N, \forall \mathbf{r} \in (0, 1)^3$. We keep the same notation $*$ as in (3) even if \mathbf{f} is a deformation from \mathbb{R}^3 onto $(0, 1)^3$ and not from \mathbb{R}^3 onto \mathbb{R}^3 .

Now if \mathbf{f}_1 and \mathbf{f}_2 solve

$$\begin{cases} \rho_1 = \mathbf{f}_1 * \rho_c \\ \rho_2 = \mathbf{f}_2 * \rho_c \end{cases}$$

then $\rho_c = \mathbf{f}_1^{-1} * \rho_1$ and $\rho_2 = \mathbf{f}_2 * (\mathbf{f}_1^{-1} * \rho_1) = (\mathbf{f}_1^{-1} \circ \mathbf{f}_2) * \rho_1$. Thus $\mathbf{f} = \mathbf{f}_1^{-1} \circ \mathbf{f}_2$ is a deformation from \mathbb{R}^3 onto \mathbb{R}^3 which solves our problem (see fig.1).

Figure 1:



III.1 The Zumbach and Maschke decomposition revisited

Let ρ be a positive function on \mathbb{R}^3 such that $\int \rho = N$. We can obtain a solution of $\rho = \mathbf{f}_\rho * \rho_c$ (i.e., $\rho(\mathbf{r}) = J_{\mathbf{f}_\rho}(\mathbf{r}) N$) using the following definition of \mathbf{f}_ρ due to Zumbach and Maschke [14]:

$$\begin{aligned} f_1(x, y, z) &= \frac{\int_{-\infty}^x dx' \rho(x', y, z)}{\int_{-\infty}^{+\infty} dx' \rho(x', y, z)} \\ f_2(x, y, z) &= \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^y dx' dy' \rho(x', y', z)}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx' dy' \rho(x', y', z)} \\ f_3(x, y, z) &= \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^z dx' dy' dz' \rho(x', y', z')}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx' dy' dz' \rho(x', y', z')} \end{aligned} \quad (6)$$

where (f_1, f_2, f_3) are the three components of \mathbf{f}_ρ .

We can also use this deformation \mathbf{f}_ρ in order to deform the set of auxiliary wave-functions of constant density N on the unit cube into the set of wave-functions of given

density ρ . This will allow us to obtain a parameterization of the set of wave-functions of a given density function.

Let \mathbf{T}_ρ be the following operator from $L_a^2((0, 1)^{3N})$ into $L_a^2(\mathbb{R}^{3N})$:

$$(\mathbf{T}_\rho \Phi)(\mathbf{r}_1, \dots, \mathbf{r}_N) = \left(\prod_{i=1}^N \frac{\rho(\mathbf{r}_i)}{N} \right)^{1/2} \Phi(\mathbf{f}_\rho(\mathbf{r}_1), \dots, \mathbf{f}_\rho(\mathbf{r}_N)) \quad (7)$$

where $L_a^2((0, 1)^{3N})$ is the space of square-integrable functions on $(0, 1)^{3N}$ that are anti-symmetric. Note that the above formula is formally the same as (1) since $J_{\mathbf{f}_\rho} = \rho/N$.

In [9] we have proved the following result:

Theorem. III.1 *Let $\rho > 0$, with $\int \rho = N$, and $\Psi \in L_a^2(\mathbb{R}^{3N})$. Then*

(i) \mathbf{T}_ρ is a unitary operator from $L_a^2((0, 1)^{3N})$ onto $L_a^2(\mathbb{R}^{3N})$.

(ii) $\rho_\Psi = \rho$ if and only if there exists $\Phi \in L_a^2((0, 1)^{3N})$ such that $\begin{cases} \Psi = \mathbf{T}_\rho \Phi \\ \rho_\Phi = N \end{cases}$

Furthermore Φ is then uniquely defined.

Actually in [9] we have proved that if $\rho \geq 0$, (ii) still holds but of course the inverse of \mathbf{T}_ρ is no more defined on $L_a^2(\mathbb{R}^{3N})$ and this rather complicates the proof.

Theorem III.1 gives a complete parameterization of the set of wave-functions of given density function ρ , where $\Phi \in L_a^2((0, 1)^{3N})$ is the parameter. Formally the proof of this theorem is simple. If we suppose that ρ is strictly positive and regular, then \mathbf{f}_ρ is a regular and invertible change of variables. So, for a given Ψ in $L_a^2(\mathbb{R}^{3N})$, there exists a Φ in $L_a^2((0, 1)^{3N})$ such that $\Psi = \mathbf{T}_\rho \Phi$ (take $\Phi = \mathbf{T}_{\mathbf{f}_\rho^{-1}} \Psi$). In particular, $\rho_\Psi = J_{\mathbf{f}_\rho} \rho_\Phi(\mathbf{f}_\rho) = \frac{\rho}{N} \rho_\Phi(\mathbf{f}_\rho)$. Then, $\rho_\Psi = \rho$ if and only if $\rho_\Phi = N$, which concludes the proof.

Now if we decompose Φ in Fourier series we then obtain the Zumbach and Maschke characterization [14], as explained in [9] (see also [19]).

III.2 The atomic case

In the atomic case, in order to respect the natural symmetry of the system, we consider the spherical coordinates (r, θ, ϕ) . Let ρ be a density function. Notice that the Jacobian problem $J_{\mathbf{f}}(x, y, z) = \frac{\rho(x, y, z)}{N}$ in Cartesian coordinates becomes $J_{\mathbf{f}}(r, \theta, \phi) = \frac{\rho(r, \theta, \phi) r^2 \sin(\theta)}{N}$ under the change of variables $\mathbf{f}(r, \theta, \phi) = \tilde{\mathbf{f}}(x, y, z)$. A solution \mathbf{f}_ρ of $J_{\mathbf{f}} = \frac{\rho r^2 \sin(\theta)}{N}$ can be obtained as follows (in the same way as in [20]):

$$\begin{aligned} f_\phi(r, \theta, \phi) &= \frac{\int_0^\phi d\phi' \mu(r, \theta, \phi')}{\int_0^{2\pi} d\phi' \mu(r, \theta, \phi')} \\ f_\theta(r, \theta, \phi) &= \frac{\int_0^\theta \int_0^{2\pi} d\theta' d\phi' \mu(r, \theta', \phi')}{\int_0^\pi \int_0^{2\pi} d\theta' d\phi' \mu(r, \theta', \phi')} \\ f_r(r, \theta, \phi) &= \frac{\int_0^r \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu(r', \theta', \phi')}{\int_0^{+\infty} \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu(r', \theta', \phi')} \end{aligned} \quad (8)$$

where

$$\mu(r, \theta, \phi) = \rho(r, \theta, \phi) r^2 \sin(\theta).$$

Furthermore, if we suppose that ρ is radial, then

$$\begin{aligned} f_\phi(r, \theta, \phi) &= \frac{\phi}{2\pi} \\ f_\theta(r, \theta, \phi) &= \frac{1 - \cos(\theta)}{2} \\ f_r(r, \theta, \phi) &= \frac{\int_0^r \rho(r') r'^2 dr'}{N/4\pi}. \end{aligned}$$

So for two radial densities ρ_1 and ρ_2 , we have a simple manner to compute the deformation \mathbf{f} which satisfies $\rho_2 = \mathbf{f} * \rho_1$. In fact, as seen in the beginning of Section III, $\mathbf{f} = \mathbf{f}_{\rho_1}^{-1} \circ \mathbf{f}_{\rho_2}$, which gives in spherical coordinates

$$\mathbf{f}(r, \theta, \phi) = \begin{pmatrix} f(r) \\ \theta \\ \phi \end{pmatrix} \quad (9)$$

where $f(r)$ is defined by

$$\int_0^{f(r)} t^2 \rho_1(t) dt = \int_0^r t^2 \rho_2(t) dt. \quad (10)$$

This is exactly the local scaling transformation as it was first defined by E.S. Kryachko and E. V. Ludeña in [3], except that sometimes the integral equation (10) is presented as a differential equation for $f(r)$:

$$r^2 \rho_2(r) = f(r)^2 \rho_1(f(r)) \frac{df}{dr}(r). \quad (11)$$

Remark that this deformation \mathbf{f} (solution of (10)) lets the origin invariant and also keeps the symmetry in the sense that $\mathbf{T}_\mathbf{f}$ transforms a wave-function in a given symmetry class into a wave-function in the same symmetry class (in the atomic case).

III.3 General case

In the linear case, it is possible to generalize formula (8) using cylindrical coordinates (r, ϕ, z) . For instance, when $\rho_i = \rho_i(r, z)$, we can solve $J_{\mathbf{f}_i} = \frac{r \rho_i(r, z)}{N}$ as follows:

$$\begin{cases} f_{i,r}(r, z) = 2\pi N^{-1} \int_0^r \int_{-\infty}^{\infty} r' \rho_i(r', z') dr' dz' \\ f_{i,\phi}(\phi) = (2\pi)^{-1} \phi \\ f_{i,z}(z) = \int_{-\infty}^z \rho_i(r, z') dz' \times \left(\int_{-\infty}^{\infty} \rho_i(r, z') dz' \right)^{-1} \end{cases}$$

However the deformation $\mathbf{f}_{\rho_1}^{-1} \circ \mathbf{f}_{\rho_2}$ does not *a priori* conserves the nuclei positions. In fact, if we want to consider non atomic cases (and non radial deformations), and if we use the solution described in this section, we face various problems, which are:

- It is physically important to keep invariant the nuclei positions. With the above method, we are only able to have one invariant point (using spherical coordinates) or two invariant points (using elliptical coordinates [12, 4]).

- In many cases we know, *a priori*, the symmetry class of the ground state. Thus we want that the deformation lets invariant the symmetry classes. In general this will not be the case with the above deformations, except in the atomic case (with radial deformations) or the diatomic case (see [12], annexe 3).
- In order that $E[\Psi]$ be well defined, we must have $\int |\nabla\Psi|^2 < \infty$, which implies a regularity condition on the deformed wave-functions. In general, since we use deformations from \mathbb{R}^3 into the unit cube, we may create singularities. (Note that in the radial case, we can obtain regular deformations, but in the diatomic case, the use of elliptical coordinates creates singularities, see [12], annexe 3).

For all these reasons, we propose another method in order to solve the Jacobian problem.

IV Moser's Procedure

IV.1 Linearization of the Jacobian problem

In this section, we recall the Moser linearization method in order to solve the Jacobian problem.

Let ρ_2 and ρ_1 be two density functions. We introduce a continuum set of intermediary density functions (ρ_t) , for $t \in [0, 1]$, as follows:

$$\rho_t := (1 - t)\rho_2 + t\rho_1.$$

We are going to deform continuously ρ_1 into ρ_2 solving the following Jacobian problems: for every $t \in [0, 1]$, find $\mathbf{f}_t : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ such that,

$$\rho_2 = \mathbf{f}_t * \rho_t. \tag{12}$$

Let us recall a classical calculation of differential geometry:

$$\frac{\partial(\mathbf{f}_t * \rho_t)}{\partial t} = \mathbf{f}_t * \left(\frac{\partial\rho_t}{\partial t} + \text{div}(\rho_t \mathbf{X}_t) \right), \tag{13}$$

where $\mathbf{X}_t : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ is the vector field associated to \mathbf{f}_t by:

$$\frac{\partial}{\partial t} \mathbf{f}_t = \mathbf{X}_t(\mathbf{f}_t) \tag{14}$$

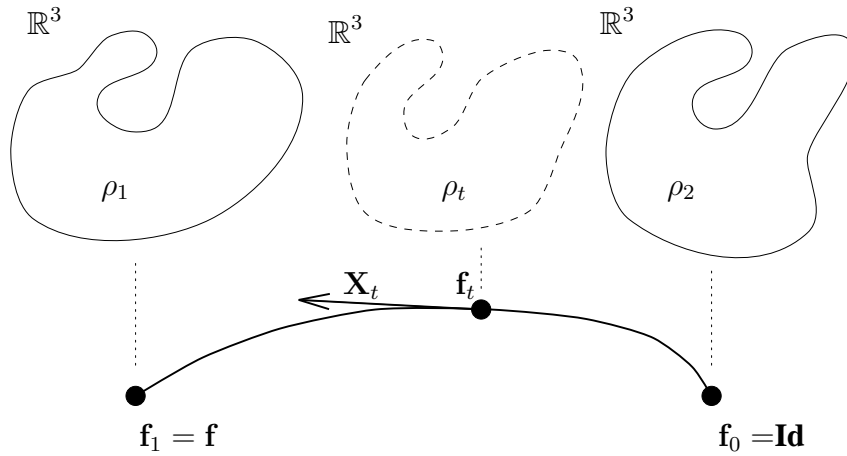
and where div denotes the divergence operator (see fig.2).

For $t = 0$, we have $\rho_0 = \rho_2$ and we can choose $\mathbf{f}_0(\mathbf{x}) = \mathbf{x}$ for the initial solution of (12). Now, if we are able to solve the following conservation equation:

$$\frac{\partial\rho_t}{\partial t} + \text{div}(\rho_t \mathbf{X}_t) = 0,$$

then by (13), we obtain that $\mathbf{f}_t * \rho_t$ is constant, so equals ρ_2 , and we are done.

Figure 2:



Note that the non-linear equation for \mathbf{f}_t has been transformed in a linear equation for the associated vector field \mathbf{X}_t . This will allow us to deal more easily with the problems related to the invariant points and the symmetries.

Finally, with our choice for ρ_t we proceed formally as follows. First we construct a field $\mathbf{V} : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ such that $\text{div}(\mathbf{V}) = \rho_2 - \rho_1$. Then we define $\mathbf{X}_t = \frac{\mathbf{V}}{\rho_t}$. Finally, we integrate the evolution equation (14) from $t = 0$ to $t = 1$.

IV.2 Construction of deformations in the case of admissible densities

In this section we show how to deform a density function into another one, using a deformation \mathbf{f} , in such a way that \mathbf{T}_f preserves some physical invariant of the system, which are:

- Invariance of the nuclei: if $\mathbf{R}_1, \dots, \mathbf{R}_P$ are the nuclei positions, we want that $\mathbf{f}(\mathbf{R}_i) = \mathbf{R}_i$ (since we want to preserve the singularity positions of the wavefunction).
- Conservation of symmetries (see [21] for general considerations on symmetry). Let G be the point group of the molecule, i.e., the group of affine transformations on \mathbb{R}^3 that preserve the molecule. If Ψ is in Γ , where Γ is a symmetry class associated to the group G , then we want that $\mathbf{T}_f \Psi$ be also in Γ . For this, it suffices (see [10]) that \mathbf{f} commutes with all the elements of G (i.e., for all $Q \in G$, $\mathbf{f} \circ Q = Q \circ \mathbf{f}$ where \circ denotes the composition product). In fact, this condition is in some sense a necessary one [11]. (For instance, for atoms, this condition implies that \mathbf{f} be a radial deformation as in (9)).
- Regularity conditions: if $E[\Psi]$ is well defined, we want that $E[\mathbf{T}_f \Psi]$ be also well defined. This implies some regularity conditions and also a particular behavior at infinity on \mathbf{f} . We do not discuss this point here and refer the reader to [10].

Such a deformation will be called an *admissible deformation*.

Nevertheless we were not able to solve the Jacobian problem $\rho_2 = \mathbf{f} * \rho_1$ for any type of density functions (ρ_i) if we want that \mathbf{f} be admissible. So we define also a class of admissible density functions as follows.

Definition. We say that a density function ρ is admissible if ρ is a continuous and strictly positive function on \mathbb{R}^3 , everywhere regular on $\mathbb{R}^3 \setminus \{\mathbf{R}_1, \dots, \mathbf{R}_P\}$, such that $(\nabla \rho)/\rho$ be bounded, and $\int_{\mathbb{R}^3} \rho = N$. Furthermore we impose that:

- (i) ρ is totally symmetric, i.e., $\forall Q \in G$, and $\mathbf{r} \in \mathbb{R}^3$, $\rho(Q\mathbf{r}) = \rho(\mathbf{r})$;
- (ii) ρ has a cusp behavior around each nuclei positions \mathbf{R}_i :

$$\rho(r, w) = a + b(w)r + o(r), \quad (15)$$

where (r, w) denotes the spherical coordinates around \mathbf{R}_i , $a > 0$ and b is continuous on the sphere S^2 ;

- (iii) ρ has an exponential fall-off at infinity:

$$\rho(r, w) = C(w)r^\beta e^{-\alpha r} + o(r^\beta e^{-\alpha r}), \quad r \rightarrow \infty \quad (16)$$

where $\alpha > 0$, $\beta \in \mathbb{R}$, and C is continuous on the sphere.

We think that all the above requirements are physically relevant, except for the totally symmetric condition. We shall come back later on this point (see Section IV.3). In fact, the theorem we state below still holds without the symmetry conditions on ρ , but clearly we then obtain a deformation that may not respect the symmetry requirement (see [10]).

Remark. IV.1 In the above definition, condition (ii), although physically reasonable, is not satisfied when Gaussian basis sets are used. However other asymptotic behavior type at infinity can be considered in the same way without modifying Theorem IV.1 below. But in this Theorem we cannot change the asymptotic behavior type at infinity by using admissible deformations.

Theorem. IV.1 If ρ_1 and ρ_2 are two admissible density functions, then there exists an admissible deformation \mathbf{f} such that

$$\rho_2 = \mathbf{f} * \rho_1.$$

Let us sketch the proof of this theorem (see [10] for a complete proof). First we construct \mathbf{f}_1 , a composition of local radial deformations around each nuclei in order that $\tilde{\rho}_1 = \mathbf{f}_1 * \rho_1$ be equal to ρ_2 in a little neighborhood of each nuclei, and $\tilde{\rho}_1 = \rho_1$ outside an other little neighborhood of the nuclei. Then we construct \mathbf{f}_2 which only deforms a neighborhood of the infinity, and such that $\tilde{\tilde{\rho}}_1 = \mathbf{f}_2 * \tilde{\rho}_1$ be equal to ρ_2 in a neighborhood of the infinity, and $\tilde{\tilde{\rho}}_1 = \tilde{\rho}_1$ outside a neighborhood of the infinity.

Now we define $\delta\rho = \rho_2 - \tilde{\tilde{\rho}}_1$ and note that $\delta\rho$ is regular, $\int_{\mathbb{R}^3} \delta\rho = 0$, and $\delta\rho$ has a compact support (for instance included in $[-R, R]^3$). We then apply the Moser procedure in order to deform $\tilde{\tilde{\rho}}_1$ into ρ_2 .

First we obtain a solution \mathbf{V} of $\operatorname{div}(\mathbf{V}) = \delta\rho$, as follows:

$$\begin{aligned} V_1(x, y, z) &= \int_{-\infty}^x \delta\rho(x', y, z) dx' - g(x) \int_{-\infty}^{+\infty} \delta\rho(x', y, z) dx' \\ V_2(x, y, z) &= g'(x) \int_{-\infty}^{+\infty} \int_{-\infty}^y \delta\rho(x', y', z) dx' dy' \\ &\quad - g'(x)g(y) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \delta\rho(x', y', z) dx' dy' \\ V_3(x, y, z) &= g'(x)g'(y) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^z \delta\rho(x', y', z') dx' dy' dz', \end{aligned}$$

where g is a regular function from \mathbb{R} into \mathbb{R} such that $g(x) = 0$ for $x \leq -R$ and $g(x) = 1$ for $x \geq R$. Remark that the set of $\mathbf{r} \in \mathbb{R}^3$ such that $\mathbf{V}(\mathbf{r}) \neq 0$ is included in $[-R, R]^3$, and that \mathbf{V} is regular.

Then, in order to obtain a deformation which preserves the nuclei positions and the symmetry, it suffices to construct a $\tilde{\mathbf{V}}$ such that $\operatorname{div}(\tilde{\mathbf{V}}) = \operatorname{div}(\mathbf{V}) = \delta\rho$, $\tilde{\mathbf{V}}(\mathbf{R}_i) = \mathbf{0}$, and $Q \circ \tilde{\mathbf{V}} = \tilde{\mathbf{V}} \circ Q$ for any $Q \in G$.

For that, we first construct a regular vector field \mathbf{W} on \mathbb{R}^3 , which does not vanish only on a neighborhood of \mathbf{R}_i , and such that $\mathbf{W}(\mathbf{R}_i) = \mathbf{V}(\mathbf{R}_i)$ and $\operatorname{div}(\mathbf{W}) = 0$ (a simple construction is done in [10]). Then we take

$$\tilde{\mathbf{V}}(\mathbf{x}) := \frac{1}{\operatorname{Card}(G)} \sum_{Q \in G} (\mathbf{V} - \mathbf{W})(Q\mathbf{x}) \quad (17)$$

Formula (17) has a natural extension in the case of continuous point groups [11].

Finally we define $\mathbf{X}_t = \tilde{\mathbf{V}}/\rho_t$ in (14). This vector field is regular and has compact support, and we can easily integrate (14) in order to obtain \mathbf{f}_3 such that $\rho_2 = \mathbf{f}_3 * \tilde{\rho}_1$. Then $\mathbf{f} = \mathbf{f}_1 \circ \mathbf{f}_2 \circ \mathbf{f}_3$ solves $\rho_2 = \mathbf{f} * \rho_1$.

Remark. IV.2 We must confess that in the above construction, we have omitted a problem concerning the matching of the deformations when we construct $\tilde{\rho}$ and $\tilde{\tilde{\rho}}$ (see for instance Lemma III.1 in [10]). So, excepted for the Moser procedure, the above construction is mainly of mathematical interest. A more applied viewpoint is given in Section V.

Remark. IV.3 In this section, we have only considered strictly positive density functions. In the case the density functions vanish, more assumptions are needed in order to find a regular deformation (see for instance [12], annexe 2).

IV.3 N-representability result and application to density functional theory

The role of symmetry and in particular of symmetry averaging has been extensively discussed in the literature (see e.g. [21], [22]). It is well-known that the energy depends only on the symmetric components of the density matrices (since the Hamiltonian \mathcal{H} is invariant under all the transformations of G). As in Görling [13], we construct at the end of this section, a functional F_{Γ} which contains all the symmetry information. That is, if

Γ is the symmetry class of the ground-state, the minimization of F_Γ over all the totally symmetric densities gives $E_{0,\Gamma}$, which denotes the ground-state energy in Γ , i.e.,

$$E_{0,\Gamma} := \inf\{E[\Psi], \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}), \int |\nabla\Psi|^2 < \infty, \text{ and } \int |\Psi|^2 = 1\}. \quad (18)$$

First, we state an N -representability result which justifies our interest in totally symmetric density functions (see definition of admissible densities).

It is well-known that for any density function ρ such that $\rho \geq 0$, $\int \rho < \infty$ and $\int |\nabla\sqrt{\rho}|^2 < \infty$, there exists a wave-function Ψ in $L_a^2(\mathbb{R}^{3N})$ with $\int |\nabla\Psi|^2 < \infty$, and such that $\rho_\Psi = \rho$ (see [2], [23]; see also [24]).

However, in general, it is not possible to impose that Ψ be in Γ , a given symmetry class.

Let us define $\tilde{\rho}$ as the totally symmetrized density function associated to ρ , i.e.,

$$\tilde{\rho}(\mathbf{r}) := \frac{1}{\text{Card}(G)} \sum_{Q \in G} \rho(Q\mathbf{r})$$

(when the cardinal of G is infinite, see [11]). Then we have the following result (proved in [11]) which answers to an underlying N -representability problem stated in [13].

Theorem. IV.2 *Let $N \geq 2$ and ρ be an admissible density function. Let Γ be a symmetry class such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$. Then there exists $\Psi \in \Gamma$, with $\Psi \in L_a^2(\mathbb{R}^{3N})$ and $\int |\nabla\Psi|^2 < \infty$, such that $\tilde{\rho}_\Psi = \rho$.*

The idea of the proof is first to find a Ψ_0 in Γ , such that $\tilde{\rho}_{\Psi_0}$ be an admissible density function (see [11] for this fact). Then, for a given admissible density function ρ , using the previous theorem we can construct an admissible deformation \mathbf{f} such that $\rho = \mathbf{f} * \tilde{\rho}_{\Psi_0}$. Now let $\Psi = \mathbf{T}_\mathbf{f}\Psi_0$. Note that Ψ is in Γ by definition of an admissible deformation, and also $\rho_\Psi = \mathbf{f} * \rho_{\Psi_0}$. Hence $\tilde{\rho}_\Psi = \mathbf{f} * \tilde{\rho}_{\Psi_0} = \rho$.

As a consequence we can define a density functional associated with the symmetry class Γ , by:

$$F_\Gamma[\rho] := \inf\{E[\Psi], \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}), \int |\nabla\Psi|^2 < \infty, \text{ and } \tilde{\rho}_\Psi = \rho\},$$

for ρ admissible. We then obtain, for $N \geq 2$, and for a given symmetry class Γ :

$$E_{0,\Gamma} = \inf \left\{ F_\Gamma[\rho], \rho \text{ admissible, } \int \rho = N \right\}, \quad (19)$$

where $E_{0,\Gamma}$ is defined in (18). We emphasize that in formula (19), we obtain $E_{0,\Gamma}$ minimizing only with respect to totally symmetric density functions, the symmetry information (the choice of Γ) is contained in F_Γ .

The deformations generated in section IV.2 allow us to generate functionals of the totally symmetric densities which are approximations of the exact functional $F_\Gamma[\rho]$. Let $\Psi_0 \in \Gamma$ normalized such that $E[\Psi_0]$ be an approximation of $E_{0,\Gamma}$. Let $\rho_0 = \tilde{\rho}_{\Psi_0}$. Then we can define the density functional $F[\rho, \Psi_0]$ as follows: for ρ an admissible density function,

we construct \mathbf{f} the admissible deformation such that $\rho = \mathbf{f} * \rho_0$ (using theorem IV.1) and we take

$$F[\rho, \Psi_0] := E[\mathbf{T}_{\mathbf{f}}\Psi_0]. \quad (20)$$

Thus in this formula we are computing the energy of the wave-function $\Psi = \mathbf{T}_{\mathbf{f}}\Psi_0$ which satisfies $\widetilde{\rho}_{\Psi} = \rho$, and in some sense, $F[\rho, \Psi_0]$ is now an approximation of $F_{\Gamma}[\rho]$:

$$E_{0,\Gamma} \leq \inf \{F[\rho, \Psi_0], \rho \text{ admissible}\} \leq E[\Psi_0].$$

This can be used for the calculation of certain excited states. Indeed, if we consider a molecule for which we already have an approximation of the first excited states, we are able to improve by deformation all energy values which correspond to different symmetry classes (using (20)).

V Applied view point

It is clear that the above construction of the functionals $F[\rho, \Psi_0]$ is not very numerically efficient (essentially because of the treatment of the cusps, see remark IV.1). In this section, in order to obtain simpler algorithms, we only deal with the deformations and we do not care about the generated density functions. So rigorously we are no longer considering the density functional theory view point, but because of the previous results, we know that if we generate a sufficiently large set of deformations, we shall also generate a large class of density functions.

V.1 A numerical example in the atomic case

The Local Scaling Transformation method has been numerically tested in several atomic cases [7, 6, 8]. However, the wave-functions considered in these papers are Slater determinants or linear combinations of Slater determinants and thus it is difficult to improve the correlation. In fact, it is not possible to create a dynamic correlation by this type of deformations if there is no dynamic correlation in the initial wave-function.

We have made various numerical tests in atomic and diatomic cases (up to $N = 4$, see [12]). Here we give one of these example, on the Helium atom. Our aim is not to obtain better energies than known results but rather to show how the deformation method can improve the correlation energy.

We choose an initial wave-function, Ψ_1 , which contains a Jastrow factor, namely:

$$\Psi_1 = \phi(r_1) \phi(r_2) J(r_{12}) | \uparrow, \downarrow |$$

where $\phi(r) = \exp(-ar)$, and with a Jastrow factor $J(r) = \exp(\frac{\alpha r}{1+\beta r})$.

Starting from the above wave-function Ψ_1 , we study the deformed wave-function $\Psi_2 = \mathbf{T}_{\mathbf{f}}\Psi_1$ where the deformation $\mathbf{f}(\mathbf{r}) = f(r) \mathbf{u}_r$ has the following form:

$$f(r) = c_0 r + \sum_{i=1}^p c_i r^{n_i} \exp(-\gamma_i r),$$

where $n_i \in \mathbb{N}^*$ and $\gamma_i > 0$ are fixed. Then we minimize the energy $E[\mathbf{T}_f \Psi_1]$ by improving the parameters of Ψ_1 (a, α, β , called the "p1" parameters) and the parameters of the deformation ((c_i) , called the "p2" parameters). Notice that we are interested by deformations which are close to the identity (because Ψ_1 is not so bad), and thus c_0 will be close to 1 and c_i ($i \geq 1$) are close to zero.

The results are given in Table. 1. We have denoted E_{HF} the optimal Hartree-Fock energy, and $E_c = E_0 - E_{HF}$ the correlation energy. The notation "p1 free, kp2" means that we have minimized the energy with respect to a, α, β and k parameters of type p2.

The energy computation and improvement of the parameters were done using a Variational Monte Carlo method (see [25]) and σ denotes the variance of the energy of the tested wave-function (the wave-function $\mathbf{T}_f \Psi_1$ is normalized in the calculation). Also, the digit in parenthesis denotes the error on the last digit of the energy value.

We see that without deformations, we obtain 64% of the correlation energy E_c , while using deformations, we are able to obtain 89% of E_c .

In the above example, we have just studied how the energy can be improved by deformation, without working directly on the density functions. In fact in the radial case, it is equivalent to work on the density function or on the deformation, because there is a one-to-one correspondence between $\rho(r)$ and $f(r)$ in (10).

The same method (using Monte Carlo) can be applied for problems with more than two electrons. We know that a Jastrow factor deteriorates the quality of the electron density of Ψ . So deformations can be used to improve the quality of this density function.

V.2 Local deformations in the general case

In the molecular case, it is not easy to generate relevant deformations. It seems simpler to consider local deformations (that we can choose of radial type) in order to improve some local behavior of the wave-function.

Our strategy would be the following. We can consider a family of deformations around the cusps which deform a given cusp behavior into another one, and then minimize the energy of $\mathbf{T}_f \Psi_0$ with respect to \mathbf{f} in this family of deformations. This would allow an optimization of the cusp behavior without moving the form of the wave-function outside of a neighborhood of the cusps. For instance, for a given cusp in \mathbf{R}_i , a family of deformations can be given by $\mathbf{f}(\mathbf{r}) = f(r_i, w_i) \mathbf{u}_{r_i}$ where (r_i, w_i) are the spherical coordinates around \mathbf{R}_i (with $r_i = |\mathbf{r} - \mathbf{R}_i|$ and $\mathbf{u}_{r_i} = \frac{\mathbf{r} - \mathbf{R}_i}{|\mathbf{r} - \mathbf{R}_i|}$ is the radial unit vector), and

$$f(r, w) = ((\lambda_0 - 1) r + \lambda_1(w) r^2) \chi(r) + r. \quad (21)$$

In (21), we have denoted λ_0 a non-negative constant, $\lambda_1(w)$ a continuous function from the sphere into \mathbb{R} , and $\chi(r)$ a regular function such that $\chi(r) = 1$ for $r \in [0, \epsilon]$ and $\chi(r) = 0$ for $r \geq r_0$ (where $0 < \epsilon < r_0$ are sufficiently small). Note that in particular $\mathbf{f}(\mathbf{r}) = \mathbf{r}$ for $|\mathbf{r} - \mathbf{R}_i| \geq r_0$.

Actually, we have obtained in [10] that if ρ has the following cusp behavior in $r = 0$:

$$\rho(r, w) = a_1 + b_1(w) r + o(r)$$

and if we let $\lambda_0 = (\frac{a_2}{a_1})^{1/3}$ and $4 \lambda_1(w) = \frac{b_2(w)}{a_2} \lambda_0 - \frac{b_1(w)}{a_1} \lambda_0^2$, then $\mathbf{f} * \rho$ will have the following cusp behavior:

$$(\mathbf{f} * \rho)(r, w) = a_2 + b_2(w) r + o(r).$$

Thus, with the family of local deformations defined by (21), we can obtain any cusp behavior.

Clearly we can adopt the same strategy in order to improve the exponential fall-off behavior, or any other local behavior.

Remark. V.1 If we want to stay in the same symmetry class, we recall that we need that $f \circ Q = Q \circ f$ for all $Q \in G$ (see [11]). This requirement is satisfied if for instance we define f as follows:

$$f(\mathbf{r}) = \mathbf{r} + \frac{1}{\text{Card}(G)} \sum_{Q \in G} Q \mathbf{V} Q^{-1}(\mathbf{r})$$

where $\mathbf{V}(\mathbf{r}) = ((\lambda_0 - 1) r_i + \lambda_1(w) r_i^2) \chi(r_i) \mathbf{u}_{r_i}$ around each nucleus \mathbf{R}_i (in fact it suffices to define such a \mathbf{V} for only one nucleus in each independent cycle $\{Q\mathbf{R}_i, Q \in G\}$).

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