

New N -representability results with symmetry in molecular quantum chemistry

Olivier Bokanowski*

*LSMA (U. Paris 7) and LAN (U. Paris 6), C.P. 7012, Université Paris 7, 16 rue Clisson,
75013 Paris, France*

Received 15 October 1997; revised 2 November 1999

We prove a new type of N -representability result: given a totally symmetric density function ρ , we construct a wavefunction Ψ such that the totally symmetric part of ρ_Ψ (its projection over the totally symmetric functions) be equal to ρ , and, furthermore, such that Ψ belongs to a given class of symmetry associated to the symmetry group of a molecule. Our proof uses deformations of density functions and which are solutions of a “Jacobian problem”. This allows us to formalize rigorously an idea of A. Görling (Phys. Rev. A 47 (1993) 2783), for Density-Functional Theory in molecular quantum chemistry, by defining a density functional that takes into account the symmetry of the molecule under study.

1. Introduction

In this paper we are interested in N -representability problems with symmetry that occur in Density-Functional Theory (DFT) methods, in molecular quantum chemistry. DFT was developed in order to find simpler models of the N -electron problem (see, for instance, [23,26,29,41] for the physical approach and [1,8,15,31,45] for some mathematical results). For a given N -electron atom or molecule, the problem is to obtain an approximation of the lowest energy E_0 of the system

$$E_0 := \inf \left\{ \langle \Psi, \mathcal{H}\Psi \rangle, \Psi \in H^1 \cap L_a^2(\mathbb{R}^{3N}), \int |\Psi|^2 = 1 \right\},$$

where \mathcal{H} is the Hamiltonian of the molecule:

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

* This work was done at the Laboratoire de Mathématiques pour l’Industrie et la Physique, UMR CNRS 5640, and also at the Laboratoire de Physique Quantique, UMR CNRS 5626 (Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex, France).

and where, for $\mathbf{x} \in \mathbb{R}^3$,

$$v(\mathbf{x}) = \sum_{j=1}^P \frac{-Z_j}{|\mathbf{x} - \mathbf{R}_j|}. \quad (2)$$

We have denoted $\langle \cdot, \cdot \rangle$ the scalar product on $L^2(\mathbb{R}^{3N})$, $\mathbf{x}_i \in \mathbb{R}^3$ the i th space variable, $L_a^2(\mathbb{R}^{3N}) = \overline{\bigwedge_{i=1}^N L^2(\mathbb{R}^3)}$ (the closed space of antisymmetric and square integrable wavefunctions), $H^1 = \{\Psi \in L^2, \nabla \Psi \in L^2\}$, Δ the Laplacian on \mathbb{R}^{3N} , and in (2) v is the Coulomb potential created by a finite set of P nuclei at (distinct) positions $\mathbf{R}_j \in \mathbb{R}^3$ and of charge $+Z_j$. In this paper we do not consider the spin variables in order to simplify the presentation of the results. (For other potentials and spin variables, see [3, chapter IV].)

Levy [30] and Lieb [31] already obtained a rigorous formalization of DFT. The key point uses the following N -representability result (initially due to Macke [35], see also [21,44]): if $N \geq 1$ and $\rho \geq 0$ is such that $\sqrt{\rho} \in H^1(\mathbb{R}^3)$, then there exists a wavefunction $\Psi \in L_a^2(\mathbb{R}^{3N}) \cap H^1$ such that $\rho_\Psi = \rho$. We have denoted ρ_Ψ the density function associated to Ψ :

$$\rho_\Psi(\mathbf{x}) := N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (3)$$

(when $N \geq 2$) and $\rho_\Psi(\mathbf{x}) := |\Psi(\mathbf{x})|^2$ when $N = 1$. Hence for any $\rho \geq 0$ such that $\sqrt{\rho} \in H^1(\mathbb{R}^3)$, we can define the density-functional

$$E[\rho] := \min \{ \langle \Psi, \mathcal{H}\Psi \rangle, \rho_\Psi = \rho, \Psi \in L_a^2(\mathbb{R}^{3N}) \cap H^1 \} \quad (4)$$

which satisfies

$$E_0 = \inf \left\{ E[\rho], \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}.$$

A general way to construct wavefunctions Ψ such that $\rho_\Psi = \rho$ is given in [5,33], for instance, and will be also used in the present paper.

One drawback of the above approach is that the symmetries of the molecule are not taken into account explicitly. In [32] (a revised version of [31]), density-functionals for excited energies are proposed, but the symmetry is not used. For *improvement* of existing density-functionals, or comparison between them, it could help to have a rigorous definition of a variational exact density-functional including symmetries. In this paper one aim is to obtain such a variational formulation of DFT.

Precisely, we also search a density-functional for

$$E_{0,\Gamma} := \inf \left\{ \langle \Psi, \mathcal{H}\Psi \rangle, \Psi \in \Gamma \cap H^1 \cap L_a^2(\mathbb{R}^{3N}), \int |\Psi|^2 = 1 \right\},$$

where Γ is a given class of symmetry (a subspace of $L^2(\mathbb{R}^{3N})$) associated to the symmetry group G of the molecule (1)–(2). In this paper G is defined by

$$G := \{Q \in O(3), v(Q) = v\}. \quad (5)$$

In (5) the center of G is assumed to be at the origin. (See section 3.1 for more precisions.) We recall that Γ can be different from the symmetry class associated to the trivial character: if $\psi \in \Gamma$ and $Q \in G$ then, in general, $\Psi(Q\mathbf{x}_1, \dots, Q\mathbf{x}_N) \neq \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$. There is a choice of Γ for which $E_{0,\Gamma}$ is equal to E_0 ; if $E_{0,\Gamma} < 0$ then it is an eigenvalue of \mathcal{H} (since the nonpositive spectrum of \mathcal{H} corresponds to eigenvalues).

In order to define a density-functional for $E_{0,\Gamma}$ of the same type as $E[\rho]$ in (4), this poses the following N -representability problem: find a wavefunction $\Psi \in L^2_a(\mathbb{R}^{3N}) \cap H^1$ such that

$$\rho_\Psi = \rho \quad \text{and} \quad \Psi \in \Gamma. \quad (6)$$

Note that this kind of question appears (more or less implicitly) in more recent DFT theories for excited states and symmetries. We refer, for instance, to Englisch et al. (see equations (1) and (2) in [14]) and Görling [18] (see equation (6) therein). In the theory of Gross et al. [20] (see equation (109)), they use a minimization over density matrices that yield a given ρ density; but some symmetry assumption should be added in the set of density matrices in the case of applications, and thus also on the densities. A similar question occurs when the Kohn–Sham potential is searched through the minimization of the kinetic energy with a fixed density constraint (quantities such as $T_s[\rho]$, see equation (112) in [20] or equation (10) in [14]). We refer to [13,19,38] and references therein for new approaches and problems with symmetry and excited states calculations in DFT.

Now we remark that (6) has been solved in particular cases. For instance, in [44], for atoms, ρ is radial and Ψ is searched in the form of a determinantal wavefunction and in Γ . In the atom case also, more general solutions were obtained in [27,42,45] using a deformation approach. For a molecule with finite symmetry group a partial answer to (6) is given in [5] when ρ is “totally symmetric”, i.e., such that

$$\rho(Q\mathbf{x}) = \rho(\mathbf{x}) \quad \text{for all } Q \in G \text{ and } \mathbf{x} \in \mathbb{R}^3,$$

and when Γ is a class of symmetry of dimension one (which means, in this paper, that the irreducible representations of Γ are of dimension one: $\Psi(Q\mathbf{x}_1, \dots, Q\mathbf{x}_N) = \lambda(Q)\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$; see section 3.1). We do not know solutions when Γ is not of dimension one, in particular if the symmetry Γ cannot be obtained by determinants.

Of course, solving (6) is not possible in general. For instance, in the atom case ($G = O(3)$), if we take ρ to be a nonradial function and if Γ is of dimension one, then ρ_Ψ is radial for any $\Psi \in \Gamma$ and thus $\rho_\Psi \neq \rho$. Also, if ρ is a radial function, and if $\Psi \in \Gamma$ where Γ is not of dimension one, then in general ρ_Ψ will not be a radial function.

In this paper we solve an alternate problem. Let μ be the Haar measure of G . We define $\tilde{\rho}$ as the projection of ρ on the totally symmetric functions, i.e.,

$$\tilde{\rho}(\mathbf{x}) := \frac{1}{\mu(G)} \int_{Q \in G} \rho(Q\mathbf{x}) \, d\mu(Q).$$

Our main result (theorem 2.1) is to show that for any ρ totally symmetric (i.e., $\tilde{\rho} = \rho$) and which satisfies, furthermore, some natural physical assumptions (cusp at the nuclei and exponential fall-off behavior, see definition 2.3), there exists a wavefunction $\Psi \in L_a^2(\mathbb{R}^{3N}) \cap H^1$ such that

$$\tilde{\rho}_\Psi = \rho \quad \text{and} \quad \Psi \in \Gamma. \quad (7)$$

The resolution of (7) is one of the implicit problems posed by Görling in [18] but not solved (yet in [18] the focus is on spin symmetry problems). Then, following the approach of Görling, we propose a formalization of DFT similar to Levy–Lieb’s formalization but that, furthermore, takes into account the spatial symmetries of the molecule (see theorem 2.3; our density-functional $E_\Gamma[\rho]$ in equation (8) corresponds to equation (22) in [18]). This approach has also been used implicitly in [34]: when the authors improve the density function of a basic wavefunction model for Li, B, and F atoms, they improve (or control) only the radial part of the density function.

Main results are stated in section 2, and proved in section 3. In order to solve (7) we shall use “deformations” of densities [5,27] as explained in section 3.4. But first, we shall need to construct a wavefunction $\Psi_1 \in \Gamma$ such that $\tilde{\rho}_{\Psi_1}$ has good regularities, does not vanish anywhere, and has other natural behavior properties (section 3.3). This may appear obvious by hand-waving arguments, still this is one of the mathematical difficulties of the paper (and not a consequence of [5]). For $N = 1$ and for an atom or a diatomic molecule, it is sometime not possible to obtain nonvanishing density functions ρ_{Ψ_1} (even after symmetrization – see section 3.7), while there is no such problem if $N \geq 2$.

At the same time, we shall also need to list precisely which symmetry classes Γ are non-empty, i.e., such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ (when Γ corresponds to a given symmetry group and character); this never happens when $N \geq 3$, happens once when $N = 2$ (in the atom case), and in several cases for $N = 1$. We were not able to find this kind of result clearly stated in some textbook. For all these reasons we have to construct almost explicitly a nonzero wavefunction $\Psi \in \Gamma$ each time this is possible (this part is mainly algebra). Finally, we shall need some density results (section 3.6) in order to obtain $E_{0,\Gamma}$ as an infimum of $E_\Gamma[\rho]$ over symmetric ρ densities.

In a concluding section (section 4) we propose more practical ways to use the ideas of the paper and give links to recent related works.

The results of the paper can be generalized in order to treat spin symmetries, and also can be applied to other symmetries (such as in periodic systems [8,9]).

2. Main results

In this section we give our main results in the setting of molecular quantum chemistry. We first define a set of density functions for which we can solve (7).

2.1. Definition of H^1 -admissible density functions

Following physical studies (as in [5]), we may characterize the behavior of the density functions at the nuclei positions $K = \{\mathbf{R}_1, \dots, \mathbf{R}_P\}$ by *cusps conditions* [25,40] and at infinity by an *exponential fall-off condition* [22,46] as follows. We denote $\mathbf{x} = (r, w)$ in the spherical coordinates ($w \in S^2$ and $r \geq 0$).

Definition 2.1 (Cusp). We say that $\rho: \mathbb{R}^3 \rightarrow \mathbb{R}^+$ has a *cusp* in $\mathbf{x} = \mathbf{0}$ if in the neighborhood of $r = 0$,

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

with $a > 0$ and $b \in C^0(S^2, \mathbb{R})$, and where $o(r)$ is uniform with respect to $w \in S^2$. Similarly, we say that ρ has a cusp in $\mathbf{x}_0 \in \mathbb{R}^3$ if $\rho(\mathbf{x} + \mathbf{x}_0)$ has a cusp in $\mathbf{x} = \mathbf{0}$.

Definition 2.2 (Exponential fall-off). We say that $\rho: \mathbb{R}^3 \rightarrow \mathbb{R}_+$ has an *exponential fall-off* at infinity if, when $r \rightarrow \infty$,

$$\rho(r, w) = A(w)r^\beta e^{-\alpha r} + o(r^\beta e^{-\alpha r}),$$

where $\alpha > 0$, $\beta \in \mathbb{R}$, $A(w) \in C^0(S^2, \mathbb{R}_+^*)$ and $o(r^\beta e^{-\alpha r})$ is uniform with respect to $w \in S^2$.

Now we can introduce:

Definition 2.3 (H^1 -admissible densities). Let G be the point group of a molecular system with nuclei K . We say that ρ is H^1 -admissible if:

- (i) $\rho \in C^0(\mathbb{R}^3, \mathbb{R}_+^*) \cap C^\infty(\mathbb{R}^3 \setminus K)$;
- (ii) ρ is totally symmetric (i.e., $\tilde{\rho} = \rho$);
- (iii) ρ has a cusp in each $\mathbf{x} \in K$;
- (iv) ρ has an exponential fall-off;
- (v) $(\nabla \rho)/\rho$ is bounded.

Note that if ρ is H^1 -admissible then $\sqrt{\rho}$ belongs to $H^1(\mathbb{R}^3)$ (using $\nabla \sqrt{\rho}/\sqrt{\rho} = \frac{1}{2} \nabla \rho/\rho$ thus bounded).

2.2. N -representability results

Our main N -representability result is:

Theorem 2.1. Let Γ be a class of symmetry such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$.

- (i) If $N \geq 2$ and if ρ is H^1 -admissible, then $\exists \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1$ such that $\widetilde{\rho_\Psi} = \rho$.
- (ii) If $N = 1$, $\rho \geq 0$, $\tilde{\rho} = \rho$ and $\rho \in L^1(\mathbb{R}^3)$, then $\exists \Psi \in \Gamma \cap L^2(\mathbb{R}^3)$ such that $\widetilde{\rho_\Psi} = \rho$.

To prove this theorem, the main problem, in this paper is to find at least one Ψ_1 in $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1$ and such that $\widetilde{\rho_{\Psi_1}}$ be H^1 -admissible (see section 3.3). Then we shall use the results of [5] in order to “deform” Ψ_1 into a Ψ_2 with the same symmetry and such that $\widetilde{\rho_{\Psi_2}} = \rho$ (see section 3.4).

We then deduce N -representability results which do not make reference to H^1 -admissible density functions.

Corollary 2.1. Let Γ be a class of symmetry such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$. The following density results hold:

- (i) For $N \geq 2$ and for the $H^1(\mathbb{R}^3)$ -topology:

$$\overline{\{\sqrt{\widetilde{\rho_\Psi}}, \Psi \in H^1 \cap L_a^2(\mathbb{R}^{3N}) \cap \Gamma\}} = \{\sqrt{\rho}, \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \rho = \tilde{\rho}\}.$$

- (ii) For $N \geq 1$ and for the $L^2(\mathbb{R}^3)$ -topology:

$$\overline{\{\sqrt{\widetilde{\rho_\Psi}}, \Psi \in L_a^2(\mathbb{R}^{3N}) \cap \Gamma\}} = \{\sqrt{\rho}, \rho \geq 0, \rho \in L^1(\mathbb{R}^3), \rho = \tilde{\rho}\}.$$

Slightly more general results are given in section 3.7. Note that for $N = 1$ and when regularity H^1 is required, the above results may be false because of the vanishing sets of the density functions (see section 3.7).

2.3. Other N -representability results (atoms, linear molecules)

When we do not require the H^1 -regularity, we can improve the results of corollary 2.1 as follows. We recall that the molecule is called an *atom* when there is only one nucleus and a *linear molecule* when $P \geq 2$ and all nuclei are aligned.

Theorem 2.2. Let $N \geq 1$ and let Γ be a class of symmetry associated to an atom or a linear molecule and such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$.

- (i) $\{\widetilde{\rho_\Psi}, \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})\} = \{\rho, \rho \geq 0, \rho \in L^1(\mathbb{R}^3), \tilde{\rho} = \rho\}$.
- (ii) $\Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \rightarrow \sqrt{\widetilde{\rho_\Psi}} \in \{\sqrt{\rho}, \rho \geq 0, \rho \in L^1(\mathbb{R}^3), \tilde{\rho} = \rho\}$ is an open map for the L^2 -topology.

In order to prove theorem 2.2 we shall use the technics of [4] where it was already proved that $\Psi \in L_a^2(\mathbb{R}^{3N}) \rightarrow \sqrt{\rho_\Psi} \in L^2(\mathbb{R}^3, \mathbb{R}_+)$ is an *open* map. This type of question was first asked by Lieb in [31]. Note that this is still an open problem from $H^1 \cap L_a^2(\mathbb{R}^{3N})$ onto $H^1(\mathbb{R}^3, \mathbb{R}_+)$.

2.4. Definition of a density functional with symmetry

Let $N \geq 2$. Let Γ be such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ (we prove this is always true except for the atom in one case, see remark 3.3). Using theorem 2.1, we can define for any ρ H^1 -admissible:

$$E_\Gamma[\rho] := \inf \{ \langle \Psi, \mathcal{H}\Psi \rangle, \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1, \widetilde{\rho_\Psi} = \rho \}. \quad (8)$$

We then show, as expected:

Theorem 2.3. Let $N \geq 2$ and Γ such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$. Then $E_\Gamma[\rho]$ is a minimum, and

$$E_{0,\Gamma} = \inf \left\{ E_\Gamma[\rho], \rho \text{ } H^1\text{-admissible, } \int_{\mathbb{R}^3} \rho = N \right\}. \quad (9)$$

Hence $E_\Gamma[\rho]$ is a density functional for $E_{0,\Gamma}$. Possible utilizations of this approach to DFT are discussed in section 4 (see also [34], and also [3, chapter IV], [5,6]).

3. Proofs

3.1. Preliminary definitions

In this section we recall some basic definitions and notations related to the symmetry [24,43] and introduce other ones more specific to the paper.

Notation. We identify $O(3)$, the group of orthonormal matrices ($Q^T Q = \text{Id}$), with the isometries of \mathbb{R}^3 that let the origin invariant. $SO(3)$ denotes the rotations of $O(3)$. We denote Id the identity function (or matrix), I the inversion in \mathbb{R}^3 ($I(\mathbf{x}) = -\mathbf{x}$), $U(d)$ the unitary matrices of dimension d .

Symmetry group. Let $\text{Isom}(\mathbb{R}^3)$ be the set of isometries of \mathbb{R}^3 . In this paper we define the symmetry group (or point group) of the molecule associated to \mathcal{H} by

$$G = \{ Q \in \text{Isom}(\mathbb{R}^3); \mathbf{T}_Q \mathcal{H} = \mathcal{H} \mathbf{T}_Q \}, \quad (10)$$

where

$$\mathbf{T}_Q \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \Psi(Q\mathbf{x}_1, \dots, Q\mathbf{x}_N). \quad (11)$$

Note also that

$$[\mathcal{H}, \mathbf{T}_Q] = \left[\left(\sum_{i=1}^N v(\mathbf{x}_i) \right), \mathbf{T}_Q \right] = \left(\sum_{i=1}^N (v(\mathbf{x}_i) - v(Q\mathbf{x}_i)) \right) \mathbf{T}_Q$$

(where $[A, B] = AB - BA$). Hence $Q \in G$ if and only if $v(Q) = v$.

Then we recall that there exists $\mathbf{x}_0 \in \mathbb{R}^3$ (the center of G) such that $\forall Q \in G$, $Q\mathbf{x}_0 = \mathbf{x}_0$. Hereafter, we assume that \mathbf{x}_0 is the origin. Thus G is a subgroup of $O(3)$ and is equivalently defined by (10) or (5).

Atoms. In the atom case, $P = 1$ ($\mathbf{R}_1 = \mathbf{0}$) and $G = O(3)$. We shall use the *spherical coordinates* (r, θ, ϕ) , where $r > 0$, $\phi \in (0, 2\pi)$, and $\theta \in (0, \pi)$, related to the Euclidean coordinates by $x = r \cos(\phi) \sin(\theta)$, $y = r \sin(\phi) \sin(\theta)$, and $z = r \cos(\theta)$. Then $\tilde{\rho}$ is radial and (with $dw = \sin(\theta) d\theta d\phi$):

$$\tilde{\rho}(r) = \frac{1}{4\pi} \int_{S^2} \rho(r, w) dw.$$

Linear molecules. When the nuclei are aligned (and $P \geq 2$), we can suppose that (Oz) , the z -axis, is confounded with the nuclei axis. We denote $SO(2)$ for the rotations of z axis, and $O(2)$ for the group generated by $SO(2)$ and a symmetry with respect to a plane which contains (Oz) . We recall that only two situations may occur.

- If the linear molecule is not symmetric with respect to any plane perpendicular to (Oz) , we have $G = O(2)$.
- Otherwise, there exists such a plane of symmetry (and we can assume it contains the origin), and we then have $G = O(2) \times \{\text{Id}, I\}$ (the group generated by $O(2)$ and the inversion I).

For instance, diatomic molecules ($P = 2$) are linear molecules. If $Z_1 \neq Z_2$, then $G = O(2)$, and if $Z_1 = Z_2$, then $G = O(2) \times \{\text{Id}, I\}$.

For linear molecules, we shall use the *cylindrical coordinates* (r, z, ϕ) such that $r > 0$, $\phi \in (0, 2\pi)$, and $z \in \mathbb{R}$, and related to the Euclidean coordinates by $x = r \cos(\phi)$, $y = r \sin(\phi)$, and with identical z component.

For $G = O(2)$:

$$\tilde{\rho}(r, z) = \frac{1}{2\pi} \int_0^{2\pi} \rho(r, z, \phi) d\phi,$$

and for $G = O(2) \times \{\text{Id}, I\}$:

$$\tilde{\rho}(r, z) = \frac{1}{4\pi} \int_0^{2\pi} (\rho(r, z, \phi) + \rho(r, -z, \phi)) d\phi.$$

Note. $O(3)$, $O(2)$ and $O(2) \times \{\text{Id}, I\}$ are also denoted O_∞ , $C_{\infty v}$, and $D_{\infty h}$ in chemistry.

Finite point groups. When the nuclei are not aligned ($P \geq 3$), we say that the molecule is nonlinear, and in this case G is finite. If $|G|$ denotes the cardinal of G , then

$$\tilde{\rho}(\mathbf{x}) = \frac{1}{|G|} \sum_{Q \in G} \rho(Q\mathbf{x}).$$

Classes of symmetry. We recall that there exists a Hilbert decomposition of $L^2(\mathbb{R}^{3N})$ into *classes of symmetry* associated to the unitary representation $Q \in G \rightarrow (\mathbf{T}_Q)^{-1}$ (see (11)). Each class of symmetry $\Gamma = \Gamma(\chi)$ can be defined by a character $\chi: G \rightarrow \mathbb{C}$ as follows:

$$\Gamma(\chi) := \{\Psi \in L^2(\mathbb{R}^{3N}), P_\chi \Psi = \Psi\},$$

where P_χ is the orthogonal projector on Γ , i.e.,

$$P_\chi \Psi := \frac{d}{\mu(G)} \int_{Q \in G} d\mu(Q) \chi(Q) \mathbf{T}_Q \Psi$$

and where $d \in \mathbb{N}^*$ is the dimension of any irreducible unitary matrix representation $Q \in G \rightarrow M(Q) \in U(d)$ such that $\forall Q \in G, \text{Tr}(M(Q)) = \chi(Q)$.

If $P_\chi \Psi = \Psi$ but Ψ is not in L^2 , we shall still say that Ψ is of symmetry Γ .

The classes of symmetry $\Gamma = \Gamma(\chi)$ such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ will be listed in section 3.3.

Dimension of a class of symmetry. In this paper we also denote $d = \dim(\Gamma)$ and say that d is the dimension of Γ (or χ). For instance, if $\Gamma = \Gamma(\chi)$ and $\dim(\Gamma) = 1$, we know that $\Psi \in \Gamma$ if and only if $\Psi \in L^2(\mathbb{R}^{3N})$ and $\forall Q \in G, \mathbf{T}_Q \Psi = \chi(Q)\Psi$ (and in this case $\tilde{\rho}_\Psi = \rho_\Psi$).

Operator A_N and Slater determinants. Let S_N be the set of permutations of $\{1, \dots, N\}$. The operator A_N is defined from $L^2(\mathbb{R}^{3N})$ into $L_a^2(\mathbb{R}^{3N})$ by

$$A_N[\Psi](\mathbf{x}_1, \dots, \mathbf{x}_N) := \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \varepsilon(\sigma) \Psi(\mathbf{x}_{\sigma(1)}, \dots, \mathbf{x}_{\sigma(N)}) \quad (12)$$

where $\varepsilon(\sigma)$ is the signature of the permutation σ .

We say that $\Psi: \mathbb{R}^{3N} \rightarrow \mathbb{C}$ is a *Slater determinant* when it is of the form

$$\Psi = A_N[\phi_1(\mathbf{x}_1) \cdots \phi_N(\mathbf{x}_N)] \quad (13)$$

(we also denote $\Psi = A_N[\phi_1 \cdots \phi_N]$), and recall that if the set (ϕ_i) is orthonormal in $L^2(\mathbb{R}^3)$ then $\rho_\Psi = \sum_{i=1}^N |\phi_i|^2$.

3.2. Preliminary results

We first establish some useful elementary inclusions and density results.

Proposition 3.1. (i) $\sqrt{\rho} \rightarrow \sqrt{\tilde{\rho}}$ is 1-Lipschitz on $L^2(\mathbb{R}^3, \mathbb{R}_+)$.

(ii) $\sqrt{\rho} \rightarrow \sqrt{\tilde{\rho}}$ is continuous for the H^1 norm, and

$$\|\nabla \sqrt{\tilde{\rho}}\|_2 \leq \|\nabla \sqrt{\rho}\|_2.$$

Proof. (i) We have $\|\sqrt{\tilde{\rho}_2} - \sqrt{\tilde{\rho}_1}\|_2^2 = \int (\tilde{\rho}_2 + \tilde{\rho}_1 - 2\sqrt{\tilde{\rho}_1}\sqrt{\tilde{\rho}_2})$. By Schwarz inequality on $L^2(G, d\mu)$,

$$\widetilde{\sqrt{\rho_1\rho_2}} \leq \sqrt{\tilde{\rho}_1}\sqrt{\tilde{\rho}_2}.$$

We have also $\int \rho = \int \tilde{\rho}$, thus

$$\|\sqrt{\tilde{\rho}_2} - \sqrt{\tilde{\rho}_1}\|_2^2 \leq \int_{\mathbb{R}^3} \tilde{\rho}_2 + \tilde{\rho}_1 - 2\sqrt{\rho_1\rho_2} = \|\sqrt{\rho_2} - \sqrt{\rho_1}\|_2^2.$$

(ii) We must take care of the points where the density functions may vanish. Let $A = \{\mathbf{x} \in \mathbb{R}^3, \rho(\mathbf{x}) = 0\}$. We recall that if $\sqrt{\rho} \in H^1$, then $\nabla \rho \in L^1$ with $\nabla \rho = 2\sqrt{\rho}(\nabla \sqrt{\rho})$, $\nabla \sqrt{\rho} = \frac{1}{2}(\nabla \rho)/\sqrt{\rho}$ a.e. on $\mathbb{R}^3 \setminus A$ and $\nabla \sqrt{\rho} = 0$ a.e. on A .

First we show that $\sqrt{\rho} \in H^1 \implies \sqrt{\tilde{\rho}} \in H^1$ and with the bound $\|\nabla \sqrt{\tilde{\rho}}\|_2 \leq \|\nabla \sqrt{\rho}\|_2$. Note that it suffices to obtain the bound for a regular ρ such that $\rho > 0$ and $\sqrt{\rho} \in H^1$ (then use density results). In fact we have, a.e. on \mathbb{R}^3 :

$$|\nabla \sqrt{\tilde{\rho}}|^2 \leq |\widetilde{\nabla \sqrt{\rho}}|^2. \tag{14}$$

To see this, write $\nabla \tilde{\rho} = \widetilde{\nabla \rho} = 2\sqrt{\tilde{\rho}}(\widetilde{\nabla \sqrt{\rho}})$. Then, by Schwarz inequality on $L^2(G, d\mu)$, $|\nabla \tilde{\rho}|^2 \leq 4|\widetilde{\nabla \sqrt{\rho}}|^2 \tilde{\rho}$. Also, $4\tilde{\rho}|\nabla \sqrt{\tilde{\rho}}|^2 = |\nabla \tilde{\rho}|^2$, and we obtain (14).

To prove the continuity of $\sqrt{\rho} \rightarrow \sqrt{\tilde{\rho}}$ on $H^1(\mathbb{R}^3)$, let $\rho_n \geq 0$ be a sequence such that $\sqrt{\rho_n} \xrightarrow{n \rightarrow \infty} \sqrt{\rho}$ in H^1 . We already have $\sqrt{\tilde{\rho}_n} \rightarrow \sqrt{\tilde{\rho}}$ in L^2 because of (i). Then, it suffices to show that from any subsequence of $\sqrt{\tilde{\rho}_n}$ we can extract a subsequence that converges in $H^1(\mathbb{R}^3)$ to the same $\sqrt{\tilde{\rho}}$. After a change in the indices, we just have to prove that there exists a subsequence of $\nabla \sqrt{\tilde{\rho}_n}$ that converges to $\nabla \sqrt{\tilde{\rho}}$ in L^2 .

We can suppose, after extraction, that $\nabla \sqrt{\tilde{\rho}_n}$ is a.e. convergent and dominated by a $g \in L^2(\mathbb{R}^3)$, with $g \geq 0$, and that $\sqrt{\tilde{\rho}_n}$ is also a.e. convergent to $\sqrt{\tilde{\rho}}$ (because $\sqrt{\tilde{\rho}_n} \rightarrow \sqrt{\tilde{\rho}}$ in $L^2(\mathbb{R}^3)$). Using the bound in equation (14), we obtain $|\nabla \sqrt{\tilde{\rho}_n}|^2 \leq |\widetilde{\nabla \sqrt{\rho_n}}|^2 \leq \tilde{g}^2$. Thus, $|\nabla \sqrt{\tilde{\rho}_n}|$ is dominated by $\sqrt{\tilde{g}^2}$ in $L^2(\mathbb{R}^3)$. In order to conclude by Lebesgue's domination theorem, we want to obtain that $\nabla \sqrt{\tilde{\rho}_n}$ is a.e. convergent towards $\nabla \sqrt{\tilde{\rho}}$.

In the case $\tilde{\rho}(\mathbf{x}) > 0$, we have $\rho_n(\mathbf{x}) > 0$ for n large enough. So $\nabla \sqrt{\widetilde{\rho_n}(\mathbf{x})} = \frac{1}{2}(\nabla \widetilde{\rho_n})(\mathbf{x})/\sqrt{\widetilde{\rho_n}(\mathbf{x})}$ converges towards $\frac{1}{2}(\nabla \tilde{\rho})(\mathbf{x})/\sqrt{\tilde{\rho}(\mathbf{x})} = \nabla \sqrt{\tilde{\rho}}$.

In the other case, let $B = \{\mathbf{x} \in \mathbb{R}^3, \tilde{\rho}(\mathbf{x}) = 0\}$ (for a representative of $\tilde{\rho}$). We know that $\nabla \sqrt{\tilde{\rho}} = 0$ on B (because $\nabla \sqrt{\tilde{\rho}} \in H^1$). In order to show that $\nabla \sqrt{\widetilde{\rho_n}} \rightarrow 0$ a.e. on B , it suffices to show that $u_n = \int_B |\nabla \sqrt{\widetilde{\rho_n}}|^2 \rightarrow 0$ (then, we obtain the result by extraction). But $u_n \leq v_n = \int_B |\nabla \sqrt{\widetilde{\rho_n}}|^2$. We have also $\nabla \sqrt{\widetilde{\rho_n}} \rightarrow \nabla \sqrt{\tilde{\rho}}$ in L^2 , so $|\nabla \sqrt{\widetilde{\rho_n}}|^2 \rightarrow |\nabla \sqrt{\tilde{\rho}}|^2$ in L^1 , and thus $|\nabla \sqrt{\widetilde{\rho_n}}|^2 \rightarrow |\nabla \sqrt{\tilde{\rho}}|^2$ in L^1 . Thus $v_n \rightarrow v = \int_B |\nabla \sqrt{\tilde{\rho}}|^2$. We know also that a.e. $(\mathbf{x}, Q) \in B \times G$ (for the measure $dx \otimes d\mu$), we have $\tilde{\rho}(\mathbf{x}) = 0$, so $\rho(Q\mathbf{x}) = 0$, and also $(\nabla \sqrt{\tilde{\rho}})(Q\mathbf{x}) = 0$. Thus a.e. on B , $|\nabla \sqrt{\tilde{\rho}}| = 0$, so $v = 0$ and $\lim(u_n) = 0$. This concludes the proof. \square

Corollary 3.1. (i) $\Psi \in L_a^2(\mathbb{R}^{3N}) \rightarrow \sqrt{\rho_\Psi} \in L^2(\mathbb{R}^3)$ is 1-Lipschitz.

(ii) $\Psi \in H_a^1(\mathbb{R}^{3N}) \rightarrow \sqrt{\rho_\Psi} \in H^1(\mathbb{R}^3)$ is continuous.

Proof. We recall that $\Psi \in L_a^2(\mathbb{R}^{3N}) \rightarrow \sqrt{\rho_\Psi} \in L^2(\mathbb{R}^3)$ is 1-Lipschitz, and that $\Psi \in H_a^1(\mathbb{R}^{3N}) \rightarrow \sqrt{\rho_\Psi} \in H^1(\mathbb{R}^3)$ is a continuous mapping [31]. Hence the result is a corollary of proposition 3.1. \square

Definition 3.1. Now we introduce the following sets:

$$\begin{aligned} D_0(\Gamma) &:= \{ \sqrt{\rho_\Psi}, \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \}, \\ D_1(\Gamma) &:= \{ \sqrt{\rho_\Psi}, \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1 \}, \\ D_0 &:= \{ \sqrt{\rho}, \rho \geq 0, \sqrt{\rho} \in L^2(\mathbb{R}^3), \rho = \tilde{\rho} \}, \\ D_1 &:= \{ \sqrt{\rho}, \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \tilde{\rho} = \rho \}. \end{aligned}$$

Then, using corollary 3.1 we obtain:

Remark 3.1. $D_0(\Gamma) \subset D_0$ and $D_1(\Gamma) \subset D_1$ are continuous embeddings.

Also, elementary verifications give:

Lemma 3.1. (i) For the L^2 -norm, $\overline{\{\sqrt{\rho}, \rho \text{ } H^1\text{-admissible}\}} = D_0$.

(ii) For the H^1 -norm, $\overline{\{\sqrt{\rho}, \rho \text{ } H^1\text{-admissible}\}} = D_1$.

3.3. Existence of a $\Psi \in \Gamma$ such that $\tilde{\rho}_\Psi$ be H^1 -admissible

This section is mainly devoted to prove the following proposition.

Proposition 3.2. Let Γ be a class of symmetry such that $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$.

(i) For $N \geq 1$, $\exists \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$ such that $\tilde{\rho}_\Psi$ be H^1 -admissible.

- (ii) For $N \geq 2$, $\exists \Psi \in \Gamma \cap L^2_{\text{a}}(\mathbb{R}^{3N}) \cap H^1$ such that $\widetilde{\rho}_{\Psi}$ be H^1 -admissible. (When $N = 1$, (ii) also holds for $G = \text{O}(3)$ and $G = \text{O}(2)$.)

At the same time, we shall obtain the following result that will be used in section 3.6.

Remark 3.2. The wavefunction Ψ in proposition 3.2 can be obtained in the following form:

$$\Psi = A_N [\Phi(w_1, \dots, w_p) \phi_1(r_1) \cdots \phi_N(r_N)],$$

where $\Phi \in C^\infty((S^2)^p)$ and is of symmetry Γ , $\int_{(S^2)^p} |\Phi|^2 = (4\pi)^p$, Φ a.e. $\neq 0$, and such that for any orthonormal set (ϕ_i) of $L^2(\mathbb{R}^3)$ of radial functions:

- (i) $\widetilde{\rho}_{\Psi} = \sum_{i=1}^N |\phi_i|^2$ for atoms and linear molecules (with $p \leq 3$),
(ii) $\widetilde{\rho}_{\Psi}(r, w) = |\Phi(w)|^2 |\phi_1(r)|^2 + (\sum_{i=2}^N |\phi_i(r)|^2)$ for nonlinear molecules (with $p = 1$).

3.3.1. Proof of proposition 3.2 in the case G is finite

We first show in lemma 3.3 that, for $N = 1$, we always have $\Gamma \neq \{0\}$. We first need the following lemma which states the existence of a subdivision of \mathbb{R}^3 into $|G|$ cones Ω_j such that G acts transitively on $\{\Omega_j, 1 \leq j \leq g\}$ (see also [2, chapter 1]).

Lemma 3.2. Let G be finite and $g = |G|$ its cardinal. There exists $\{\Omega_j\}_{1 \leq j \leq g}$ convex and disjoint open cones of \mathbb{R}^3 , centered at the origin, and such that:

- (i) $\mathbb{R}^3 \setminus \bigcup_{j=1}^g \Omega_j$ is included in a finite union of planes of \mathbb{R}^3 ,
(ii) $\forall Q \in G, \forall i, \exists j, Q\Omega_i = \Omega_j$,
(iii) $\forall Q \in G, \forall i, Q\Omega_i = \Omega_i \Rightarrow Q = \text{Id}$.

Proof. The proof is left to the reader. It can be obtained by graphical arguments and going through all the possible finite subgroups of $\text{O}(3)$ (for a review of such groups, see [28, p. 416]). \square

Lemma 3.3. Let G be a finite subgroup of $\text{O}(3)$, $N = 1$, χ a character. Then $\Gamma = \Gamma(\chi)$ is not reduced to $\{0\}$. More precisely:

- (i) $\forall \rho \in L^1(\mathbb{R}^3, \mathbb{R}_+)$ such that $\widetilde{\rho} = \rho$, $\exists \Psi \in \Gamma$, $\widetilde{\rho}_{\Psi} = \rho$.
(ii) $\exists \Phi \in C^\infty(S^2)$, Φ of symmetry Γ and $\Phi(w) \neq 0$ a.e.
(iii) $\exists \Psi \in \Gamma \cap C^\infty(\mathbb{R}^3)$, $\Psi \neq 0$ and Ψ of compact support.

Proof. (i) Let $d = \dim(\Gamma)$ and let f be the function such that $f(\mathbf{x}) = \sqrt{d \rho(\mathbf{x})}$ for $\mathbf{x} \in \Omega_1$ and $f(\mathbf{x}) = 0$ for $\mathbf{x} \notin \Omega_1$. Let $Q \in G \rightarrow M(Q) \in U(d)$ be an irreducible

matrix representation associated to χ (i.e., $\chi(Q) = \sum_{i=1,d} m_{ii}(Q)$). Let $\Psi_{ij}(\mathbf{x}) = \sum_{Q \in G} m_{ij}(Q)f(Q\mathbf{x})$.

We recall that $\Psi_{ij} \in \Gamma$, and that $\forall Q \in G, T_Q \Psi_{ik} = \sum_{j=1}^d m_{ij}(Q)\Psi_{jk}$ (using $M(PQ) = M(P)M(Q)$ for P, Q in G). We use this for $i = k = 1$ and obtain, by a classical calculation, $\widetilde{\rho_{\Psi_{11}}} = |\Psi_{11}|^2 = (1/d) \sum_{j=1}^d |\Psi_{j1}|^2$. Furthermore, if $\mathbf{x} \in \Omega_1$, then $\Psi_{j1}(\mathbf{x}) = \delta_{j1}f(\mathbf{x})$ because $M(\text{Id}) = \text{Id}$ and for $Q \neq \text{Id}, Q\Omega_1 \cap \Omega_1 = \emptyset$ (use lemma 3.2). So $\widetilde{\rho_{\Psi_{11}}}(\mathbf{x}) = \rho(\mathbf{x})$ on Ω_1 . Since $\widetilde{\rho_{\Psi_{11}}}$ and ρ are totally symmetric, we obtain $\widetilde{\rho_{\Psi_{11}}} = \rho$ on \mathbb{R}^3 (use lemma 3.2).

(ii) We follow the proof of (i) but using $f(w) \in C^\infty(S^2)$, with $f(w) > 0$ for $\mathbf{x} = (1, w) \in \Omega_1$, and $\text{supp}(f) = \overline{\Omega_1} \cap S^2$. We obtain $\Phi = \Psi_{11} \in C^\infty(S^2)$, of symmetry Γ , and also, $\Phi(w) = f(w) \neq 0$ for $\mathbf{x} = (1, w) \in \Omega_1$, so $\Phi(w) \neq 0$ on $\Omega_1 \cap S^2$. In order to obtain $\Phi(w)$ a.e. $\neq 0$, we may consider a sum of such functions (using functions f with different supports).

(iii) It suffices to take $\Psi(r, w) = g(r)\Phi(w)$, where Φ is the solution of (ii) and g is radial, regular and of compact support. □

Now we finish the proof of proposition 3.2 in the case $|G|$ is finite. If $N = 1$, we obtain (i) as a consequence of lemma 3.3 (i). Then, for $N \geq 2$, it suffices to prove (ii). To this end, we consider the Slater determinant $\Psi = A_N[\phi_1 \cdots \phi_{N-1}(\phi_N\Phi)]$ with $\phi_1 = ce^{-r}$ (where c is a normalization factor), and where (ϕ_2, \dots, ϕ_N) are radial and regular functions with compact support, such that $(\phi_j)_{1 \leq j \leq N}$ is an orthonormal set in $L^2(\mathbb{R}^3)$, and $\Phi \in C^\infty(S^2)$ as in lemma 3.3 (ii) and such that $\int_{S^2} |\Phi|^2 = 4\pi$. So $(\phi_1, \dots, \phi_{N-1}, \phi_N\Phi)$ is also an orthonormal set. Hence $\Psi \in \Gamma \cap H^1$ and, in spherical coordinates,

$$\widetilde{\rho_\Psi}(r, w) = \left(\sum_{j=1}^{N-1} |\phi_j(r)|^2 \right) + |\phi_N(r)|^2 \times |\widetilde{\Phi(w)}|^2.$$

When $r \rightarrow \infty, \widetilde{\rho_\Psi}(r) = |\phi_1(r)|^2 = c^2 e^{-2r}$. Also, $\widetilde{\rho_\Psi}(r) \geq |\phi_1(r)|^2 > 0$. Thus $\widetilde{\rho_\Psi}$ is H^1 -admissible, which concludes the proof for G finite.

3.3.2. Proof of proposition 3.2, case $G = O(3)$.

In table 1, we recall the character tables of $SO(3)$ and $O(3) = SO(3) \times \{\text{Id}, I\}$. We have listed the character values for Id, R_θ (a rotation of angle θ) and of the inversion I , and we have denoted

$$\chi_\ell(R_\theta) = \frac{\sin[(2\ell + 1)\theta/2]}{\sin(\theta/2)} \quad \text{for } \ell \in \mathbb{N}.$$

Table 1
Character tables for $SO(3)$ and $O(3)$ (or O_∞).

$SO(3)$	Id	R_θ	$O(3)$	Id	R_θ	I
Γ_ℓ	$2\ell + 1$	$\chi_\ell(R_\theta)$	Γ_ℓ^+	$2\ell + 1$	$\chi_\ell(R_\theta)$	1
			Γ_ℓ^-	$2\ell + 1$	$\chi_\ell(R_\theta)$	-1

Thus for $G = O(3)$, for each $\ell \in \mathbb{N}$, there exist exactly two characters χ_ℓ^+ and χ_ℓ^- , of dimension $(2\ell + 1)$, defined by $\chi_\ell^\varepsilon(R_\theta) = \chi_\ell(R_\theta)$ and $\chi_\ell^\varepsilon(I R_\theta) = \varepsilon \chi_\ell(R_\theta)$ ($\varepsilon = \pm 1$). We denote $\Gamma_\ell^\varepsilon = \Gamma(\chi_\ell^\varepsilon)$ the corresponding class of symmetry (it is a subspace of $L^2(\mathbb{R}^{3N})$), and ε is called the *parity* of Γ_ℓ^ε . In particular, if $\Psi \in \Gamma_\ell^\varepsilon$ then $\Psi(-x) = \varepsilon \Psi(x)$.

In the following lemma, we list the cases when the space $\Gamma_\ell^\varepsilon \cap L_a^2(\mathbb{R}^{3N})$ is not reduced to $\{0\}$, construct a wavefunction Ψ in this space and calculate its density function ρ_Ψ .

Lemma 3.4. Let $G = O(3)$, $\ell \in \mathbb{N}$, $\varepsilon = \pm 1$, and $\Gamma = \Gamma_\ell^\varepsilon$.

- (i) When $N = 1$, $\Gamma_\ell^\varepsilon \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ if and only if $\varepsilon = (-1)^\ell$.
- (ii) When $N = 2$, $\Gamma_\ell^\varepsilon \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ if and only if $\Gamma \neq \Gamma_0^-$.
- (iii) When $N \geq 3$, $\Gamma_\ell^\varepsilon \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$.
- (iv) In all cases, if $\Gamma_\ell^\varepsilon \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$, then $\exists \Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$ of the form

$$\Psi = A_N [\Phi(w_1, \dots, w_p) \phi_1(r_1) \cdots \phi_N(r_N)], \tag{15}$$

where $p \leq 3$, $\Phi \in C^\infty((S^2)^p)$, $\Phi(x)$ a.e. $\neq 0$, and where the (ϕ_i) can be any radial functions of $L^2(\mathbb{R}^3)$.

- (v) If $\Phi \in L^2((S^2)^p)$ is such that $\int_{(S^2)^p} |\Phi|^2 = (4\pi)^p$, if ϕ_1, \dots, ϕ_N is an orthonormal set of radial functions in $L^2(\mathbb{R}^3)$, then for Ψ as in (15):

$$\widetilde{\rho}_\Psi(r) = \sum_{j=1}^N |\phi_j(r)|^2.$$

Proof. (i) is immediate because on $L^2(S^2)$, there is only one class of symmetry of dimension $2\ell + 1$, spanned by the spherical harmonics $(Y_{\ell m})$, $m \in [-\ell, \ell]$, and of parity $\varepsilon = (-1)^\ell$ (see [28]). Then we can take $\Psi = Y_{\ell m} \phi$ with ϕ a radial function.

Thus for $N \geq 1$, when $\varepsilon = (-1)^\ell$, it is easy to conclude $\Gamma_\ell^\varepsilon \neq \{0\}$ and to prove (iv), using a function of the form $\Psi = A_N [Y_{\ell m}(w_1) \phi_1(r_1) \cdots \phi_N(r_N)]$. But for the general case we need other arguments.

(ii) *Case $\ell = 0$.* $\Gamma_0^+ \neq \{0\}$ is obtained using $\Psi = A_2[\phi_1 \phi_2]$, ϕ_i radial and orthonormal in $L^2(\mathbb{R}^3)$. Also, $\Gamma_0^- = \{0\}$, because if $\Psi \in \Gamma_0^-$, then note that Ψ is of the form $\Psi = \Psi_1(r_1, r_2, r_{12})$ where $r_i = |\mathbf{x}_i|$ and $r_{12} = |\mathbf{x}_1 - \mathbf{x}_2|$ (use the invariance by rotations). On the other hand, $\Psi(-\mathbf{x}_1, -\mathbf{x}_2) = -\Psi(\mathbf{x}_1, \mathbf{x}_2)$ and therefore $\Psi = 0$.

Case $\ell \geq 1$. We recall that given two non-negative integers $\ell_2 \geq \ell_1$, the following decomposition holds (see [24]):

$$D_{\ell_1}^{(1)} \otimes D_{\ell_2}^{(1)} = D_{\ell_2 - \ell_1}^{(2)} \oplus D_{\ell_2 - \ell_1 + 1}^{(2)} \oplus \cdots \oplus D_{\ell_2 + \ell_1}^{(2)}. \tag{16}$$

We have denoted $D_{\ell_1}^{(1)} \otimes D_{\ell_2}^{(1)}$ the subspace of $L^2(S^2 \times S^2)$ spanned by the $(2\ell_1 + 1) \times (2\ell_2 + 1)$ functions $Y_{\ell_1 i}(w_1) Y_{\ell_2 j}(w_2)$, and $D_\ell^{(2)}$ are some subspaces of $L^2(S^2 \times S^2)$,

of dimension $2\ell + 1$ (thus non-empty), of symmetry Γ_ℓ^ε where $\varepsilon = (-1)^{\ell_1 + \ell_2}$ (because it is the parity of the functions of $D_{\ell_1}^{(1)} \otimes D_{\ell_2}^{(1)}$).

If $\varepsilon = 1$, we take $\ell_1 = \ell_2 = \ell$ in (16). We have $\ell \in [0, 2\ell]$, therefore there appears a $D_\ell^{(2)}$ in (16), and it is of parity $(-1)^{2\ell} = 1$.

If $\varepsilon = -1$, and $\ell \geq 1$, we take $\ell_1 = \ell$ and $\ell_2 = \ell + 1$. Since $\ell \geq 1$, we still have $\ell \in [1, 2\ell + 1]$ and we obtain now a $D_\ell^{(2)}$ of parity -1 .

In all cases, we choose $\Phi \in \mathcal{D}_\ell^{(2)}$ so that $\Phi \in L^2(S^2 \times S^2)$, $\Phi \neq 0$, and of symmetry Γ_ℓ^ε . Finally we can take $\Psi = A_2[\Phi(w_1, w_2)\phi_1(r_1)\phi_2(r_2)]$, where (ϕ_i) are radial functions, and orthonormal in $L^2(\mathbb{R}^3)$. So $\Psi \neq 0$, $\Psi \in L^2_a(\mathbb{R}^3 \times \mathbb{R}^3)$, and $\Psi \in \Gamma_\ell^\varepsilon$.

(iii) *Case $N \geq 3$.* If $\Gamma \neq \Gamma_0^-$, we know from the study of (ii) that there exists $\Phi \in L^2((S^2)^2)$, normalized and of symmetry Γ . We then extend Φ on $L^2((S^2)^3)$ by $\Phi(w_1, w_2, w_3) = \Phi(w_1, w_2)$.

If $\Gamma = \Gamma_0^-$, for $N = 3$ we define on $(S^2)^3$: $\Phi(w_1, w_2, w_3) = \det(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, where \mathbf{x}_i is the vector $(1, w_i)$. Thus Φ is of symmetry Γ_0^- .

In all cases, we have obtained $\Phi \in C^\infty((S^2)^p)$ (with $p \leq 3$), $\Phi \neq 0$ and of symmetry Γ .

Then let be N radial functions ϕ_1, \dots, ϕ_N , orthonormal in $L^2(\mathbb{R}^3)$, and consider Ψ as in (15). Note that $\Psi \in \Gamma$ is straightforward, and also $\Psi \neq 0$ (for instance using (v)).

(iv) Follows from (i), (ii) and (iii). In fact, we have obtained, furthermore, $\Phi \neq 0$ a.e. on $(S^2)^p$, because otherwise Φ is an analytical function which would vanish on a set of positive measure, so we would have $\Phi \equiv 0$.

(v) For simplicity of presentation, we prove only the case $p = 2$. Note that if $\sigma \in S_N$, then $\prod_{j=1}^N \phi_j(r_{\sigma(j)}) = \prod_{j=1}^N \phi_{\sigma^{-1}(j)}(r_j)$. So up to a change of σ into σ^{-1} , and if we denote $r_i = |\mathbf{x}_i|$ and $w_i = \mathbf{x}_i/r_i \in S^2$, we obtain

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \varepsilon(\sigma) \Phi(w_{\sigma^{-1}(1)}, w_{\sigma^{-1}(2)}) \prod_{j=1}^N \phi_{\sigma(j)}(r_j).$$

Then

$$\widetilde{\rho}_\Psi = \frac{N}{4\pi} \int_{(S^2)^N} dw_1 \cdots dw_N I, \tag{17}$$

where

$$\begin{aligned} I &= \int_{[0, \infty]^{N-1}} r_2^2 dr_2 \cdots r_N^2 dr_N |\Psi|^2 \\ &= \frac{1}{N!} \sum_{\sigma, \tau \in S_N} \varepsilon(\sigma)\varepsilon(\tau) \Phi(w_{\sigma^{-1}(1)}, w_{\sigma^{-1}(2)}) \overline{\Phi}(w_{\tau^{-1}(1)}, w_{\tau^{-1}(2)}) \\ &\quad \times \phi_{\sigma(1)}(r_1) \overline{\phi_{\tau(1)}}(r_1) \prod_{j=2}^N \left(\frac{1}{4\pi} \langle \phi_{\sigma(j)}, \phi_{\tau(j)} \rangle \right). \end{aligned} \tag{18}$$

Since $\langle \phi_i, \phi_j \rangle = \delta_{ij}$, the only nonvanishing terms in (18) are obtained when $\sigma(j) = \tau(j)$, $\forall j = 2, \dots, N$, and thus only when $\sigma = \tau$. Therefore,

$$I = \frac{1}{N!} \frac{1}{(4\pi)^{N-1}} \sum_{\sigma \in S_N} |\Phi(w_{\sigma^{-1}(1)}, w_{\sigma^{-1}(2)})|^2 |\phi_{\sigma(1)}(r_1)|^2. \tag{19}$$

If we introduce (19) into (17) and use $\int_{(S^2)^2} |\Phi|^2 = (4\pi)^2$, we obtain

$$\widetilde{\rho}_\Psi(r_1) = \frac{1}{(N-1)!} \sum_{\sigma \in S_N} |\phi_{\sigma(1)}(r_1)|^2 = \sum_{j=1}^N |\phi_j(r_1)|^2. \quad \square$$

Now we can conclude the proof of proposition 3.2 for $G = O(3)$. Since $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$, by lemma 3.4 we can take Ψ as in equation (15). Then using (v) we obtain $\widetilde{\rho}_\Psi = \sum_{j=1}^N |\phi_j|^2$ for any set of N radial and orthonormal functions (ϕ_j) in $L^2(\mathbb{R}^3)$. We can choose (ϕ_j) such that furthermore $\Psi \in H^1$ and $\widetilde{\rho}_\Psi$ be H^1 -admissible. This concludes the proof.

3.3.3. Proof of proposition 3.2 in the case of linear molecules

We list the classes of symmetry and see which ones are not reduced to $\{0\}$; the results are summarized in the character tables (tables 2 and 3) and in lemma 3.5. This lemma, and the proof of proposition 3.2 in the linear case, can be proved using arguments of the same type as in the atom case (this is left to the reader).

To the left in tables 2 and 3, we have listed the classes of symmetry, and we recall the corresponding character values. We have denoted C^θ the rotation $\phi \rightarrow \phi + \theta$, and σ the symmetry $\phi \rightarrow -\phi$ (in the cylindrical coordinates (r, z, ϕ)). To the right, the columns $N = 1$ and $N = 2$ contain an example of a function in $\Gamma \cap L_a^2(\mathbb{R}^{3N})$ in the case $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$, otherwise contains “0” (so $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$ as soon as $N \geq 2$).

For $O(2)$, in table 2, we see three different types of classes of symmetry: Γ_{A_1} and Γ_{A_2} , of dimension one, and the classes of dimension two, Γ_{E_k} (with $k \in \mathbb{N}^*$). We have denoted ψ_0 a function of $L^2(\mathbb{R}^3)$ such that $\psi_0(\mathbf{x}) = \psi_0(r, z)$, i.e., that does not depend of the cylindrical coordinate ϕ .

For $G = O(2) \times \{\text{Id}, I\}$, in table 3, we have denoted by $\varepsilon = \pm$ the parity of Γ ($\varepsilon = \chi(I)$ for $\Gamma = \Gamma(\chi)$). Also, in table 3, ψ_0 and ψ_1 are two functions of $L^2(\mathbb{R}^3)$ which are ϕ -independent and such that $\psi_1(r, -z) = -\psi_1(r, z)$ and $\psi_0(r, -z) = \psi_0(r, z)$ (and A_2 is the operator A_N for $N = 2$, see (12)).

Table 2
Character tables for $O(2)$ (or $C_{\infty v}$).

$O(2)$	Id	C^θ	σ	$N = 1$	$N = 2$
Γ_{A_1}	1	1	1	ψ_0	
Γ_{A_2}	1	1	-1	0	$\psi_0(\mathbf{x}_1)\psi_0(\mathbf{x}_2) \sin(\phi_1 - \phi_2)$
Γ_{E_k}	2	$2 \cos(k\theta)$	0	$\psi_0 e^{ik\phi}$	

Table 3
Character tables for $O(2) \times \{\text{Id}, I\}$ (or $D_{\infty h}$).

$O(2) \times \{\text{Id}, I\}$	Id	C^θ	σ	I	$N = 1$	$N = 2$
$\Gamma_{A_1}^+$	1	1	1	1	ψ_0	
$\Gamma_{A_1}^-$	1	1	1	-1	ψ_1	
$\Gamma_{A_2}^+$	1	1	-1	1	{0}	$\psi_0(\mathbf{x}_1)\psi_0(\mathbf{x}_2) \sin(\phi_1 - \phi_2)$
$\Gamma_{A_2}^-$	1	1	-1	-1	{0}	$\psi_1(\mathbf{x}_1)\psi_0(\mathbf{x}_2) - \psi_0(\mathbf{x}_1)\psi_1(\mathbf{x}_2)$
$\Gamma_{E_k}^+$	2	$2 \cos(k\theta)$	0	1	$\psi_0 e^{ik\phi}$	
$\Gamma_{E_k}^-$	2	$2 \cos(k\theta)$	0	-1	$\psi_1 e^{ik\phi}$	

Lemma 3.5. Let $G = O(2) \times \{\text{Id}, I\}$ or $G = O(2)$, and Γ a class of symmetry.

- (i) For $N \geq 2$, $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$.
- (ii) For $N = 1$, we have $\Gamma \neq \{0\}$ except for $\Gamma = \Gamma_{A_2}, \Gamma_{A_2}^+, \text{ or } \Gamma_{A_2}^-$.
- (iii) If $N \geq 2$, then there exists Ψ in $\Gamma \cap L_a^2(\mathbb{R}^{3N})$ of the following form:

$$\Psi = A_N [\Phi(\phi_1, \phi_2)\psi_1(r_1, z_1) \cdots \psi_N(r_N, z_N)], \tag{20}$$

where $\Phi \in C^\infty((S^1)^2)$, $\Phi \neq 0$, a.e. and where the (ψ_i) can be any functions of the form $\psi_i = \psi_i(r, z)$ (and furthermore, if $G = O(2) \times \{\text{Id}, I\}$ and if Γ is of parity ε , with $\psi_1(r, -z) = \varepsilon \psi_1(r, z)$ and $\psi_i(r, -z) = \psi_i(r, z)$ for $i \geq 2$).

- (iv) If $\int_{(S^1)^2} |\Phi|^2 = (2\pi)^2$ and the ψ_j are orthonormal, then for Ψ as in (20):

$$\widetilde{\rho_\Psi}(r, z) = \sum_{j=1}^N |\psi_j(r, z)|^2.$$

To conclude, note that the results of this section imply also the following:

Remark 3.3. If $N \geq 2$ then $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1 \neq \{0\}$ except in one case: when $N = 2$, $G = O(3)$ (atom) and with $\Gamma = \Gamma_0^-$.

3.4. Proof of theorem 2.1 and corollary 2.1

Note that corollary 2.1 will be a consequence of theorem 2.1 and of lemma 3.1. Thus we have only to prove theorem 2.1. Also, we only prove part (i) because the second part (ii) can be obtained using the same method.

First, using proposition 3.2, we obtain the existence of a $\Psi_1 \in \Gamma \cap L_a^2(\mathbb{R}^{3N}) \cap H^1$ such that $\widetilde{\rho_{\Psi_1}}$ be H^1 -admissible. The idea is then “to deform Ψ_1 into a Ψ_2 ” such that $\widetilde{\rho_{\Psi_2}} = \rho$. We proceed as in [5] and introduce the following unitary operator on $L_a^2(\mathbb{R}^{3N})$:

$$(\mathbf{T}_f \Psi)(\mathbf{x}_1, \dots, \mathbf{x}_N) = \left(\prod_{i=1}^N J_f(\mathbf{x}_i) \right)^{1/2} \Psi(\mathbf{f}(\mathbf{x}_1), \dots, \mathbf{f}(\mathbf{x}_N)), \tag{21}$$

where $J_{\mathbf{f}} = |\det(\partial f_i / \partial x_j)|$ is the absolute value of the Jacobian determinant of \mathbf{f} (for a regular \mathbf{f}). Using the change of variable formula one can obtain the following fundamental property of $\mathbf{T}_{\mathbf{f}}$:

$$\text{if } \Psi_2 = \mathbf{T}_{\mathbf{f}}\Psi_1 \quad \text{then } \rho_{\Psi_2} = \mathbf{f} * \rho_{\Psi_1}, \quad (22)$$

where we have denoted

$$(\mathbf{f} * \rho)(\mathbf{x}) := J_{\mathbf{f}}(\mathbf{x}) \rho(\mathbf{f}(\mathbf{x})).$$

Note. $\mathbf{f} * \rho$ represents the density ρ “deformed” by \mathbf{f} .

We also need the following definition:

Definition 3.2. We say that $\mathbf{f} : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ is *symmetric* if

$$\forall Q \in G, \quad \mathbf{f}(Q) = Q(\mathbf{f}).$$

Note that in [5] it was proved that if \mathbf{f} is symmetric then $\mathbf{T}_{\mathbf{f}}(\Gamma) \subset \Gamma$. Also, we recall that using a combination of results of [5], we have obtained a constructive proof for the following

Theorem 3.1. If ρ_1 and ρ_2 are two H^1 -admissible density functions such that $\int \rho_1 = \int \rho_2$, then there exists a $C^1(\mathbb{R}^3)$ -diffeomorphism \mathbf{f} such that:

- (i) $\rho_2 = \mathbf{f} * \rho_1$,
- (ii) \mathbf{f} is symmetric,
- (iii) $\mathbf{T}_{\mathbf{f}}(H^1) \subset H^1$,
- (iv) $\mathbf{f}(\mathbf{R}_j) = \mathbf{R}_j$ for $j = 1, \dots, P$,
- (v) $D\mathbf{f} = (\partial f_i / \partial x_j)$ is bounded on \mathbb{R}^3 .

Note. Solving $\rho_2 = \mathbf{f} * \rho_1$ (for given densities ρ_1, ρ_2) is known as the *Jacobian problem* [12,37]. Although in [5] theorem 3.1 was only stated for nonlinear molecules (and atoms), it can be checked that it still holds for linear molecules.

Now let $\Psi_2 = \mathbf{T}_{\mathbf{f}}\Psi_1$ where \mathbf{f} is a solution of $\rho = \mathbf{f} * \widetilde{\rho_{\Psi_1}}$ as in the above theorem. (By changing Ψ_1 by a constant factor, we can always suppose $\int \rho = \int \widetilde{\rho_{\Psi_1}}$.) We have also $\rho_{\Psi_2} = \mathbf{f} * \rho_{\Psi_1}$ using (22).

Since \mathbf{f} is symmetric, note that $J_{\mathbf{f}}(Q\mathbf{x}) = J_{\mathbf{f}}(\mathbf{x})$ for $Q \in G$. Hence $\widetilde{\rho_{\Psi_2}} = \mathbf{f} * \widetilde{\rho_{\Psi_1}} = \rho$. Furthermore, $\Psi_2 \in \Gamma \cap H^1$ using theorem 3.1, (ii) and (iii). Finally, $\Psi = \Psi_2$ is a solution of our problem.

3.5. Proof of theorem 2.2

Let us introduce the following natural extension of a Jacobian problem, i.e., via a change of variable formula.

Definition 3.3. Let ρ_i be in $L^1(\mathbb{R}^3, \mathbb{R}_+)$ and let $\mathbf{f}: \mathbb{R}^3 \rightarrow \mathbb{R}^3$ be a measurable function. We say that \mathbf{f} solves the Jacobian problem $\rho_2 = \mathbf{f} * \rho_1$ in the measure sense, if, for any measurable $u: \mathbb{R}^3 \rightarrow \mathbb{R}_+$ (bounded),

$$\int_{\mathbb{R}^3} u(\mathbf{f})\rho_2 = \int_{\mathbb{R}^3} u\rho_1.$$

We first establish the existence of symmetric solutions for the Jacobian problem, as in [4], but here in the *measure sense* (see below, and see also [17,39] for fundamental results without symmetry). We were not able to extend this result to nonlinear molecules.

Theorem 3.2. Let G be the point group of an atom or a linear molecule. Let ρ_1, ρ_2 be in $L^1(\mathbb{R}^3, \mathbb{R}_+)$, totally symmetric, with $\rho_1 > 0$ (almost everywhere), and such that $\int \rho_1 = \int \rho_2$. Then there exists a measurable $\mathbf{f}: \mathbb{R}^3 \rightarrow \mathbb{R}^3$, symmetric (see definition 3.2) and solution of $\rho_2 = \mathbf{f} * \rho_1$ in the measure sense.

Proof. In the atom case, the density functions are radial and there is a solution of the form $\mathbf{f} = f(r)\mathbf{u}_r$ (with $\mathbf{u}_r = \mathbf{x}/r$ and $r = |\mathbf{x}|$), where $f(r)$ is defined by (see [4, section V])

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

In the linear case, we proceed as in [4, section V], but using the cylindrical coordinates $(r, z, \phi) \in \mathbb{R}_+ \times \mathbb{R} \times (0, 2\pi)$. The correspondence with the Euclidean coordinates $(x, y, z) = \mathbf{G}(r, z, \phi)$ is defined by $x = r \cos(\phi)$ and $y = r \sin(\phi)$. We denote $\rho_i = \rho_i(r, z)$ the density functions (they are totally symmetric, so are ϕ -independent). Let $C = \int \rho_i$ for $i = 1, 2$. We have $\int_0^\infty \int_{-\infty}^\infty dr dz r \rho_i(r, z) = 2\pi/C$.

Then we solve $\rho_i = \mathbf{f}_i * C$ (i.e., $J_{\mathbf{f}_i} = \rho_i/C$) in the measure sense, as follows. First, a solution of $J_{\mathbf{g}_i} = r \rho_i(r, z)/C$ is given by

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

Then we define \mathbf{f}_i by $\mathbf{g}_i = \mathbf{f}_i(\mathbf{G})$. The case of vanishing density functions is in fact not important in the definition of \mathbf{g}_i (except for inversion, see [4]). Finally, $\mathbf{f} = \mathbf{f}_1^{-1}(\mathbf{f}_2)$ solves $\rho_2 = \mathbf{f} * \rho_1$ in the measure sense.

Now we must check that \mathbf{f} is symmetric. Note that in cylindrical coordinates, \mathbf{f} is represented by $\mathbf{g} = \mathbf{g}_1^{-1}(\mathbf{g}_2)$ and thus is of the form $(r, z, \phi) \rightarrow (r_g(r), z_g(r, z), \phi)$, where (r_g, z_g) are implicitly defined by

$$\int_0^{r_g} \int_{-\infty}^{\infty} r' \rho_1(r', z') \, dr' \, dz' = \int_0^r \int_{-\infty}^{\infty} r' \rho_2(r', z') \, dr' \, dz'$$

and

$$\frac{\int_{-\infty}^{z_g} \rho_1(r_g, z') \, dz'}{\int_{-\infty}^{\infty} \rho_1(r_g, z') \, dz'} = \frac{\int_{-\infty}^z \rho_2(r, z') \, dz'}{\int_{-\infty}^{\infty} \rho_2(r, z') \, dz'}.$$

Hence, \mathbf{g} is symmetric in the case $G = \mathbf{O}(2)$.

If $G = \mathbf{O}(2) \times \{\text{Id}, I\}$, we have to check furthermore that $r_g(r, -z) = r_g(r, z)$ and $z_g(r, -z) = -r_g(r, z)$. This is a simple verification using the fact that in this case $\rho_i(r, -z) = \rho_i(r, z)$, which concludes the proof. \square

Now we come to the proof of theorem 2.2. To prove (i), let $\rho \in D_0$ (see definition 3.1) be such that $\int \rho > 0$. We look for $\Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$ such that $\widetilde{\rho_\Psi} = \rho$. First, we choose $\Psi_1 \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$ such that $\widetilde{\rho_{\Psi_1}} > 0$ a.e. on \mathbb{R}^3 (proposition 3.2). Let $\rho_1 = \widetilde{\rho_{\Psi_1}}$. We can also modify Ψ_1 such that $\int \rho_1 = \int \rho$. By theorem 3.2 there exists \mathbf{f} symmetric, solution of $\rho = \mathbf{f} * \rho_1$ in the measure sense. We define $\Psi = \mathbf{T}_f \Psi_1$ (where $J_f = \rho/\rho_1(\mathbf{f})$) and obtain $\Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$ and $\widetilde{\rho_\Psi} = \rho$ (see [4]).

To prove (ii), i.e., the openness of the map $\Psi \rightarrow \sqrt{\rho_\Psi}$, we adapt the proof of [4]. We recall that it is equivalent to show the following. Given $\Psi \in \Gamma \cap L_a^2(\mathbb{R}^{3N})$, $\rho = \widetilde{\rho_\Psi}$ and $\rho_n \in D_0$ a sequence such that $\sqrt{\rho_n} \rightarrow \sqrt{\rho}$ in $L^2(\mathbb{R}^3)$, find a sequence (Ψ_n) of $L_a^2(\mathbb{R}^{3N})$ such that $\Psi_n \in \Gamma$, $\widetilde{\rho_{\Psi_n}} = \rho_n$, and $\Psi_n \rightarrow \Psi$ in L^2 . For simplicity of presentation we suppose $\int \rho_n = N$ for all n .

We keep the constructions used in the proof of theorem 3.2, and we denote $\mathbf{f}[\rho_i]$ our solution of $J_f = \rho_i/N$. Note that as in proposition 3.1 and theorem 3.1 of [4] we can obtain that if $\mathbf{T}_{\mathbf{f}[\rho]}$ is defined as in equation (21) (except that $J_{\mathbf{f}[\rho]}$ must be replaced by ρ/N), then $\mathbf{T}_{\mathbf{f}[\rho]}$ is a unitary operator from $\bigwedge_{i=1}^N L^2((0, 1)^3)$ onto K_ρ defined by

$$K_\rho = \{ \Psi \in L_a^2(\mathbb{R}^{3N}); (\rho(x) = 0) \Rightarrow (\rho_\Psi(x) = 0) \text{ a.e.} \}$$

(for given representatives of ρ and ρ_Ψ). In order to stay in $L_a^2(\mathbb{R}^{3N})$, we introduce the density function $\rho_0(\mathbf{x}) = ae^{-r-|z|}$ (i.e., totally symmetric and > 0), where $a > 0$ is such that $\int \rho_0 = N$, and define $\mathbf{f}[\rho_0]$ and $\mathbf{T}_{\mathbf{f}[\rho_0]}$ in the same way. We obtain that $U(\rho) = \mathbf{T}_{\mathbf{f}[\rho]}(\mathbf{T}_{\mathbf{f}[\rho_0]})^{-1} = \mathbf{T}_{\mathbf{f}[\rho_0]^{-1} \circ \mathbf{f}[\rho]}$ is a unitary operator from $L_a^2(\mathbb{R}^{3N})$ onto K_ρ .

In particular, for $\rho = \widetilde{\rho_\Psi}$ we see that $\rho = 0 \implies \rho_\Psi = 0$ (a.e. on \mathbb{R}^3), and thus there exists $\Phi \in L_a^2(\mathbb{R}^{3N})$ such that $\Psi = U(\rho)\Phi$. Then we define $\Psi_n = U(\rho_n)\Phi$.

Let us check that Ψ_n is a solution of our problem. First note that $U(\rho) = \mathbf{T}_f$ and $U(\rho_n) = \mathbf{T}_{\mathbf{f}_n}$ where $\mathbf{f} = \mathbf{f}[\rho_0]^{-1} \circ \mathbf{f}[\rho]$ and $\mathbf{f}_n = \mathbf{f}[\rho_0]^{-1} \circ \mathbf{f}[\rho_n]$. By construction, \mathbf{f} and \mathbf{f}_n are symmetric and solve $\rho = \mathbf{f} * \rho_0$ and $\rho_n = \mathbf{f}_n * \rho_0$ in the measure sense. Also, $\rho_{\Psi_n} = \mathbf{f}_n * \rho_\Phi$ in the measure sense. Thus $\widetilde{\rho_{\Psi_n}} = \mathbf{f}_n * \rho_0 = \rho_n$. Note that $\Phi \in \Gamma$

because $\Psi \in \Gamma$ and $U(\rho)^{-1} = (\mathbf{T}_f)^{-1}$ keeps the symmetry (using that \mathbf{f} is symmetric). Also, $\Psi_n \in \Gamma$ because $U(\rho_n) = \mathbf{T}_{f_n}$ keeps the symmetry (since \mathbf{f}_n is symmetric).

Finally, we can check as in proposition 3.3 and proposition 3.4 of [4] that $\sqrt{\rho} \rightarrow U(\rho)\Phi$ is a continuous map from D_0 into $L^2_a(\mathbb{R}^{3N})$. So $\Psi_n = U(\rho_n)\Phi$ converges towards $U(\rho)\Phi = \Psi$ in L^2 , which concludes the proof of theorem 2.2. \square

3.6. Proof of theorem 2.3

We first establish a density result. Let $H^1_a(\mathbb{R}^{3N}) := L^2_a(\mathbb{R}^{3N}) \cap H^1$.

Proposition 3.3. Let $N \geq 2$ and Γ a class of symmetry such that $\Gamma \cap L^2_a(\mathbb{R}^{3N}) \neq \{0\}$. Then, for the H^1 -norm:

$$\overline{\{\Psi, \Psi \in \Gamma \cap H^1_a(\mathbb{R}^{3N}) \cap C^\infty(\mathbb{R}^{3N}), \widetilde{\rho}_\Psi \text{ } H^1\text{-admissible}\}} = \Gamma \cap H^1_a(\mathbb{R}^{3N}).$$

Proof. Let $\varepsilon > 0$ and $\Psi \in \Gamma \cap H^1_a(\mathbb{R}^{3N})$. There exists $\Psi_0 \in H^1_a(\mathbb{R}^{3N}) \cap C^\infty$ with compact support and such that $\|\Psi_0 - \Psi\|_{H^1} \leq \varepsilon/2$ (where we define $\|\Psi\|_{H^1}^2 = \|\Psi\|_2^2 + \|\nabla\Psi\|_2^2$). Let $R > 0$ such that $\text{supp}(\Psi_0) \subset [-R, R]^{3N}$. Let $\Psi_1 = P_\chi \Psi_0$ (χ the character associated with Γ). By definition of P_χ we obtain easily $\Psi_1 \in \Gamma \cap H^1_a(\mathbb{R}^{3N}) \cap C^\infty$, $\text{supp}(\Psi_1) \subset [-R, R]^{3N}$, and $\|\Psi_1 - \Psi\|_{H^1} \leq \|\Psi_0 - \Psi\|_{H^1} \leq \varepsilon$ (since $\Psi_1 - \Psi = P_\chi(\Psi_0 - \Psi)$).

We then consider for $\lambda > 0$, $\Psi_2 = \Psi_1 + \lambda\Theta$, where Θ is of the form

$$\Theta = A_N [\Phi(w_1, \dots, w_p)\phi_1(r_1) \cdots \phi_N(r_N)].$$

We are going to search for λ and Θ such that Ψ_2 be an approximation of Ψ and $\widetilde{\rho}_{\Psi_2}$ be H^1 -admissible.

Using remark 3.2, we know that, given orthonormal (ϕ_i) in $L^2(\mathbb{R}^3)$ (radial functions), there exists a $\Phi \in C^\infty((S^2)^p)$ and of symmetry Γ , such that $\widetilde{\rho}_\Theta = \sum_{i=1}^N |\phi_i|^2$ in the atom and linear cases, and $\widetilde{\rho}_\Psi = \sum_{i=2}^N |\phi_i|^2 + |\phi_1|^2 |\Phi|^2$ in the nonlinear case (with $p = 1$).

We have $\rho_{\Psi_2} = \rho_{\Psi_1} + \lambda^2\rho_\Theta + 2N\text{Re}(I)$ where

$$I(\mathbf{x}_1) = \int_{\mathbb{R}^{3N-3}} \Psi_1(\mathbf{x}_1, \mathbf{x}_2, \dots) \overline{\Theta}(\mathbf{x}_1, \mathbf{x}_2, \dots) d\mathbf{x}_2 \dots d\mathbf{x}_N. \tag{23}$$

Then we choose regular functions (ϕ_i) such that $\phi_N > 0$ and $\phi_N(r) = e^{-r}$ for $r \geq 1$, and $(\phi_i)_{1 \leq i \leq N-1}$ with compact support included in $\mathbb{R}^3 \setminus [-R, R]^3$, and such that (ϕ_1, \dots, ϕ_N) be orthonormal in $L^2(\mathbb{R}^3)$. Since $N > 1$ and because of the disjoint supports, we obtain $I = 0$.

Note also that $\widetilde{\rho}_\Theta$ is H^1 -admissible, and that $\widetilde{\rho}_{\Psi_1}$ is of compact support. Then, we choose $\lambda > 0$ small enough so that $\|\Psi_2 - \Psi\|_{H^1} \leq \varepsilon$. We have $\Psi_2 \in \Gamma$, regular, and we can check that $\widetilde{\rho}_{\Psi_2} = \widetilde{\rho}_{\Psi_1} + \lambda^2\widetilde{\rho}_\Theta$ is also H^1 -admissible. \square

Using similar arguments as in Lieb [31] (theorem 3.3), and corollary 3.1, we can also obtain the following lemma:

Lemma 3.6. Let $\Psi_j \in L^2_a(\mathbb{R}^{3N})$ and $\rho_j = \widetilde{\rho_{\Psi_j}}$, such that

- (i) $\Psi_j \rightarrow \Psi$ weakly in $L^2_a(\mathbb{R}^{3N})$ and strongly in $L^2(\Omega)$ for any bounded Ω ,
- (ii) $\rho_j \rightarrow \rho$ weakly in $L^1(\mathbb{R}^3)$.

Then $\Psi_j \rightarrow \Psi$ strongly in $L^2_a(\mathbb{R}^{3N})$, and, in particular, $\rho = \widetilde{\rho_\Psi}$.

Now we can prove theorem 2.3. First, we obtain (9) using proposition 3.3. Then, in order to show that $F_\Gamma[\rho]$ is a minimum when ρ is an H^1 -admissible density function, let Ψ_j be a minimizing sequence for $E[\Psi_j]$ (where we denote $E[\Psi] = \langle \Psi, \mathcal{H}\Psi \rangle$) and such that $\rho = \widetilde{\rho_{\Psi_j}}$. Since $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ in (1), we have $\|\Psi_j\|_{H^1}$ bounded as soon as $E[\Psi_j]$ is bounded. So we may extract a subsequence (Ψ_j) that is weakly convergent to a Ψ in H^1 , and strongly convergent to Ψ in $L^2(\Omega)$ for any bounded set $\Omega \subset \mathbb{R}^{3N}$.

We apply lemma 3.6 to (Ψ_j) (with $\rho_j = \rho$), and obtain that $\Psi_j \rightarrow \Psi$ in $L^2_a(\mathbb{R}^{3N})$ and $\rho = \widetilde{\rho_\Psi}$. The state Ψ still has the symmetry Γ . So $F_\Gamma[\rho] \leq E[\Psi]$.

Also, there exists a constant $C > 0$ such that $q(\Phi) = E[\Phi] + C\|\Phi\|_2$ is a positive quadratic form. So $q(\Psi) \leq \liminf q(\Psi_j)$, and we obtain $E[\Psi] \leq \lim E[\Psi_j] = F_\Gamma[\rho]$. Hence $F_\Gamma[\rho] = E[\Psi]$ with $\rho = \widetilde{\rho_\Psi}$ which concludes the proof of theorem 2.3.

3.7. Miscellaneous results and remarks

In the following theorem, we give slight improvements of theorem 2.1, corollary 2.1 and proposition 3.3, by demanding more regularity on the wavefunctions Ψ . Let E be the following subset of \mathbb{R}^{3N} :

$$E := \{(\mathbf{x}_1, \dots, \mathbf{x}_N) \in \mathbb{R}^{3N}, \exists i, \mathbf{x}_i \in K\}.$$

Theorem 3.3. Let $N \geq 2$ and let Γ be a class such that $\Gamma \cap L^2_a(\mathbb{R}^{3N}) \neq \{0\}$.

- (i) Let ρ be H^1 -admissible. There exists $\Psi \in \Gamma \cap L^2_a(\mathbb{R}^{3N}) \cap H^1 \cap C^\infty(\mathbb{R}^{3N} \setminus E)$, with Ψ and $\nabla\Psi$ bounded on \mathbb{R}^{3N} , such that $\widetilde{\rho_\Psi} = \rho$.
- (ii) $\{\sqrt{\widetilde{\rho_\Psi}}, \Psi \in \Gamma \cap L^2_a(\mathbb{R}^{3N}) \cap H^1 \cap C^\infty(\mathbb{R}^{3N}), \widetilde{\rho_\Psi} \text{ } H^1\text{-admissible}\}$ is dense in $D_1 = \{\sqrt{\rho}, \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \widetilde{\rho} = \rho\}$ for the H^1 -topology.

Proof. (i) We proceed as in section 3.4 and search for Ψ in the form $\Psi := \mathbf{T}_f\Psi_1$. In order to obtain the regularity on Ψ , we start from a $\Psi_1 \in C^\infty(\mathbb{R}^{3N})$ (in Γ), with Ψ_1 and $\nabla\Psi_1$ bounded, and such that $\rho_1 = \widetilde{\rho_{\Psi_1}}$ be H^1 -admissible (using remark 3.2). We consider the solution \mathbf{f} of $\rho = \mathbf{f} * \rho_1$ as in theorem 3.1, which gives $\widetilde{\rho_\Psi} = \rho$. Then, the deformation \mathbf{T}_f keeps the regularity except possibly at the nuclei positions, so $\Psi \in C^\infty(\mathbb{R}^{3N} \setminus E)$. By theorem 3.1 we have also $D\mathbf{f} = (\partial f_i / \partial x_j)$ (and J_f) bounded in \mathbb{R}^3 . Using $J_f = \rho_1 / \rho(\mathbf{f})$ and the fact that $\nabla\rho/\rho$ and $\nabla\rho_1/\rho_1$ are bounded, we deduce from

$$\frac{\nabla J_f}{J_f} = \frac{\nabla\rho_1}{\rho_1} - D\mathbf{f}^T \frac{\nabla\rho(\mathbf{f})}{\rho(\mathbf{f})}$$

that $\nabla J_{\mathbf{f}}$ is bounded in \mathbb{R}^3 . We then conclude easily that Ψ and $\nabla\Psi$ are bounded.

(ii) This is a consequence of proposition 3.3 and corollary 3.1 and the fact that if θ is a continuous application and if A is dense in B then $\theta(A)$ is dense in $\theta(B)$. (Furthermore, in order to have $\Psi \in C^\infty$, we consider here only functions ρ that are regular and H^1 -admissible.) \square

Remark 3.4. In the case $N = 1$, we have $\rho_\Psi = |\Psi|^2$ and theorem 2.1 (i) may not hold because of vanishing density functions.

To illustrate the above remark, we give an example. Let $G = \{\text{Id}, \sigma\}$ where $\sigma(x, y, z) = (x, y, -z)$ is the symmetry of plane $\Pi = \{(x, y, z) \in \mathbb{R}^3, z = 0\}$. There are two classes of symmetry: $\Gamma_{A_1} = \{\Psi \in L^2(\mathbb{R}^3), \Psi(\sigma) = \Psi\}$ and $\Gamma_{A_2} = \{\Psi \in L^2(\mathbb{R}^3), \Psi(\sigma) = -\Psi\}$. Note that if $\Psi \in \Gamma_{A_2} \cap H^1$, then $\Psi(x, y, \cdot)$ is well-defined in $L^2(\mathbb{R}^2)$ by the usual trace theorem, and $\Psi(x, y, 0) = 0$. So $\widetilde{\rho_\Psi} = \rho_\Psi = |\Psi|^2$ vanishes on Π . Reciprocally, if $\rho \geq 0$, $\sqrt{\rho} \in H^1(\mathbb{R}^3)$ and $\sqrt{\rho}|_\Pi = 0$. Then we can define $\Psi = \sqrt{\rho}$ for $z > 0$ and $\Psi = -\sqrt{\rho}$ for $z < 0$, and check that $\Psi \in \Gamma_{A_2} \cap H^1(\mathbb{R}^3)$. Thus

$$\{\widetilde{\rho_\Psi}, \Psi \in \Gamma_{A_2} \cap H^1(\mathbb{R}^3)\} = \{\rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \rho = \widetilde{\rho}, \sqrt{\rho}|_\Pi = 0\}.$$

Characterizations of the same type can be obtained for the other classes of symmetry when $N = 1$.

4. Some applications

A first way to approximate the energy $E_{0,\Gamma}$ from the theoretical definition (8) is the following. Take $\Psi_0 \in \Gamma$ to be a given reference wavefunction (an initial guess of the exact eigenvector associated to $E_{0,\Gamma}$). Define

$$E[\mathbf{f}; \Psi_0] := \langle \mathbf{T}_{\mathbf{f}}\Psi_0, \mathcal{H}\mathbf{T}_{\mathbf{f}}\Psi_0 \rangle / \langle \mathbf{T}_{\mathbf{f}}\Psi_0, \mathbf{T}_{\mathbf{f}}\Psi_0 \rangle, \tag{24}$$

where \mathbf{f} is assumed to be any symmetric deformation of \mathbb{R}^3 (see section 3.4). Note that $E_{0,\Gamma} \leq E[\mathbf{f}; \Psi_0]$ because $\mathbf{T}_{\mathbf{f}}\Psi_0 \in \Gamma$, so equation (24) is variational.

Then the energy $E[\mathbf{f}; \Psi_0]$ (energy of the wavefunction $\Psi = \mathbf{T}_{\mathbf{f}}\Psi_0$) can be calculated for instance using a variational Monte Carlo method [47]. In this case we can take $\Psi_0 = Q_J\Psi_0^{\text{det}}$, a product of a Jastrow factor Q_J (which does not affect symmetry) and of a determinant $\Psi_0^{\text{det}} \in \Gamma$ (or a simple linear combination of determinants). It is known that the Jastrow factor, introduced in order to take into account dynamic correlation, deteriorates the density function of Ψ_0^{det} . Thus the deformation \mathbf{f} can be used to recover a better density (with only few parameters to optimize for \mathbf{f}). Numerical examples are given in [6] for helium and [3] for atoms and a diatomic molecule.

Furthermore, if $\mathbf{f} = \mathbf{f}_\rho$ is a solution of the Jacobian problem $\rho = \mathbf{f} * \widetilde{\rho_{\Psi_0}}$ for symmetric ρ densities then

$$\rho \rightarrow E[\mathbf{f}_\rho; \Psi_0] \tag{25}$$

becomes a true variational density functional for the energy $E_{0,\Gamma}$. A natural question is then how to compute the energy in (25) (solving the Jacobian problem in the same time)?

We mention here that this task has been considerably simplified in the case of a periodic crystal model, where Ψ_0 is a plane wave determinant in some Bloch space and where \mathbf{f}_ρ is a “periodic deformation” of the lattice cell (\mathbf{f}_ρ is closed to the identity deformation; periodicity corresponds here to symmetry with respect to the cell). In [7–10] it is shown, using almost explicit calculations, how to recover rigorously the usual DFT approximations in the slowly varying density limit (ρ closed to the average density) and assuming the number of electrons N is large. In particular, we show how to recover Thomas–Fermi, Von–Weisäcker and Slater–Dirac functionals, within the same deformation approach.

Finally, we also mention the work and Ludeña et al. [34], an approach that uses deformations in order to deal with the density constraint in $T(\rho)$ (also denoted $T_s[\rho]$, the infimum of the kinetic energy of the free-electron gas with constraint density ρ). For the “exact” ρ density, this minimization procedure is believed to give the “exact” exchange–correlation potential V_{xc} (as a Lagrange parameter associated to the ρ constraint, see [11,41,48]). In this approach we should also take care of the symmetry. In [34] radially symmetric situations are studied (atoms). Looking carefully at this work shows that indeed it is only the radially symmetric part of the densities that are constrained to keep a given radial density. So indeed a better formulation for $T(\rho)$ could be (for totally symmetric ρ ’s):

$$T_\Gamma(\rho) := \inf\{T_{\text{kin}}(\Psi), \rho_\Psi = \rho, \Psi \in \Gamma \cap H^1, \Psi = \det\}$$

(the notation $\Psi = \det$ meaning determinantal wavefunctions) in the case the class Γ is of dimension one or can be reached by determinant wavefunctions. Otherwise we could use

$$T_\Gamma(\rho) := \inf\{T_{\text{kin}}(\Psi), \widetilde{\rho}_\Psi = \rho, \Psi \in \Gamma \cap H^1\}$$

(eventually $\Psi \in \Gamma$ and is a small linear combination of determinant). Anew, *using the results of the paper*, the above quantities are well defined as soon as $N \geq 2$ and $\Gamma \cap L_a^2(\mathbb{R}^{3N}) \neq \{0\}$. They could also be approximated, in principle, using a deformation approach as above, and we hope to be able to study these energies in a periodic model as in [8].

Acknowledgements

It is a pleasure to thank A. Savin for many inspiring discussions, C. Bigorgne and P. Labastie for very useful remarks, and B. Grébert for various advices. The author also thanks J. Bellissard for suggesting some questions on the symmetry, and V. Bach, N. Mauser and H.K.H. Siedentop for showing various references.

References

- [1] V. Bach, Accuracy of mean field approximations for atoms and molecules, *Commun. Math. Phys.* 155 (1993) 295.
- [2] M. Berger, *Géométrie*, Tome 1 (Natan, 1990).
- [3] O. Bokanowski, Thèse de Doctorat de l'Université Paul Sabatier n° 2374 (Université Paul Sabatier, Toulouse, France, 1996).
- [4] O. Bokanowski and B. Grébert, A decomposition theorem for wave functions in molecular quantum chemistry, *Math. Models Methods Appl. Sci.* 6(4) (1996) 437.
- [5] O. Bokanowski and B. Grébert, Deformations of density functions in molecular quantum chemistry, *J. Math. Phys.* 37 (1996) 1553.
- [6] O. Bokanowski and B. Grébert, Utilization of deformations in molecular quantum chemistry and application to density-functional theory, *Internat. J. Quant. Chem.* 68 (1998) 221–231.
- [7] O. Bokanowski, B. Grébert and N.J. Mauser, Approximations de l'énergie cinétique en fonction de la densité pour un modèle de Coulomb périodique, *C. R. Acad. Sci. Paris Math. Phys.* 329 (1999) 85–90.
- [8] O. Bokanowski, B. Grébert and N.J. Mauser, Rigorous derivation of the “ $X\alpha$ ” exchange potential: a deformation approach, in: *Theo. Chem.*, ed. Nagy (1999) (to appear).
- [9] O. Bokanowski, B. Grébert and N.J. Mauser, *Proc. Theor. Chem.* (submitted).
- [10] O. Bokanowski and N.J. Mauser, Local approximation for the Hartree–Fock exchange potential: a deformation approach, *Math. Models Methods Appl. Sci.* 9(6) (1999) 941–961.
- [11] O. Bokanowski, I. Schindler and H. Zidani, On the minimization of the energy of a free-electron gas with constrained density function, *Analyse Non Lin.*, TMA 35 (1998) 1073–1090.
- [12] B. Dacorogna and J. Moser, On a partial differential equation involving the Jacobian determinant, *Ann. Inst. Henri Poincaré (Analyse non linéaire)* 7(1) (1990) 1–26.
- [13] J.P. Daudey and J.P. Malrieu, Quantum chemistry in front of symmetry-breakings, in: *Strategies and Applications in Quantum Chemistry*, eds. Y. Ellinger and M. Defranceschi (Kluwer, 1996) pp. 103–108.
- [14] H. Englisch, H. Fieseler and A. Haufe, Density-functional calculations for excited-state energies, *Phys. Rev. A* 37 (1988) 4570–4576.
- [15] Fefferman and Seco, On the Dirac and Schwinger corrections to the ground-state energy of an atom, *Advances in Math.* 107 (1994) 1–185.
- [16] G. Friesecke, Pair correlation and exchange phenomena in the free electron gas, *Comm. Math. Phys.* 184 (1997) 143–171.
- [17] C. Goffman and G. Pedrick, A proof of the homeomorphism of Lebesgue–Stieltjes measure with Lebesgue measure, *Proc. Amer. Math. Soc.* 52 (1975) 196–198.
- [18] A. Görling, Symmetry in density-functional theory, *Phys. Rev. A* 47 (1993) 2783.
- [19] A. Görling, Density functional theory for excited states, *Phys. Rev. A* 54 (1996) 3912–2915.
- [20] E.K.U. Gross, L.N. Oliveira and W. Kohn, Density-functional theory for ensembles of fractionally occupied states, *Phys. Rev. A* 37 (1988) 2809–2820.
- [21] J.E. Harriman, Orthonormal orbitals for the representation of an arbitrary density, *Phys. Rev. A* 24 (1981) 680.
- [22] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, Schrödinger inequalities and asymptotic behavior of the electron density of atoms and molecules, *Phys. Rev. A* 16 (1977) 1782.
- [23] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev. B* 136 (1964) 864.
- [24] I.G. Kaplan, *Symmetry of Many-Electron Systems*, Physical Chemistry, Vol. 34 (Academic Press, 1975).
- [25] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, *Comm. Pure Appl. Math.* 10 (1957) 151–157.
- [26] W. Kohn and L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev. A* 140 (1965) 1133.

- [27] E.S. Kryachko and E.V. Ludeña, *Energy Density Functional Theory of Many-Electron Systems* (Kluwer, Dordrecht, 1990).
- [28] L. Landau and E. Lifschitz, *Physique Théorique, Tome 3: Mécanique Quantique* (Mir, 1975).
- [29] C. Lee, W. Yang and R.G. Parr, Development of the Colle–Salvetti correlation energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785.
- [30] M. Levy, *Proc. Natl. Acad. Sci. USA* 76 (1979) 6062.
- [31] E. Lieb, Density functional for Coulomb systems, in: *Physics as Natural Philosophy: Essays in Honor of Laszlo Tisza on his 75th Birthday*, eds. H. Feshback and A. Shimony (MIT Press, Cambridge, MA, 1982) pp. 111–149. See also *Internat. J. Quant. Chem.* 24 (1983) 243.
- [32] E. Lieb, in: *Density Functional Methods in Physics*, eds. R.M. Dreizler and J. da Providencia (Plenum, New York, 1985) p. 31. (Same as [31] but with a supplementary section on excited states.)
- [33] E.V. Ludeña, R. López-Boada, J. Maldonado, E. Valderrama, E.S. Kryachko, T. Koga and J. Hinze, Local-scaling transformation version of density functional theory, *Internat. J. Quant. Chem.* 56 (1995) 285–301.
- [34] E.V. Ludeña, R. López-Boada and R. Pino, Approximate kinetic energy density functionals generated by local-scaling transformations, *Can. J. Chem.* 74 (1996) 1097–1105.
- [35] V.W. Macke, Zur wellenmechanischen Behandlung von Vielkörperproblemen, *Ann. Phys. (Leipzig)* 17 (1955) 1.
- [36] N.H. March and W.H. Young, Variational methods based on the density matrix, *Proc. Phys. Soc.* 72 (1958) 182.
- [37] J. Moser, On the volume elements on a manifold, *Trans. Amer. Math. Soc.* 120 (1965) 286–294.
- [38] A. Nagy, Excited states in density functional theory, *Internat. J. Quant. Chem.* 70 (1998) 681–691.
- [39] J.C. Oxtoby and S.M. Ulam, Measure-preserving homeomorphisms and metrical transitivity, *Ann. of Math.* 42 (1941) 874–920.
- [40] R.T. Pack and W. Byers Brown, Cusp conditions for molecular wave functions, *J. Chem. Phys.* 45(2) (1966) 556.
- [41] R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).
- [42] I. Petkov, M. Stoitsov and E. Kryachko, Method of local-scaling transformation and DFT in quantum chemistry, part I, *Internat. J. Quant. Chem.* 29 (1986) 149; see also *Internat. J. Quant. Chem.* 32 (1987) 467.
- [43] J.-P. Serre, *Représentations linéaires des groupes finis* (Hermann, 1967).
- [44] H.K.H. Siedentop, On the relation between the Hellmann energy functional and the ground state energy of an N -fermion system, *Z. Phys. A – Atoms and Nuclei* 302 (1981) 213.
- [45] H.K.H. Siedentop and R. Weikard, A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators, *Ann. Scient. Éc. Norm. Sup., 4^{ie} série* 24 (1991) 215.
- [46] Y. Tal, Asymptotic behavior of the ground-state charge density in atoms, *Phys. Rev. A* 18 (1978) 1781.
- [47] C.J. Umrigar, K.G. Wilson and J.W. Wilkins, Optimized trial wave functions for quantum Monte Carlo calculations, *Phys. Rev. Lett.* 60 (1988) 1719.
- [48] Q. Zhao and R. Parr, Quantities $T_s[n]$ and $T_c[n]$ in density-functional theory, *Phys. Rev. A* 46 (1992) 2337–2343.
- [49] G. Zumbach and K. Maschke, New approach to the calculation of density functionals, *Phys. Rev. A* 28 (1983) 544.