

A mathematical discussion on density and shape functions, vector semispaces and related questions

Patrick Bultinck

Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S-3),
B-9000 Gent, Belgium

Ramon Carbó-Dorca*

Institute of Computational Chemistry, University of Girona, Campus Montilivi,
17071 Girona, Catalonia, Spain

Received 5 November 2004; revised 16 April 2004

Density and shape functions are studied from the point of view of vector semispace structure and properties. Useful characteristics based on the shell structure of vector semispaces are used to analyze some properties of both functions. Fukui functions and quantum similarity indices are also studied when basic applications of the theory are discussed. Construction of approximate density functions and pseudo wave functions is also outlined. Finally, the original DFT variational theorem is reformulated within the frame of the shape function.

KEY WORDS: Density function, shape function, DFT, quantum similarity, vector semispaces, space shell structure, fukui functions, convex sets, Pseudo wave functions, variational DFT theorem

1. Introduction

Some time ago and with respect to the application possibilities of DFT, several authors, starting with Parr and Bartolotti [1] have introduced the *shape function* definition. The interest in the shape function has continued up to the present time [2]. On the other hand, there has developed the description of the *vector semispace*, as the most suitable structure able to contain density functions and probability distributions in general [3]. The manipulation of quantum mechanical density functions, as well as their generalization and approximation, was worked out at the same time [4] within a research framework intended to develop the basic theoretical ideas associated to *quantum similarity* [5]. The scope

* Corresponding author.

E-mail: quantunqsar@hotmail.com

of the present discussion is to set the nature of shape functions with respect to the structure of vector semispaces and to obtain useful insight about the significance of linking density and wave functions within a DFT framework.

Quantum mechanical probability density functions, $\rho(\mathbf{r})$, are positive definite functions, that usually are given with a *vector sum*, which in this case is coincident with a *Minkowski norm*, associated to the number of particles, N , conserving in this way a thermodynamically well known property [6]. That is

$$\langle \rho \rangle = \int_D \rho(\mathbf{r}) d\mathbf{r} = N.$$

The shape function is defined alternatively as positive definite, Minkowski normalized density function, $\sigma(\mathbf{r})$ which fulfils the trivial property

$$\sigma(\mathbf{r}) = N^{-1} \rho(\mathbf{r}) \rightarrow \langle \sigma \rangle = \int_D \sigma(\mathbf{r}) d\mathbf{r} = 1.$$

2. Vector semispaces

Once set these basic definitions, one can introduce both density and shape functions as elements of a vector semispace. An N -dimensional vector semispace [3] $V_N(\mathbf{R}^+)$, is simply defined as a subset of a N -dimensional vector space, $V_N(\mathbf{C})$, where the additive group has been substituted by a *semigroup* [7]. A semigroup is a group which lacks reciprocal elements. So, in a semispace no negative vectors or vector differences appear, but shall be associated to the related vector space structure, which in turn has to supposedly contain a given semispace. In this sense, the null vector does not need to be introduced as a semispace element. Vector semispaces are compulsively defined over the positive real number set, \mathbf{R}^+ , excluding the zero element. The vector semispace including the zero element will be denoted \mathbf{R}_0^+ . According to this vector semispace definition, both density and shape functions belong to some functional vector semispace, $V_\infty(\mathbf{R}^+)$, which can be attached in the most general situation to a Hilbert space $V_\infty(\mathbf{C})$.

2.1. Vector sum and Minkowski norm

The suitable norm and some special metric structure in vector semispaces, being constituted by positive definite elements, have to be based on the formalism of a *Minkowski norm* [8], which can be defined easily in a discrete vector domain as just the sum of the vector elements, called the *vector sum*

$$\forall \mathbf{x} = \{x_I\} \in V(\mathbf{R}^+) : \langle \mathbf{x} \rangle = \sum_I x_I \in \mathbf{R}^+,$$

while in a continuous functional framework it can be written by means of the integral

$$\forall f(\mathbf{r}) \in V_\infty(\mathbf{R}^+) : \langle f \rangle = \int_D f(\mathbf{r}) \, d\mathbf{r} \in \mathbf{R}^+.$$

2.2. Shell structure

It is readily seen that vector semispaces can be partitioned into special sets, whose elements possess the same Minkowski norm value denoted as λ . Such common vector characteristic defines a λ -shell, $S(\lambda)$ [8]. That is

$$\forall l \in S(\lambda) \subset V(\mathbf{R}^+) \rightarrow \langle l \rangle = \lambda \in \mathbf{R}^+.$$

According to this shell definition, density functions belong to some N -shell, $S(N)$, while shape functions belong necessarily to the *unit shell* $S(1)$. The unit shell, on the other hand, generates any λ -shell, just by employing the homothecy

$$\forall h \in S(1) \subset V(\mathbf{R}^+) \rightarrow l = \lambda h \in S(\lambda) \subset V(\mathbf{R}^+).$$

On the other hand, any λ -shell element can be transformed into a unit shell one

$$\forall l \in S(\lambda) \subset V(\mathbf{R}^+) \rightarrow h = \lambda^{-1}l \in S(1) \subset V(\mathbf{R}^+).$$

Thus, the unit shell in vector semispaces can be seen as a fundamental subset, which can generate any shell element by the appropriate homothecy. The unit shell, from the statistical theory point of view, also contains the set of all the probability distributions of the associate semispace dimension. From this perspective, the shape function should be considered as the generating element of the possible set of all N particle density functions.

These definitions and obvious results have interesting consequences in many aspects of the density function properties and structure. Some of them will be discussed below.

3. Density functions difference, Fukui functions and quantum dissimilarity indices

A controversial point associated to DFT applications regards the definition and values of Fukui functions [2,9]. Although the original definition of Fukui [10] implies a density-like set of functions belonging to the unit shell, the DFT environment definition [9] sometimes produces negative results, as recently discussed [11–13].

3.1. The zero shell

In order to discuss the issue of Fukui functions, one can analyze the possible extension of vector semispaces, relaxing the possibility of performing differences among the elements of the same shell. This induces the appearance of a *zero shell*. Indeed, assume that a given semispace λ -shell is known, one can define the following construction

$$\forall \rho_A, \rho_B \in S(\lambda) \rightarrow d = \rho_A - \rho_B \in \Sigma(0).$$

Here the notation $\Sigma(0)$ is used to distinguish it from the notation $S(\lambda)$ since $\Sigma(0) \subset V(\mathbf{R})$ and $S(\lambda) \subset V(\mathbf{R}^+)$. The meaning of the zero shell becomes clear when the vector sum of the difference is computed

$$\langle d \rangle = \langle \rho_A - \rho_B \rangle = \langle \rho_A \rangle - \langle \rho_B \rangle = 0.$$

Such a result was already described by Parr and Bartolotti in another context [1] when density functions are the semispace elements studied.

3.2. Fukui functions

Suppose now that, within the same spirit of the semispace extension leading to the 0-shell, one analyzes first a reduced density function, $\rho_A^{(N)}$, associated to some N particle quantum system A , then one will have: $\langle \rho_A^{(N)} \rangle = N \rightarrow \rho_A^{(N)} \in S(N)$. In the same manner, suppose known the homogeneous reduced density function for the same quantum system with an extra electron on it, that is: $\langle \rho_A^{(N+1)} \rangle = N + 1 \rightarrow \rho_A^{(N+1)} \in S(N + 1)$. The well-defined difference between both densities generates nothing but the vector space unit shell, as

$$f_A = \rho_A^{(N+1)} - \rho_A^{(N)} : \langle \rho_A^{(N+1)} - \rho_A^{(N)} \rangle = 1 \rightarrow f_A \in \Sigma(1).$$

In fact, the function f_A is the approximate Fukui function associated to the system A , as according to the usual DFT framework definition [9] one can write

$$\left(\frac{\partial \rho_A}{\partial N} \right)_V \approx \frac{\rho_A^{(N+1)} - \rho_A^{(N)}}{(N+1) - N} = \rho_A^{(N+1)} - \rho_A^{(N)} = f_A,$$

and this result proves that Fukui functions have to belong to the unit shell. This does not imply that they are positive definite functions since they do not belong to the semispace unit shell $S(1)$. They do, however, if a Koopmans approach is taken. If all orbitals are considered frozen, the Fukui function will correspond to the electron density of the first orbital available, which is naturally positive definite and belongs to $S(1)$. Allowing relaxation infers that the shell to which Fukui functions belong may change from $S(1)$ to $\Sigma(1)$.

3.3. *Vector spaces generated throughout semispace element subtraction*

At this stage of the discussion and as a previous step to further analysis it can be briefly studied how the difference of two elements of a vector semispace can generate the elements of the associated vector space. Suppose known two elements of a vector semispace, belonging to a pair of different shells, as the same shell case has been already discussed

$$S(\alpha); S(\beta) \subset V(\mathbf{R}^+) \wedge a \in S(\alpha); b \in S(\beta),$$

then, a difference between both semispace elements can be written, leading to a real vector sum

$$d = a - b \rightarrow \langle d \rangle = \langle a \rangle - \langle b \rangle = \alpha - \beta = \delta \in \mathbf{R} \rightarrow d \in \Sigma(\delta) \subset V(\mathbf{R}).$$

This property can be considered as to permit construction of real vector space elements from the corresponding vector semispace shell structure. Realizing that the vector semispace elements can be constructed by homothetic manipulations of the unit shell, then one can consider the unit shell as the generating nuclear structure in vector spaces [14]. Complex vector spaces can be constructed in the same homothetic way.

3.4. *Quantum dissimilarity indices*

Quantum dissimilarity indices were proposed already in 1980 [15] in the form of the Euclidian distance between two homogeneous density functions belonging to distinct systems. Certainly, this needed difference between density functions can be performed when both densities, even if they are associated to different shells, have the same number of variables. One can have

$$\rho_A \in S(\alpha) \wedge \rho_B \in S(\beta) \rightarrow \rho_A - \rho_B \in \Sigma(\alpha - \beta)$$

in the same way as in the previous discussion, providing a function which generally speaking belongs to the associated vector space. The difference function can be reversely transformed into a semispace element again by computing the square power of the difference $|\rho_A - \rho_B|^2 \in V(\mathbf{R}_0^+)$. In this way, the squared Euclidian distance between both densities can be written as a Minkowski norm of the squared difference function

$$D^2(\rho_A; \rho_B) = \langle |\rho_A - \rho_B|^2 \rangle = \langle \rho_A^2 \rangle + \langle \rho_B^2 \rangle - 2 \langle \rho_A \rho_B \rangle,$$

where the symbol $\langle \rho_A \rho_B \rangle$ stands for the overlap integral

$$\langle \rho_A \rho_B \rangle = \int_D \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) \, d\mathbf{r},$$

which as a measure appears to be one of the basic tools employed in quantum similarity [5, 15].

Minkowski norm structure has been used into the expression above in order to stress the direct dependence of higher order norms from the Minkowski norm definition.

3.5. Quantum similarity index: Carbó index

An often used similarity index, known as the Carbó index [15] is given by

$$C(\rho_A; \rho_B) = \langle \rho_A \rho_B \rangle (\langle \rho_B^2 | \rho_B^2 \rangle)^{1/2}.$$

The Carbó index can easily be related to a distance measure [5a] and is invariant about the character of the shells, where both density functions have to belong. It is readily seen how this occurs using unit shell homotheties to express the density functions

$$\text{iff : } \rho_A = \alpha \sigma_A \wedge \rho_B = \beta \sigma_B \rightarrow C(\rho_A; \rho_B) = C(\sigma_A; \sigma_B).$$

This property enhances once more the fundamental role of the unit shell elements in vector semispaces.

4. Convex linear combinations within the same shell and the construction of density functions

4.1. Convex sets of scalars

A set of scalars $\{w_I\}$ or the elements of a vector \mathbf{w} can be called *convex* and noted as $K(\{w_I\})$ or $K(\mathbf{w})$, whenever they are positive definite real numbers and their sum is one, or alternatively the vector is a semispace element belonging to the unit shell. That is

$$K(\{w_I\}) = \left\{ \forall w_I \in \mathbf{R}^+ \wedge \sum_I w_I = 1 \right\},$$

alternatively

$$K(\mathbf{w}) = \{ \mathbf{w} \in V(\mathbf{R}^+) \wedge \langle \mathbf{w} \rangle = 1 \}.$$

4.2. Convex linear combinations within vector semispace shells

A convex linear combination of elements of a vector semispace belonging to the same shell results into a new element belonging to this shell, meaning that

$$\{\rho_I\} \subset S(\lambda) \subset V(\mathbf{R}^+) \wedge K(\{w_I\}) \rightarrow \rho = \sum_I w_I \rho_I \in S(\lambda).$$

This is true because

$$\langle \rho \rangle = \left\langle \sum_I w_I \rho_I \right\rangle = \sum_I w_I \langle \rho_I \rangle = \sum_I w_I \lambda = \lambda \sum_I w_I = \lambda.$$

That is: any vector semispace shell is *closed* upon convex linear combinations of its elements. Such a property constitutes the basic idea employed to construct approximate molecular density functions in the *promolecular* form [16]. The *atomic shell approximation* [17], which has been systematically employed to obtain approximate, but accurate atomic density functions is based in the same fundamental closeness property of vector semispaces shell structure.

It easy to prove that closure under convex linear combinations also holds into shells defined within vector spaces.

5. Pseudo wave functions

The vector semispace properties so far disclosed may be employed to seek for any useful connection between vector semispaces and the associated vector spaces. Such relationship is of capital interest to rely DFT resulting density functions and wave function theoretical structure. Such a possible connection has been preliminarily put recently forward by one of us [6].

5.1. Norm variation and Fukui functions

Suppose a quantum system whose state density function, $\rho_A^{(\alpha)}$ belongs to some vector semispace shell, $S(\alpha)$. Suppose that the same system has underwent some change which produces as a result a new density function, $\rho_A^{(\alpha+\delta\alpha)}$, where $\delta\alpha$ is a suitable variation of the vector sum, then one has the possibility to construct the density difference as a semispace $\delta\alpha$ -shell element

$$\rho_A^{(\alpha+\delta\alpha)} - \rho_A^{(\alpha)} = \rho_A^{(\delta\alpha)} \in S(\delta\alpha),$$

which can be written in terms of an homothecy of some appropriate shape function, $\sigma_A^{(1)}$ belonging to the unit shell, or

$$\rho_A^{(\delta\alpha)} = (\delta\alpha) \sigma_A^{(1)}.$$

It is interesting to note, at this moment, that one can arrive at an equivalent expression to the one defining a Fukui function, that is

$$\sigma_A^{(1)} = \frac{\delta \rho_A^{(\delta\alpha)}}{\delta\alpha},$$

which can be related to the discussion about possible non-integer particle time fluctuations, studied by Perdew et al. [18].

5.2. Pseudo wave functions

Then, based on this shell characteristic vector sum variation, one can seek for some function, Ψ_A of the same number of variables as both used densities, which fulfils

$$|\Psi_A|^2 = \rho_A^{(\delta\alpha)},$$

or also, taking into account the previous homothety, after a trivial rearrangement

$$|(\delta\alpha)^{-1/2} \Psi_A|^2 = \sigma_A^{(1)} \rightarrow \left\langle \left| (\delta\alpha)^{-\frac{1}{2}} \Psi_A \right|^2 \right\rangle = \langle \sigma_A^{(1)} \rangle = 1,$$

so, defining the function

$$\varphi_A = (\delta\alpha)^{-1/2} \Psi_A \rightarrow |\varphi_A|^2 = \sigma_A^{(1)}$$

it is seen in this way how such a Minkowski normalized function provides a density probability according to the quantum mechanical setup [19] and how it can be obtained, as

$$\varphi_A = \left(\sigma_A^{(1)} \right)^{1/2}.$$

Such a function can be named *pseudo wave function*, as it is just provided with the same number of variables as the shape function, however it must be kept in mind that such a function can be obtained from any density function reduction level.

6. DFT variational theorem over shape functions

The possibility to use the shape function to set up the DFT variational theorem [20] has apparently not attracted research attention in DFT field and related problems. There, to complete this review of the shape functions in relation to the vector semispace structure, a reformulation of the DFT variational theorem will be given in terms of the unit shell elements.

It has been shown that, owing to the possible definition of extended wave functions⁴, the energy $E^{(N)}$ of a N particle quantum system associated to a Hamiltonian $H^{(N)}$ and described by some state density function $\rho^{(N)}$ can be formally expressed by means of the integral

$$E^{(N)} = \langle H^{(N)} \rho^{(N)} \rangle = \int_D H^{(N)}(\mathbf{r}) \rho^{(N)}(\mathbf{r}) \, d\mathbf{r}.$$

Using the shape function homothecy

$$\rho^{(N)} = N\sigma^{(1)},$$

and substituting one arrives to the definition of a *single electron energy* form

$$E^{(N)} = \langle H^{(N)} (N\sigma^{(1)}) \rangle = N \langle H^{(N)} \sigma^{(1)} \rangle = NE^{(1)}.$$

Then, the DFT variational principle, which can be written by means of the expression

$$\delta [E^{(N)}(\rho^{(N)}; V) - \mu (\langle \rho^{(N)} \rangle - N)] = 0,$$

where V is the external potential and μ a Lagrange multiplier, can be rewritten in terms of the shape function as

$$\delta [E^{(1)}(\sigma^{(1)}; V) - \lambda (\langle \sigma^{(1)} \rangle - 1)] = 0.$$

Of course, this DFT unit shell variational theorem corresponds to the homothetical counterpart of the original one, associated to the N particle density and has to provide derivation algorithms furnishing comparable results as well.

7. Conclusions

The definition of the shell structure in vector semispaces has permitted to reformulate several concepts attached to DFT and quantum similarity frameworks in reference to the use of the shape function.

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